SYNTHESIS AND CHARACTERIZATION OF FUNCTIONALIZED NAPHTHALENES AND ANTHRACENES

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SYNTHESIS AND CHARACTERIZATION OF FUNCTIONALIZED NAPHTHALENES AND ANTHRACENES

THESIS

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

By
Guang Zhang
Lexington, Kentucky

Director: Dr. Mark D. Watson, Associate Professor of Chemistry
Lexington, Kentucky
2012
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ABSTRACT OF THESIS

SYNTHESIS AND CHARACTERIZATION OF FUNCTIONALIZED NAPHTHALENES AND ANTHRACENES

Organic electronics have received significant development in the last few decades. p-Type materials are much more in availability than n-type now. There are only a few examples of air-stable n-type materials. The design and synthesis of novel air-stable n-type materials is still a focus of research. Herein is described a study to evaluate the effectiveness of a novel electron-withdrawing group, composed of three electron-withdrawing groups connected in series, to impart material properties known to be favorable for obtaining air-stable n-types. The smaller acenes, naphthalene and anthracene, carrying these electron-withdrawing groups were prepared and studied by UV-Vis absorption spectroscopy and solution electrochemical measurements to estimate changes in frontier molecular orbital energies and single crystal X-ray diffraction to determine packing motif. These measurements suggest that the new materials could be promising as n-type semiconductors in organic field effect transistor (OFET) and as acceptors for organic photovoltaic (OPV) cells. The reasons are based on: (1) the close intermolecular contacts seen in X-ray crystal structures, some of them showing 3D face-to-face stack. (2) Electrochemical measurements indicate LUMO energy levels suitable for air-stable n-type materials.

KEYWORDS: organic electronics, OFET, acceptor, n-type, cofacial pi-stack

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January 30th, 2012
SYNTHESIS AND CHARACTERIZATION OF FUNCTIONALIZED NAPHTHALENES AND ANTHRACENES

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Chapter One-Introduction

Organic semiconductors have attracted significant attention over the last few decades because of the practical application in electronic devices\(^1\), like organic light emitting diodes(OLED)\(^2\), organic field effect transistors(OFET)\(^3\) and organic photovoltaic (OPV) cells\(^4\). Based on the basic devices, like OLED and OFET, more complicated devices can be made, like OLED displays which have already been commercialized, sensors\(^5\), and simple radio-frequency identification tags(RFID)\(^6\). Even though the performance of organic semiconductor based devices can not compete with the inorganic single crystal based ones in demanding high-performance applications, they can be used in lower performance applications with much lower cost, and show big prospect in application in the near future.

Introduction to Organic Field Effect Transistors (OFET)

Organic field effect transistors (OFET), like traditional inorganic transistors, may display p-type (hole transport) and n-type (electron transport) charge behavior. The device comprises of source and drain electrodes usually made of metal, like Au and Al, the organic semiconductor which is deposited onto the dielectric by either vacuum deposition or solution processing, gate dielectric made of inorganic material like SiO\(_2\) or organic polymers, and gate electrode and substrate, both of which are commonly made of heavily doped silicon. Both top contact and bottom contact devices are commonly used (Figure1.1), including devices also with the gate electrode on top or bottom. When there is no gate voltage applied, \(V_G=0\), there is minor current flow between source and drain electrodes, the state of which is called “off” state. When gate voltage is applied \((V_G\neq 0)\), if
$V_G>0$ and electrons accumulate at the interface between the organic active layer and the dielectric, it is called n-type transistor and if $V_G<0$ and holes accumulate in the active layer, it is called p-type. Then, if drain voltage ($V_D$) is applied, charge carriers (electrons or holes) start to transport from source to drain electrode, the state of which is called “on” state. The source- drain current ($I_{SD}$) can be calculated by two equations (linear regime and saturation regime):

\[
I_{SD, \text{linear}} = C_i W \mu / L (V_G - V_T) V_D
\]

\[
I_{SD, \text{sat}} = C_i W \mu / 2L(V_G - V_T)^2
\]

Where, $C_i$ is the capacitance per unit area of gate dielectric, $W$ is the width of the channel, $L$ is the length of the channel, and $V_T$ is the threshold voltage.

Therefore, charge carrier mobility can be deduced with these equations, and the results generated may have considerable difference, so they are noted $\mu_{\text{linear}}$ and $\mu_{\text{sat}}$ respectively. Besides field effect mobility $\mu$, $I_{on}/I_{off}$ ratio and $V_{th}$ are important parameters to evaluate the overall OFET performance. Normally the higher the values of $\mu$ and $I_{on}/I_{off}$, the better is the performance and the performance is even improved if $V_{th}$ is reduced.

![Figure 1.1: Schematics of bottom gate OFET Device architectures: top contact(left) and bottom contact (right)](image)
General factors for better performance of organic materials include high intermolecular overlap and close intermolecular contacts in the crystal structure for charge hopping transfer, high chemical purity to reduce charge carrier doping and/or trapping, and highly ordered film microstructure for OFET.\textsuperscript{7}

Right now, high performance, p-type OFETs are readily available with charge carrier mobility, $\mu>1\text{cm}^2\text{V}^{-1}\text{s}^{-1}$.\textsuperscript{8-10}

One of the most well-known p-type small molecule organic semiconductors is pentacene. The highest field effect mobility could reach $3\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for thin film pentacene\textsuperscript{11} at ambient temperature. A single crystal pentacene based OFET could reach even higher field effect mobility\textsuperscript{12}, like $15\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ at ambient temperature. The reason for its high performance is not clear yet now, but packing arrangement in crystal structure is an important contributor (larger intermolecular orbital overlap, and denser packing results in higher mobility\textsuperscript{13-14}) Pentacene crystallizes with a herringbone-like arrangement\textsuperscript{15} with face to edge contacts by C-H…π interactions (Figure 1.2). Many unsubstituted conjugated organic molecules, like anthracene and sexithiophene(Figure 1.2 and Figure 1.4), also assemble to herringbone-like arrangements for the most efficient way to accommodate space-filling and quadrupolar interactions.\textsuperscript{7}
Slightly changing the molecular structure can significantly modify the packing motif. Some typical motifs like 1 D cofacial stack, 1 D slipped cofacial stack, 2 D herringbone-like stack and brick-work stack are shown in Figure 1.3. For example, partially replacing hydrogen atoms with fluorine atoms can change the electron density distribution in the acene backbone, thus facilitating the cofacial stack for the favorable ArH-ArF interactions (Figure 1.4). As shown in Figure 1.4, crystal structures of naphthalene and anthracene both show typical herringbone-like stacks but after fluorination of one benzene ring, the packing transformed to anti-parallel face-to-face π-π stack.
Figure 1.3: Some typical crystal motifs of organic semiconductors looking through the molecular axis: a. 1D cofacial stack, b. 1D slipped cofacial stack, c. 2D herringbone stack (looking through long molecular axis), and d. 2D brick-work stack$^{18}$
Introducing bulky groups on the pi-backbone can transfer herringbone to cofacial stack as well by blocking edge-to-face interactions. For example, the Anthony group introduces triisopropylsilyethyl groups to the peri positions of pentacene, making it 2D brick work stack, because the bulky group effectively prevent the interaction between C-H…π system along the long edges of the molecules. In addition, bigger pi-core units normally prefer cofacial stack rather than herringbone stack which is not favorable because it will result in lots of space between interacting molecules. For example, the Müllen’s group reported superphenalene-based material which shows cofacial stack.

Cofacial stacks can increase intermolecular π-π overlap compared to herringbone stack. So it is expected that charge carrier mobility can be enhanced in some cases by changing herringbone stack into cofacial stack according to the hopping transport mechanism. For example, Yamashita and coworkers reported an n-type small molecule organic semiconductor: 2, 2'-bis (4-trifluoromethylphenyl)-5, 5'-bithiazole(Figure 1.5). It showed high performance for n-type OFET with charge carrier mobility as high as 1.83cm²/Vs measured under vacuum, which is attributed to the close contacts between overlapping molecules as close as 3.37Å, 2D brick-work packing, and completely planar molecular geometry with torsion angle=0, facilitating efficient intermolecular π-π interactions.
**Figure 1.5:** X-ray crystal structure of 2, 2'-bis (4-trifluoromethylphenyl)-5, 5'-bithiazole: a. molecular structure, b. crystal packing parallel to molecular plane, c. crystal packing perpendicular to molecular plane.

Even though it sounds reasonable that cofacial stack is better than herringbone stack in charge carrier mobility, it is not conclusive now because the typical herringbone stack material, like pentacene, still dominates the highest charge carrier mobility rather than cofacial stack materials. So, lots of work still needs to be done on the structure and property relationship for organic semiconductors.

Recently, Takimiya’s group reported high performance, small molecule semiconductors for p-type OFET: alkylated dinaphtho[2,3-b:2',3'-f]thieno[3,2-
b) thiophenes (Cn-DNTTs) which show charge carrier mobility at 3.0 cm²V⁻¹s⁻¹ for (C₈-DNTT) on simple Si/SiO₂ substrate. By using octadecyltrichlorosilane (ODTS) treated substrate, the mobility reaches 7.9 cm²V⁻¹s⁻¹ and it shows good air stability ³⁰.

Polymers for organic thin-film transistors are extensively explored due to favorable solution processability, mechanical flexibility, low cost and ability to form continuous films over large areas. Poly(3-hexylthiophene) (P3HT) was probably mostly investigated. It is shown that regioregular polymers provide better electronic performance than regioirregular polymers ³¹. Besides that, it is found that charge carrier mobility is increased with increased molecular weight of P3HT, which is believed due to the better morphology for longer chains ³²-³³. Many similar thiophene based polymers appeared afterwards. For example, the Ong group reported the regioregular poly (3,3‴-dialkyl-quaterthiophene)s (PQTs), showing higher mobility around 0.14 cm²V⁻¹s⁻¹, and better stability in ambient conditions due to good structured thin film and controlled length of conjugation ³⁴. Recently, Muellen’s group reported an ultrahigh mobility polymer, poly [2, 6-(4, 4-bis-alkyl-4H-cyclopenta-[2, 1-b;3,4-b0]-dithiophene)-alt-4, 7-(2,1,3-benzothiadiazole)(cyclopentadithiophene-benzothiadiazole) donor-acceptor copolymer (CDT-BTZ) with charge carrier mobility of up to 3.3 cm²V⁻¹s⁻¹ measured under N₂. The authors concluded that polymer molecular weight strongly influences performance in transistors. It was found higher solid-state order was obtained with increased molecular weight. Also it was proposed that donor-acceptor interactions between adjacent polymer chains may be crucial for charge transport ¹⁰.

n-Type OFETs on the other hand have not developed as fast as p-type due partly to the poor air stability of organic anions while in device operation ³⁵. However, it was
reported that many published p-type materials could show electron transport property when measured under vacuum, just by changing the dielectric material. It is because dielectric itself could trap electrons based on the composition of the dielectric or dielectric could change the energy levels of FMOs (Frontier Molecular Orbitals) of the semiconducting materials to some level, under which electron transport becomes favorable. However, the electron transport property disappears under oxygen or moisture\textsuperscript{36}.

There are two main ways to design air stable n-type OFET materials: 1) engineer the LUMO to some value to limit redox chemistry with atmospheric dopants (thermodynamic barrier), and 2) provide some physical barrier to prevent penetration of oxygen or water, like fluorinated side chains and close intermolecular stacking (kinetic barrier). A general characteristic of n-type materials is that they usually contain electron withdrawing groups, like cyano, perfluoroalkyl, perfluoroaryl and carbonyl groups which reduce LUMO of the molecules and facilitate electron injection. Recently, Zhu’s group reported a high mobility n-type semiconductor based on a core-expanded naphthalene diimide fused with 2-(1, 3-dithiol-2-ylidene)malonitrile groups (NDI2OD-DTYM2) with good ambient stability and easy solution processability. The mobility is as high as 1.2cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1}, which is high enough for application in low cost large area electronics\textsuperscript{37}. More examples of n-type small molecule materials are listed in Chart 1 of Chapter 2.

For n-type polymers, only a few kinds of polymers are reported by now\textsuperscript{38}. One of the most promising recent developments is the polymer poly(N, N’-dialkylbithiophene) first reported by the Watson group\textsuperscript{39}, and followed by Polyera Corporation and coworkers with \( \mu \) as high as 0.85cm\textsuperscript{2}/Vs and high
air stability and good solubility, which paves the way for polymeric complementary circuits. \textsuperscript{40}

**Introduction of OPV**

The energy conversion mechanism in organic photovoltaics (OPV) involves several steps. First, an exciton (bound electron-hole pair) is generated in the donor material in the active layer (consists of donor and acceptor) by absorption of photon after irradiation with light. Then, the exciton diffuses to the interface of donor and acceptor to dissociate itself into free charge carriers (hole and electron). Then electrons are transported in the acceptor phase to cathode and holes within donor material are transported to the anode by some driving forces, thus generating electricity. The most efficient structure of OPV is called bulk heterojunction structure (BHJ) in which donor and acceptor are mixed thoroughly\textsuperscript{41}, ideally producing an interpenetrating network with domains on the length scale of the exciton diffusion length, facilitating the breaking apart of excitons over recombination. The active layer is sandwiched between a cathode normally made of aluminum or other metal with low work function matching the LUMO value of PCBM(1-(3-methoxycarbonyl) propyl-1-phenyl [6, 6] C\textsubscript{61} ) (most commonly used acceptor) and anode normally made of transparent indium-tin-oxide (ITO) which closely matches the HOMO value of many donor organic materials. The anode usually is coated with a hole transport layer PEDOT: PPS (poly (3,4-ethylendioxythiophene)-polystyrene-parasulfonic acid), which could improve the surface quality of ITO and hole extraction\textsuperscript{42}. 


Two parameters are mostly used to evaluate the performance of OPV. They are power conversion efficiency (PCE or η) and fill factor (FF):

$$\eta = \frac{P_{\text{out}}}{P_{\text{in}}} = \frac{(J_{\text{sc}})(V_{\text{oc}})\text{FF}}{P_{\text{in}}}$$

$$\text{FF} = \frac{(J_{m})(V_{m})}{(J_{\text{sc}})(V_{\text{oc}})}$$

where, $P_{\text{out}}$ is the power generated after light irradiation, $P_{\text{in}}$ means the incident light power (usually use 1000W/m² which matches the sun spectral intensity distribution with an incident angle of 48.2° on the surface of the earth, called the AM 1.5 spectrum$^{43}$), $J_{m}$ and $V_{m}$ are the current and voltage at maximum power point(MPP), $J_{\text{sc}}$ and $V_{\text{oc}}$ are short circuit current and open circuit voltage, respectively.

Figure 1.6: Structure of BHJ solar cell
The donor materials are often the same or similar to the p-type semiconductors described above for OFET applications, such as poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylen]-alt-(vinylene) (MDMO-PPV) and P3HT, both of which are widely investigated for polymeric donors. The nearly exclusively used acceptors are C$_{60}$ derivatives, like PCBM because better performance of OPV is commonly reached using PCBM than using other kinds of acceptors. This is possibly due to several reasons: 1) the high electron affinity, facilitating electron transfer from donor to acceptor$^{44}$; 2) up to 6 electrons can be accepted at the same time, indicating high stability of its anion form$^{45}$; 3) high charge carrier mobility, quickly transferring electrons to the cathode$^{46}$; 4) its spherical shape is unique among the conjugated materials, which probably is more efficient than other materials for charge separation and transfer at the interface of donor and acceptor.

With most researchers using PCBM as acceptor, most of the improvement in molecular design has focused on donor materials. It is predicted that by choosing the appreciate donor blended with PCBM, up to 10% PCE is possible to reach, which is realized by controlling the LUMO and band gap of the donor polymer$^{47}$. The idealized donor polymer is proposed, considering the LUMO of PCBM as -4.2eV to have energy levels shown in Figure 1.4. Another factor involves the morphology of the active layer which includes the physical interaction between donor and acceptor. The ideal morphology may include maximum interfacial area between donor and acceptor domains and maximum ordering with phase segregation on a suitable length scale of donor and acceptor, which will result in better performance.$^{48}$ Several factors may improve
morphology, like thermal annealing\textsuperscript{49}, selection of solvent for casting film\textsuperscript{50}, and the inherent miscibility of the two components.\textsuperscript{51}

**Figure 1.7:** Design rule for OPV towards PCE of 10\%\textsuperscript{48}

For MDMO-PPV as donor, power conversion efficiency $\eta=3\%$ could be reached, using C\textsubscript{70} as the acceptor\textsuperscript{52}. For P3HT, power conversion efficiency as high as $5.2\%$ is reached with PCBM as acceptor\textsuperscript{53}. Recently, the Li group reported P3HT power conversion efficiency could reach $6.48\%$ with an indene-C\textsubscript{60} bisadduct(ICBA) as acceptor by optimizing conditions. The reason for that is ICBA has higher LUMO compared to PCBM, resulting in higher $V_{oc}$\textsuperscript{54}. 

![Diagram of material properties and energy levels](image-url)
Recently, many other new kinds of donor for high performance OPV are reported and one of the most successful example is the fluorinated thieno[3,4-b]thiophene-benzodithiophene polymer with PCE of up to 7.4% by optimizing the morphology using mixed solvents and PC$_{71}$BM as the acceptor.

Examples of small molecule donors for OPV are widely available now. Small molecules could also work in BHJ with some characteristics different from polymer donors, like higher purity, monodispersity but often-poorer film-forming. For instance, the Nguyen group reported diketopyrrolopyrrole based material (DPP) as donor which blends with PC$_{71}$BM, reaching up to 4.4% efficiency after optimizing the film morphology by annealing.

Recently, OPV development is becoming faster, with 8% energy conversion efficiency reported by the companies, Solarmer(polymer material) and Heliatek(small molecule material) respectively, approaching the performance of amorphous silicon based solar cells. Commercialization could occur in the next couple of years because of their much lower cost in manufacturing process (like spin coating and inkjet-printing for polymer material; vacuum deposition for small molecule material, which is said to be cost effective for massive production), flexibility and massive availability.

Although fullerene derivatives have many good characteristics for OPV, they also have drawbacks, such as not feasible for large amount production and donors have to be designed with energy levels appropriate for fullerene only, limiting the choice of donors. Thus design of new kinds of acceptors is valuable to allow more choice of donors. Right
now, many kinds of new acceptors are reported, such as perylene derivatives\textsuperscript{64} and some polymers.\textsuperscript{38} But none of them can surpass the performance of fullerene derivatives.

Based on the previous research on n-type materials, it is proposed that air-stability problem for OFETs can be solved by introducing both thermodynamic and physical barriers into the material. New acceptors for OPV’s could replace PCBM if designed with appropriate energy levels, molecular geometry, suitable packing arrangements, and miscibility with donor materials. The goal of the research project described here is to design and synthesize some novel n-type materials with both thermodynamic and physical barriers, hopefully to solve the air-stability problem for OFET and engineer suitable properties for acceptor in OPV.
Chapter Two-Synthesis and Characterization of Smaller Acenes with Novel Electron-Withdrawing Groups

As briefly described in chapter 1, air-stability in operation is still a problem for n-type materials in OFETs as only a few successful cases are reported by now (Chart 1) and the OPV field could benefit from new n-types as acceptors for OPV’s. Air-sensitivity can be decreased thermodynamically by engineering FMO energy levels or kinetically by closer crystal packing and including substituents that make a barrier.

To prevent the oxidation of the anion of organic semiconductor by water, the reduction potential of the material must be bigger than -0.658eV vs SCE (the reduction potential of water), which means the LUMO should be lower than -3.7eV. To prevent the oxidation of the anion of organic semiconductor by oxygen, the reduction potential of the material should be bigger than +0.571eV (vs SCE) (the reduction potential of oxygen), meaning the LUMO should be lower than -5.0eV. Thus, theoretically, semiconducting materials with LUMO below -5.0eV are desirable for air-stable n-type OFET, but very rare materials could reach this value as far as I know. In reality, overpotentials should exist, which is an energy barrier for redox. Thus, materials with LUMO values higher than -5.0eV could give air-stable n-type OFET. For example, N,N′-cyclohexane-perylene diimide carrying cyano groups (PDI-CN$_2$) was an air stable n-type material with LUMO at -4.3eV, without physical barrier of perfluorinated substituents. It is predicted that the onset LUMO level between -4.0eV and -4.3eV promises air-stable n-type materials considering an overpotential versus oxygen reduction between 0.7V and 1.0V based on experimental results. Even though, the LUMO could go lower beyond -4.3eV to prevent oxidization by oxygen, it is reported that if it is too low, then it
is difficult to turn the transistor off while in operation. Some state-of-the-art air stable n-type materials are listed in Chart 1. They are perfluorinated copper phthalocyanine (CuF16Pc)\(^{71}\), N,N’-fluorocarbon substituted naphthalene diimide (NDI-F)\(^{72}\), cyano-substituted naphthalene diimide (NDI-8CN\(_2\))\(^{69}\), N,N’-fluorocarbon-functionalized, cyano-substituted perylene diimide (PDI-FCN\(_2\)), PDI-CN\(_2\)\(^{65}\), thiophene-dicyanomethylene substituted indenofluorene (TIFDMT)\(^{73}\), and dicyanomethylene substituted terthienoquinoid (DCMT)\(^{74}\). All of them show LUMO values deeper than -4.0eV. Some well-known n-type materials with high \(\mu\) but which are not stable in air while in operation are listed in Chart 2. They are \(\text{C}_6\text{O}_{75-76}\), N,N’-dialkyl substituted perylene (PDI-13)\(^{77}\), perfluoroalkylcarbonyl substituted quaterthiophene (DFHC0-4T)\(^{78}\) and (4-trifluoromethyl)phenyl substituted bithiazole (bithiazole)\(^{29}\). All of them are generally in the scope of LUMO shallower than -4.0eV.

Another approach to induce air-stable n-type organic materials is to create physical barrier to prevent film penetration by oxygen and water. This could be realized by attaching perfluoroalkyl groups to the core structure as has been described for rylene based materials.\(^{69,72,79}\) Also, materials with densely packed crystalline structure usually show higher air-stability, which is presumably due to their physical barrier as well.\(^{80}\)

This latter approach is essentially like encapsulating the material but without the additional processing costs. For example, \(\text{C}_6\text{O}\) is an air-unstable n-type material but by covering it with a layer of alumina, the stability in air is greatly improved so that no performance degradation is detected in air for more than one month.\(^{81}\) Thus, it makes \(\text{C}_6\text{O}\) a promising n-type material but only if encapsulated. Later, optimization on such \(\text{C}_6\text{O}\)
OFET’s was reported to give \( \mu \) as high as 6 cm\(^2\)V\(^{-1}\)s\(^{-1}\) and devices like inverters and ring oscillators were made.\(^{76}\)

**Chart 2.1: Structures of some n-type air stable organic semiconductors, their LUMO values and FET mobilities\(^{69}\)**

<table>
<thead>
<tr>
<th>Structure</th>
<th>LUMO (eV)</th>
<th>( \mu ) (cm(^2)V(^{-1})s(^{-1}))</th>
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<tr>
<td>CaF(_2 )Pc</td>
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</tr>
<tr>
<td>NDI-F</td>
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<td>0.05</td>
</tr>
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<td>PDI-FCN(_2)</td>
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<td>0.6</td>
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<td>PDI-CN(_2)</td>
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<td>0.1</td>
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<table>
<thead>
<tr>
<th>Structure</th>
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<th>( \mu ) (cm(^2)V(^{-1})s(^{-1}))</th>
</tr>
</thead>
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</tr>
<tr>
<td>DCMT</td>
<td>-4.2</td>
<td>0.16</td>
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Synthetic Targets in this Thesis and Rationale

The purpose of this project is to couple novel electron-withdrawing groups to small molecules for potential applications in n-type air-stable transistors and replacements for PCBM in OPVs. Based on the seemingly additive effects of electron withdrawing groups in reducing the LUMO of published molecules such as quaterthiophenes, we proposed to linearly combine perfluoroalkyl, carbonyl, and alkynyl groups to drastically lower the LUMOs of small molecules like naphthalene and anthracene to around -4.0 to -4.3eV. The perfluorinated alkyl group helps to lower LUMO (thermodynamic stability) and can provide a kinetic barrier to atmospheric species; the carbonyl group shows relatively high electron-withdrawing ability and serves as a bridge to alkynyl group which further

<table>
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<th>LUMO(eV)</th>
<th>μ (cm²V⁻¹s⁻¹)</th>
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<tr>
<td>C₆₀</td>
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<td>6</td>
</tr>
<tr>
<td>PDI-13</td>
<td>-4.0</td>
<td>2.1</td>
</tr>
<tr>
<td>DFHCO-4T</td>
<td>-4.0</td>
<td>1.7</td>
</tr>
<tr>
<td>bithiazole</td>
<td>-2.8</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Chart 2.2: Structures of some n-type air unstable organic semiconductors, their LUMO values and FET mobilities

Air unstable n-Type Organic semiconductors
lowers LUMO with relatively little effect on HOMO\textsuperscript{83}. The combined functional group is denoted as perFAcCC.

The hypothesis and the later experimental estimates of perFAcCC substituent effects on FMO energy levels have been supported by DFT calculations from a collaborator, Johannes Gierschner (Figure 2.14). The calculations suggest that perFAcCC functionalized anthracene has the LUMO energy level as low as -4.22eV, which is in the range to give air-stable n-type materials, due to the cumulative electron withdrawing effects of functional groups. It is found that 2 acetylene groups reduce LUMO by 0.61eV, 2 carbonyl groups reduce LUMO by around 1eV and 2 perfluoromethyl groups reduce LUMO by 0.55eV (Figure 2.1)

![Calculated HOMO and LUMO molecular orbital energy levels of anthracene with partial and full perFAcCC groups](image)

**Figure 2.1:** Calculated HOMO and LUMO molecular orbital energy levels of anthracene with partial and full perFAcCC groups
Based on the desirable LUMO values for the peFACCC- functionalized anthracene, various naphthalenes and anthracenes carrying the perFACCC groups at different positions were targeted (Figure 2.2)

Figure 2.2: Molecular structures of targets 1 to 4b

**Synthesis of functionalized naphthalenes and anthracenes**

The targets could generally be prepared in 2 to 3 steps (Scheme 2.1). Targets 1, 2, 3a and 3b were synthesized with the following procedures. First, trimethylsilylacetylene (TMSA)-substituted products were made from the corresponding acene quinones by nucleophilic addition of metallated TMSA followed by reduction with tin(II) chloride. After purification, the resulting TMSA-functionalized acenes were reacted with MeLi·LiBr to give organometallic intermediates for reaction with fluorinated esters, either ethyl perfluorobutanoate or methyl perfluoroacetate. Compounds 4a and 4b required a different strategy involving dihalonaphthalenes. The starting material, 1, 5-diaminonaphthalene was subjected to a Sandmeyer reaction to give 1, 5-diiodonaphthalene in moderate yield, which was readily converted to 1, 5-bis(trimethylsilylthynyl) naphthalene by Sonogashira reaction in very high yield (90%).
The TMS groups were transformed to perfluoroacyl groups in a manner similar to that for compounds 1-3b in moderate to good yields (more than 60%) (Scheme 2.2).

Scheme 2.1: Synthetic routes for compounds 1, 2, 3a and 3b. (1) TMSA, BuLi, THF; (2) SnCl₂·2H₂O, 10% HCl, THF; (3) MeLi·LiBr, DME, 0°C; (4) EtO₂CC₃F₇ or MeO₂CCF₃, Et₂O·BF₃, -61 °C; (5) saturated NH₄Cl (aq)

Scheme 2.2: Synthetic route of compounds 4a and 4b. (1) NaNO₂, conc. H₂SO₄, (2) KI; (3) TMSA, Pd (Ph₃)₂Cl₂, CuI, Et₂NH; (4) MeLi·LiBr, DME, 0°C; (5) EtO₂CC₃F₇ or MeO₂CCF₃, (Et₂O)BF₃, -61 °C; (6) saturated NH₄Cl (for quenching)

The yields shown in the schemes are all after flash chromatography and drying under reduced pressure. The first step to introduce TMSA groups was done according to modified published procedure⁸⁴ but did not reach high yield, especially for anthracene
derivatives, possibly due to desilylation of the product while running flash chromatography. The TMS-Li exchange during conversion to compound 1 was monitored by TLC, which indicated that desilylation was complete 2 h after adding MeLi·LiBr. After addition of the fluorinated ester, reaction progress seemed to cease after 3 hours. Purification of compound 3 proved the most difficult. Various eluents for flash chromatography were tried, but in the end no good separation was obtained, and further purification was given up. Some needle-shaped crystals formed from the oil. No further purification was done and the yield was not known.

Compounds 1, 3a, 3b, and 4b were further purified by vacuum sublimation or recrystallization. They were purified first by vacuum sublimation at relative low temperatures (40-65 °C) for more than 10 h at approximately 10⁻² mm Hg. The sublimate on the cold finger normally had a higher level of impurities (¹H and ¹⁹F NMR) and was discarded, except for compound 3a that the cold finger part was more pure (¹H and ¹⁹F NMR). For compound 1, sublimation of the majority of the remaining material at a higher temperature (110 °C) for 3 hours results in increased purity in the cold finger part as indicated by a decrease in high-field ¹H NMR signals. However, small spurious peaks are still present in the ¹⁹F NMR. Recrystallization does not improve it. For compound 3b, recrystallization is a successful method for purification as indicated by ¹H NMR and ¹⁹F NMR. Compound 4a was further purified by recrystallization. Compound 2 showed high purity after flash chromatography and no further purification was carried out.

The reaction efficiency was further evaluated because of the very low yields in some cases. The relatively high temperature (0 °C) and long reaction time for the TMS-Li exchange might result in decomposition and possible competing deprotonation at other
positions. The reaction condition of desilylation followed published procedures, in which the starting material was bi-silylacetylene.\textsuperscript{85} MeLi·LiBr is a strong base and could react with several positions in the molecule as the pKa of several proton positions are not far apart and not too high (around 30)\textsuperscript{86}. Based on these assumptions, some modifications to the reaction condition were tried, such as first desilylating in a separate step, then deprotonating and acylating the terminal acetylenes in a separate step at lower temperature. The solvent was changed to THF because lowering the temperature to -78 °C causes the reaction mixture in DME to become a slurry that is difficult to stir. These modifications were tried and exciting results were obtained.

Based on the literature and work by a prior member of our group, it was believed that the desilylated TMSA-acenes were relatively unstable, which is the reason we used one-pot, \textit{in situ} TMS-Li exchange and reaction with fluorinated esters. However, I found that deprotected acetylenes were stable enough to work with. After several months’ storing in refrigerator, \textsuperscript{13}C NMR was measured and it looked stable. Using standard procedures, TMSA-functionalized acenes were desilylated and the bis-acetylenes were isolated in near quantitative yields (Scheme 2.3).

The products were then deprotonated with MeLi·LiBr and reacted with the esters, both at -78°C. We used -78°C for all the steps rather than -61°C for the second step as mentioned before. Compound 2 and compound 3\textit{a} were again prepared in this way; as a result, much higher yields were obtained for both after flash chromatography (65.9% and 65.2% respectively) (Scheme 2.3). Consequently, this procedure is better than the original one with higher yield of final products.
Scheme 2.3: Improved synthetic routes for compounds 2 and 3a. (1) K₂CO₃, THF, MeOH (2) MeLi·LiBr, THF, -78 °C, (3) ester: EtO₂CCF₇ or MeO₂CCF₃, (Et₂O) BF₃, -78°C, (4) saturated NH₄Cl (for quenching)

Crystal structure analysis for compounds 1, 2, 3a, 3b, 4a, and 4b

Compound 1

The crystal structure of compound 1 exemplifies a 1D cofacial stack(Figure 2.3). The closest pi-contact was determined to be 3.33Å (Figure 2.3), which is the distance between one carbon atom of carbonyl group and one carbon atom of acene backbone. The reason for the short distance is probably due to the attraction between partially electron positive carbonyl carbon and partially electron negative acene backbone. The average distance between two pi-systems is around 3.45 Å with large overlap between adjacent molecules (Figure 2.3). It is also shown the perfluoroalkyl groups accumulate to form domains surrounding acene backbones as predicted, which probably influences the way of acene backbone packing.
Figure 2.3: X-ray crystal packing of compound 1 parallel to the acene plane (left) and perpendicular to the acene plane (right)

There are two different molecular arrangements in the crystal packing (Figure 2.4). Carbonyl oxygen atoms of one kind clearly distorts out of the molecular planes with the torsion of 46.8°, but for the other kind, they do not distort nearly with torsion angle of only about 3°. The molecule without distortion of oxygen atom was found to be in very close-contact with symmetry-related molecule(not shown), but it is merely a consequence of correlated disorder of the groups that appear to be in contact. The occupancy factor of each component of the disorder is 0.5.

As shown in Figure 2.4, there is close contact between oxygen atoms and carbon or hydrogen atoms of nearby molecule. The oxygen atom without distortion( label: O1B) shows 2 close contacts with one carbon atom and one hydrogen atom of nearby molecule, namely 2.95 and 2.69Å , both of which are less than the sum of van der waals radii of corresponding atoms(3.22Å for C and O atoms, 2.72Å for H and O atoms87). There is close contact between the distorted oxygen atom(lable: O1A) and one hydrogen atom of adjacent molecule as close as 2.52Å. This interaction possibly contributes to the
distortion of this oxygen atom. These close contacts may contribute to 3 D stack(Figure 2.5)

Figure 2.4: X-ray crystal structure of compound 1: distortion of oxygen atom(O1A)

Figure 2.5: X-ray crystal structure of compound 1: close contacts

**Compound 2**

For compound 2, the crystal structure is not able to be determined by now because the single crystal grown was too thin for X-ray diffraction.
**Compound 3a**

It is found that the acene backbone, acetylene and carbonyl groups are all in the same plane for all molecules (Figure 2.6) and show 2 D brick work stack nearly along b axis at first sight. The average pi-stacking distance is around 3.40Å and the minimum distance is found to be 3.34 Å between two carbon atoms in acene backbones(Figure 2.7). This highly regular arrangement and close interplanar contacts are consistent with spontaneous crystallization and generation of large size single crystals of compound 3a after being heated in solution and cooled down.

It is found large amount of atoms may contribute to intermolecular conjugation even though there is little overlap between the acene backbones but there is substantial overlap between acene backbone and acetylene and carbonyl groups of adjacent molecule (Figure 2.6).

Similar to compound 1, there are specific close contacts between oxygen atoms and carbon atoms for compound 3a. These contacts are within one molecular plane, which is different from compound 1(Figure 2.7). One such contact is as close as 3.20Å and the other is 3.21Å. Both of them are slightly less than the sum of van der waals radii between carbon and oxygen atom (3.22Å). These contacts may contribute to 3 D π-π stack. There are huge amounts of hydrogen bonds, especially the O…H-C hydrogen bond, and there are also F…H-C hydrogen bonds. For the central molecule, there are totally 10 hydrogen bonds formed by oxygen atoms or fluorine atoms of adjacent molecules (Figure 2.7). The bond lengths for O…H-C are between 2.50Å and 2.85Å. The bond length for F…H-C is 2.54Å consistently. These bond lengths are within strong to moderate hydrogen bond spectrum, thus these strong interactions probably play a significant role in the specific
packing style. Perpendicular to the molecular plane, there are 3 close contacts between carbon and carbon atoms of adjacent molecules as close as 3.34Å, all of them are within the sum of van der waals radii of carbon atoms, possibly due to polar-polar interactions(Figure 2.5-top).

**Figure 2.6:** X-ray crystal packing of compound 3a parallel to the molecular plane (top) and perpendicular to the molecular plane (down)
Figure 2.7: X-ray crystal structure of compound 3a: close contacts in the direction of stack (top), in the molecular plane (bottom)

Compound 3b

In the crystal structure of compound 3b (Figure 2.8), the packing shows 2D brickwork stack nearly along b axis at first sight, similar to compound 3a and the overlaps between molecules are similar to compound 3a as well. Acene backbone has overlaps with acetylene and carbonyl groups. The closest interplane distance is 3.28Å which is even shorter than that of compound 3a (Figure 2.8), probably due to the longer perfluoroalkyl chain which makes better self assembly of acene backbone.  

It is observed that the close contacts in the packing direction are generally shorter than those of compound 3a and the number of close contacts is bigger than that of
compound 3a(Figure 2.5-top and Figure 2.7-top). They further reflect the effect of longer perfluoroalkyl chains.

Similar to compound 1 and 3a, there are close interactions between oxygen atoms and carbon atoms of adjacent molecules and there are hydrogen bonds of O…H-C (Figure 2.9). One kind of oxygen atom has close contact with carbon atom of adjacent molecule with the distance of 3.19Å which is less than the sum of van der waals radii of them and it may contribute to 3 D π-π stack like compound 1 and 3a. It also forms hydrogen bonds of O…H-C with the bond length of 2.51 and 2.72Å respectively. The other kind of oxygen atom forms 2 hydrogen bonds of O…H-C with the hydrogen atoms of adjacent molecule of the same plane as well and the bond length of them are 2.54 and 2.82Å respectively (Figure 2.9). These interactions within the molecular plane probably contribute to the specific packing structure.

Perpendicular to the molecular plane, four close contacts are within the sum of van der waals radius of involved atoms. They are 3.28, 3.30, 3.31 and 3.36 Å respectively, possibly due to polar-polar interactions or the large amounts of close F…F interactions between adjacent molecules, some of them as close as 2.85 Å. All of these interactions should contribute to the formation of the specific crystal structure.

One oxygen atom is distorted from the molecular plane (Figure 2.8) with torsion angle of 26.6°, possibly due to its close contact of 3.26 Å with one carbon atom of adjacent molecule of adjacent plane. For the other oxygen atom with torsion angle of only 2°, its contacts with carbon atoms of different planes are much farther than the
previous one (closest distance is 3.47Å). Probably its strong in planar contacts(two close contacts) makes it stay within the plane.

Figure 2.8: X-ray crystal packing of compound 3b parallel to the molecular plane (top) and perpendicular to the molecular plane (down)
Figure 2.9: X-ray crystal packing of compound 3b: close contacts in the direction of packing(top) and in molecular plane(bottom)
**Compound 4a**

Compound 4a shows 1 D slipped cofacial π-π stack. The average distance between two pi-systems is around 3.44Å. There is big overlap between acene backbone and acetylene groups, similar to compound 3a and 3b (Figure 2.10).

For compound 4a, the close contacts within the molecular plane reach maximum (Figure 2.11-bottom). Each hydrogen atom in the molecule forms one hydrogen bond with either fluorine or oxygen atoms, the bond length ranging from 2.60 to 2.70Å. Also oxygen atom has close contact with one fluorine atom as close as 2.90Å, besides forming two hydrogen bonds. Perpendicular to the pi-system plane, there is only one close contact; that is F...F contact, the only close F...F close contact in this crystal structure, with the distance of 2.80Å (Figure 2.11-top).
Figure 2.10: X-ray crystal packing of compound 4a parallel to the molecular plane (top) and perpendicular to the molecular plane (bottom) in one unit cell
Figure 2.11: Close contacts of compound 4a in crystal structure, parallel to the molecular plane (top) and parallel to the molecular plane (bottom) in one unit cell

**Compound 4b**

The final crystal structure was not determined because diffraction was too poor to generate a structure of sufficient quality and the diffraction data do not contain enough information to refine the structure properly. But it’s packing may be discussed reliably.
In the crystal structure of compound 4b, it is interesting that in a single cell there are 8 molecules with highly symmetric and unique conformation (Figure 2.13), probably due to the close contacts of perfluoroalkyl groups in the molecular structure resulting in self-assembly of acene backbones and highly symmetric structure of molecular cluster as large number of F…F contacts are found in the center of the unit cell. It forms a 1D slipped cofacial π-π stack along c axis with high pi-overlap between two molecules, probably the highest among all the compounds giving a column like stack (Figure 2.12). Two adjacent molecules form a pair in the stack direction with the same spacing between two adjacent molecules.

The conformation of molecular cluster makes better barrier for acene backbone with more protections from perfluoroalkyl groups surrounding the acene backbones compared to molecules mentioned above, which may promise better air-stability in application (Figure 2.14). The distance between adjacent molecular planes is normally between 3.5 to 3.6 Å which is relatively large distance among all the compounds, but still could promise high performance in OFETs.

Figure 2.12: X-ray crystal packing of compound 4b parallel to the molecular plane (left) along c axis and perpendicular to the molecular plane (right)
Figure 2.13: X-ray crystal packing of compound 4b: perpendicular to the molecular plane in one unit cell
**Figure 2.14:** X-ray crystal packing of compound 4b: perpendicular to the molecular plane in two unit cell

**Electrochemistry for compounds 1 to 4b**

LUMO energy levels for all the final targets were estimated from solution electrochemical measurements. The electrochemistry is measured by DPV (differential pulse voltammetry) with the internal standard of ferrocene. It is assumed that the HOMO of ferrocene is -4.8eV. By measuring the reduction potential of the compound and oxidization potential of ferrocene, the LUMO of the compound could be deduced from the following equation: \( \text{LUMO (eV)} = (-4.8V - E_{\text{red}}) \) with \( E_{\text{red}} \) versus Fe/Fe\(^+\). The HOMOs of the compounds were estimated from the following equation: \( \text{HOMO} = \text{LUMO} - E_g \), with \( E_g \) the optical energy gap taken from the onset of absorption in solution UV/Vis spectra.
Also LUMO of naphthalene and anthracene were estimated from published results\textsuperscript{89} for comparison. The results of optical and electrochemical measurements are summarized in Table 2.1.

**Table 2.1: Electrochemistry of anthracene and naphthalene derivatives**

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{red,onset}}$ (V)$^a$</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>LUMO (eV)$^c$</th>
<th>$E_g$ (eV)$^d$</th>
<th>HOMO (eV)$^e$</th>
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<tr>
<td>naphthalene</td>
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</tr>
<tr>
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<td>2.83</td>
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<td>-7.04</td>
</tr>
</tbody>
</table>

$^a$ Versus Fc/Fc$^+$. $^b$ Solution absorption spectra. $^c$ Estimated from reduction wave onset with $\text{LUMO} = -4.8V - E_{\text{red}}$. $^d$ Estimated from the absorption edge. $^e$ Estimated from HOMO = LUMO - $E_g$. $^f$ vs SCE, from ref 89.

As expected from calculations, the LUMOs of the molecules are in the range of -4.00 to -4.30eV, which probably is good for air-stable n-type transistors. The electron withdrawing effect is well demonstrated by the strong lowering in LUMO comparing the compounds with the parent naphthalene and anthracene. Comparing anthracene with 1 and 2, there is totally 1.8eV lowering of LUMO. Also there is 1.9 to 2.0eV lowering of LUMO comparing naphthalene and its derivatives. Thus it may be safe to conclude that this specific combined functional group shows an effect in reduction of LUMO by approximately 1.8eV. It is interesting to note that the positions of perFAcCC groups
influence LUMO by comparing 3a and 4a or 3b and 4b, with LUMO raised approx 0.1 eV going from 3a to 3b or 4a to 4b. This suggests 1, 4-substitution of naphthalene is more effective in lowering LUMO than 1, 5-substitution, consistent with larger energy gap for the latter. Comparing 1 and 2, this effect seems to disappear, however, considering experimental error. Comparing anthracene derivatives with naphthalene derivatives, like 2 and 3b, LUMO differs by around 0.15eV, but HOMO increased by around 0.53eV from 3b to 2.

Considering solution UV-Vis absorption measurements $\lambda_{\text{max}}$ predictably red-shifts on going from the naphthalene to the more extended anthracene cores. Comparing anthracene derivatives, there is distinct difference in $\lambda_{\text{max}}$, around 25nm apart. In naphthalene derivatives, the difference is little from 3a to 3b and from 4a to 4b, but there is around 40nm difference between compounds 3 and 4 in absorption edge.

It was found that the lower energy profile of the absorption spectra for compound 2 is featureless, which is different from compound 1 which is more structured. In addition, 3a and 3b showed more fine structure than 4a and 4b in the lower energy region (Figure 2.16), which should be related to the symmetry of the molecular structures. Related calculations are under way to explain this and will be included when this study is published.

It appears that going from CF$_3$ to C$_3$F$_7$ groups has little effect on LUMO. Further investigation into the difference between perfluoropropyl and perfluoromethyl on electron withdrawing effect is focused on proton NMR. For example, we can compare proton NMR between compound 3 and 4, between which the only difference is perfluoro
group (Figure 2.15). For compound 3, the three kinds of protons are at 7.80, 7.96, and 8.34ppm respectively and for compound 4, they are at 7.81, 7.97, and 8.33ppm respectively. These two sets of data are essentially the same, only 0.01 different. Thus, it can be concluded as well that perfluoropropyl and perfluoromethyl show nearly the same effect in electron withdrawing through the perFAcCC linkage. This is further supported by the pK\(a\) values of perfluoroalkyl carboxylic acids with different length of perfluoroalkyl chains. Increasing the length of perfluoroalkyl chains does not significantly influence the pK\(a\) values as these acids all have pK\(a\) essentially between 0 and 1 by different calculation methods.\textsuperscript{90-91}
Figure 2.15: Proton NMR for compound 3a(top) and compound 3b(bottom)
Figure 2.16: UV-Vis absorption spectra: after normalization(top) and before normalization(bottom) for compounds 1 to 4b (1×10^{-5}M in DCM)

HOMO and LUMO energy levels for representative targets carrying F₃CCOCC groups were estimated via the Gaussian03 program, using density functional theory (DFT), B3LYP functional and 6-311+G* basis set. Trifluoromethyl group is used to calculate for the final products rather than trifluoropropyl group to lower the computational cost.

Comparing calculated and empirically estimated LUMO energy levels, the trends of change are the same that 1, 5-substituted naphthalene has higher level than that of 1, 4-substituted one, and normally anthracene derivatives show lower LUMO level than naphthalene ones with the same functional groups and corresponding HOMO levels increase. Also, comparing compounds 1 and 2, the calculated FMOs for 2, are higher than those of 1, consistent with the experimental results. Even though, it is observed that it is not perfectly matching with the empirical results because it seems there is generally
around at least 0.1eV difference in LUMO from calculation and that from experiment (Table 2.2), it is a good estimate of LUMO energy for future targets before synthesis. In addition there is very good correlation for HOMOs between calculation and experimental results, such as compound 1, 2 and 4a, whose HOMO values in experiment are almost the same as those in calculation (Table 2.2).

Based on this analysis, 2, 6-substituted naphthalene which is calculated as well (Table 2.2), probably could have around -4.0eV for LUMO energy level or even lower level in experiment. Thus it is promising for air-stable n-type material as well.

**Table 2.2:** Calculated and empirical results for some naphthalene and anthracene derivatives

<table>
<thead>
<tr>
<th>R</th>
<th>HOMO</th>
<th>LUMO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>calculated</td>
<td>empirical</td>
</tr>
<tr>
<td>H</td>
<td>-6.121 eV</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>-7.295 eV</td>
<td>NA</td>
</tr>
<tr>
<td>C=C-COCF3</td>
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<td>-7.18eV</td>
</tr>
<tr>
<td>C=C-COCF3</td>
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</tr>
<tr>
<td>C=C-COCF3</td>
<td>-6.607 eV</td>
<td>-6.61eV</td>
</tr>
<tr>
<td>C=C-COCF3</td>
<td>-6.47 eV</td>
<td>-6.46eV</td>
</tr>
</tbody>
</table>

**Device measurements**
Compounds 1 and 3b were sent to Polyera Corporation for OFET device measurements. However, our collaborators stated that the crystalline films were damaged when electrodes were deposited on top. One possibility is the lower melting compound 3b actually was melted as heat was released during metal electrode deposition. However, I cannot understand if enough heat is produced to melt the higher melting compound 1. Future studies should include bottom contact OFETs where the electrodes are already deposited on the substrate before the organic active layer.
Chapter Three- Conclusion and Future Work

Six compounds carrying the perFAcCC groups were synthesized in relatively few steps. All could be prepared in moderate to high yields after optimization of reaction conditions. Purification methods, like flash chromatography, vacuum sublimation and recrystallization may have to be combined in order to obtain a purity sufficient for device applications. These compounds all show high stability at ambient condition with melting points ranging from 80 to 177°C.

Most of the final products could be crystallized to grow single crystals suitable for X-ray diffraction. All the crystal structures show face to face slipped close stacks looking through the molecular plane. One-dimensional, two-dimensional and three-dimensional stacks were obtained respectively with many close contacts which are within the sum of van der Waals radii. The specific molecular packing is probably due to the interactions between atoms of adjacent molecules, like O…H-C, C…C, F…F, O…C. It is found that oxygen atoms of carbonyl group in the compounds interact with adjacent molecules, resulting in close contacts, which may be a good candidate for design of air stable n-type transistors. The electrochemically estimated LUMO values are all within the desired range as expected from calculations using DFT method with slight difference from experimental results. The HOMO values are more accurately predicted. Also it is found the electron withdrawing effect of perfluoromethyl group and perfluoropropyl group are approximately the same.

Further research on device measurement is valuable because some of the compounds show close packing and 3-dimensional charge transport possibility, which promises high charge carrier mobility of OFET. In addition, all the compounds have the LUMO values
in the range of -4.0 to -4.3eV, which are presumably promising candidates for air stable n-type materials. Device measurements should be conducted using bottom contact device.

Besides device measurements, other promising small molecules should be synthesized as well, like 2, 6-substituted naphthalene and anthracene, tetracene derivatives, and oligothiophene based derivatives. Some of the work has already started but will have to be carried on by future group members.

**Figure 3.1:** Suggested future targets on this project
Chapter four-Experimental Part

Materials and Methods.

All reagents were used as received except where noted. Diethyl ether, THF, dimethoxyethane ether (DME), ethyl heptafluorobutanoate, methyl trifluoroacetate and boron trifluoride etherate (BF₃·Et₂O) were distilled with appropriate drying agents and stored under dry argon or nitrogen. Unless otherwise stated, all reactions and manipulations were carried out under argon atmosphere with standard Schlenk techniques. Electrochemical results were obtained using a BAS-100A electrochemical analyzer under nitrogen or argon environment. The solvent (anhydrous DCM) was thoroughly purged by N₂ or Ar prior to each measurement. 0.1 M tetra-n-butylammonium hexafluorophosphate was used as supporting electrolyte. The scan rate for DPV was 100mVs⁻¹. A platinum working electrode, silver wire counter electrode, and platinum reference electrode were used. Ferrocene/ferrocenium (Fc/Fc⁺) worked as an internal reference throughout the measurements. ¹H, ¹³C and ¹⁹F NMR spectra were acquired using a Varian INOVA 400 MHz spectrometer (purchased under the CRIF Program of the National Science Foundation, grant CHE-9974810). Chemical shifts were referenced by CDCl₃ solvent signals for ¹H (at 7.24ppm) and ¹³C(at 77.0ppm) spectra; for ¹⁹F spectra, CCl₃F was added as internal standard and set as δ= 0.0ppm. Crystallographic data were collected from Bruker-Nonius X8 Proteum (purchased under NSF MRI program grant number 0319176). UV-VIS data were recorded on an Agilent technologies 8453 UV-Visible spectrophotometer. GC-MS data were collected from an Agilent technologies 6890N GC with 5973 MSD. Crystals suitable for single-crystal x-ray analysis were grown as follows:
Compound 1: slow cooling of warm toluene solution; compound 2: suitable single crystal for X-ray is not obtained; compound 3a: slow evaporation of a DCM/hexane solution; compound 3b: slow cooling of a hot heptane solution; compound 4a: slow evaporation of a DCM/heptane solution; compound 4b: slow evaporation of a DCM/heptane solution

**Synthetic Procedures**

**Compound 1c**

\[
\text{O} \quad \text{O} \\
\begin{array}{c}
\text{1c}
\end{array}
\]

n-BuLi (24ml, 0.060mol) was added dropwise to an ice-cooled, stirred solution of (trimethylsilyl)acetylene (8.5ml, 0.060mol) in 50ml dry THF in a 100ml Shlenk flask. After 30 minutes, 9,10-anthraquinone (5.0g, 0.024mol) was added, and the whole was allowed to warm to room temperature overnight with stirring. The mixture was then combined with 100 ml saturated SnCl$_2$ in 10% HCl solution in a 250ml flask and stirred for 2h. The reaction mixture was then extracted with DCM and the combined organic layers were dried with MgSO$_4$, filtered and concentrated via rotary evaporation. Target 1b was isolated as bright yellow colored solid following flash chromatography (silica gel, 10% DCM/pentane) in 22.5% yield. Spectral data were consistent with published data.$^{92}$
Compound 1

MeLi·LiBr (4.0ml, 1.5M in diethyl ether, 6.0mmol) was added dropwise to stirred, ice-cooled solution of 1c (1.0g, 2.7mmol) in 100ml anhydrous DME. After 1 hour, the reaction vessel was transferred to a chloroform-dry ice bath (-58 °C) and ethyl heptafluorobutyrate (1.5ml, 8.65mmol) and BF3·Et2O(1ml, 8.1mmol) were added in rapid succession. After 3 hours, 10ml sat’d NH4Cl (aq) was added with rapid stirring and the cooling bath was removed. After warming to room temperature, the reaction mixture was extracted with DCM and the combined organic layers were dried over MgSO4, filtered, and concentrated via rotary evaporation. Target 1 was isolated as a red solid following flash chromatography (silica gel, 10%DCM/pentane) in 36% yield and was further purified by placing under reduced pressure at 65 °C for 48 hours followed by 110 °C for 3 hours. 1H NMR(400MHZ, CDCl3) δ: 8.53 (m, 4H), 7.80 (m, 4H). 19F NMR (376MHz, CDCl3) δ: -80.88 (t, 6F, J=8Hz), -119.35 (m, 4F), -126.42 (s, 4F). GC-MS: m/z: 618(M+), 449(100%) MP: 177°C(dec).
1, 4-Anthraquinone\textsuperscript{93}

NaBH\textsubscript{4} (3.2g, 83.3mmol) was added to quinizarin (5g, 20.8mmol) in 100ml dry MeOH with ice cooling. After 4h with stirring, 50ml 6N HCl was added dropwise, and the resulting orange precipitate was filtered. The product was isolated following flash chromatography (silica gel, CHCl\textsubscript{3}) in 89.4\% yield. Spectral data were consistent with published data.

**Compound 2c\textsuperscript{94}**

Compound 2c was prepared and isolated in similar fashion to compound 1c and received as bright yellow solid in 34.7\% yield. Spectra data were consistent with that previously published.
THF/MeOH (1:1) solution (20ml) was added to a schlenk flask containing 2c (1g, 2.7mmol), and K$_2$CO$_3$ (0.037g, 0.27mmol) and stirred at room temperature. After 5 hours, the reaction mixture was extracted with DCM, the combined organic layers were dried over MgSO$_4$, filtered and concentrated via rotary evaporation to get a brown yellow colored solid in 98.4%. $^1$H NMR(400MHz, CDCl$_3$) δ: 8.93 (s, 2H), 8.07(dd, 2H, J=3.3, 6.5Hz), 7.67(s, 2H), 7.53(dd, 2H, J=3.3, 6.5Hz), 3.66(s, 2H). $^{13}$C NMR(100MHz, CDCl$_3$) δ: 132.62, 130.79, 130.33, 128.70, 126.68, 125.87, 121.32, 84.30, 82.01. GC-MS: m/z: 226(M+), 226(100%).

**Compound 3d**
Compound 3d was prepared and purified in fashion similar to compound 2d and received as a dark red colored solid in 100%. Spectra data were consistent with published data.\textsuperscript{92}

**Compound 2**

Method 1:

\[
\begin{array}{c}
\text{2c} \\
\text{TMS} \\
\end{array}
\quad \rightarrow \quad
\begin{array}{c}
\text{TMS} \\
\text{2} \\
\text{C}_3\text{F}_7 \\
\text{C}_3\text{F}_7 \\
\end{array}
\]

Compound 2 was prepared in similar fashion to compound 1, and purified via flash chromatography (silica gel, 15\% DCM/pentane) and received as a red solid in 20\% yield.

Method 2:

\[
\begin{array}{c}
\text{2d} \\
\text{H} \\
\end{array}
\quad \rightarrow \quad
\begin{array}{c}
\text{2} \\
\text{H} \\
\text{C}_3\text{F}_7 \\
\text{C}_3\text{F}_7 \\
\end{array}
\]
MeLi·LiBr (0.67ml, 1.3M in diethyl ether, 0.88mmol) was added dropwise to a rapidly stirred solution of 2d in 10ml dry THF, in acetone-dry ice bath (-75°C). After two hours, ethyl heptafluorobutyrate (0.23ml, 1.3mmol) and BF₃·Et₂O (0.22ml, 1.8mmol) were added in rapid succession. After stirring for 2.5h, 10ml sat’d NH₄Cl(aq), was added with rapid stirring and the cooling bath was removed. After warming to room temperature, the reaction mixture was extracted with DCM, the combined organic layers were dried over MgSO₄, filtered and concentrated via rotary evaporation. Target 2 was isolated following flash chromatography (silica gel, 10% DCM/Hexane) as a dark red solid in 65.9% yield. 

\( ^1H \) NMR(400MHz, CDCl₃) \( \delta \): 8.89(s, 2H), 8.12(dd, J=3, 4.5HZ, 2H), 7.98(s, 2H), 7.67(dd, 2H, J=3, 4.5Hz). \( ^19F \) NMR (376MHz, CDCl₃) \( \delta \): -80.90 (t, 6F, J=8.6Hz), -119.50(m, 4F), -126.43 (s, 4F). GC-MS: m/z: 618(M+), 449(100%) mp: 148-150°C.

**Compound 3c**

\[
\begin{array}{c}
\text{O} \\
\text{3c} \\
\text{TMS}
\end{array}
\quad \rightarrow \\
\begin{array}{c}
\text{O} \\
\text{TMS}
\end{array}
\]

Compound 3c was prepared in fashion similar to compound 1c, purified via flash chromatography (silica gel, 10% DCM/pentane) and received as a yellow colored solid in 61.4% yield. Spectra data were consistent with published data.⁹²

**Compound 3a**

Method 1:
Compound 3a was prepared in fashion similar to compound 1. Yellow colored oil formed after extraction with DCM and rotary evaporation. No further purification was done because of the difficulty in finding a good eluent for flash chromatography.

Method 2:

MeLi·LiBr (4.35ml, 1.3M in diethyl ether, 5.68mmol) was added dropwise to a rapidly stirred solution of 3d (0.50g, 2.8mmol) in 50ml dry THF while cooling with an acetone-dry ice bath (-75°C). After one hour, methyl trifluoroacetate (0.86ml, 8.5mmol), and BF₃·Et₂O (1.4ml, 11.4mmol) were added in rapid succession. After stirring for 2.5h, 10ml sat'd NH₄Cl (aq) was added with rapid stirring and the cooling bath was removed. After warming to room temperature, the reaction mixture was extracted with DCM, the
combined organic layers were dried over MgSO₄, filtered and concentrated via rotary evaporation. Target 3a was isolated following flash chromatography (silica gel, 50% EtOAc/Hexane) as yellow colored solid in 65% yield and was further purified by placing under reduced pressure at 60°C for 16 hours. ¹H NMR(400MHZ, CDCl₃) δ: 8.34(dd, 2H, J=3, 4.5HZ), 7.95 (s, 2H), 7.79 (dd, 2H, J=3, 4.5HZ). ¹⁹F NMR (376MHz, CDCl₃) δ: -78.04(s, 6F). GC-MS: m/z: 368(M⁺), 399(100%) mp:80-81°C.

Compound 3b

![Compound 3b](image)

Compound 3b was prepared in fashion similar to compound 1, purified with flash chromatography (silica gel, 10% DCM/pentane) and further purified by placing under reduced pressure at 40 °C for 24 hours, followed by recrystallization from heptane and it was finally received as a yellow solid in 50.5% yield. ¹H NMR(400MHz, CDCl₃) δ: 8.33(m, 2H), 7.95 (s, 2H), 7.81 (m, 2H). ¹⁹F NMR (376MHz, CDCl₃) δ: -81.00 (t, 4F, J=8.6Hz), -119.35 (q, 4F, J=8.6Hz), -126.53 (s, 6F). GC-MS: m/z: 568(M⁺), 399(100%) mp: 83-84°C.

Compound 4d
1, 5-diaminonaphthalene (2.00g, 12.6mmol) in 15ml glacial acetic acid was added dropwise to a stirred solution of 15 ml conc.H\textsubscript{2}SO\textsubscript{4} and NaNO\textsubscript{2} (1.93g, 28.0mmol) while cooling with an ice bath. After that, 40g ice and urea (0.250g, 4.16mmol) were added. Then, potassium iodide(60g, 0.361mol) in 60ml water was added slowly followed by stirring at room temperature overnight. The mixture was filtered and the solid was purified by flash chromatography (silica gel, 10%DCM/ pentane) yielding the target as a white solid in 50% yield. Spectral data were consistent with published data.

**Compound 4c\textsuperscript{92}**

A solution of trimethylsilylacetylene (1.00ml, 7.04mmol) in 50ml diethyl amine was sparged with N\textsubscript{2} while cooling with an acetonitrile-dry ice bath(-45°C). After 10 minutes, it was transferred into a schlenk flask containing 1, 5-diiodonaphthelene (1.00g, 2.63mmol), Pd(PPh\textsubscript{3})\textsubscript{2}Cl\textsubscript{2} (0.09g, 0.13mmol) and CuI (0.08g, 0.41mmol), and stirred at room temperature overnight. The reaction mixture was concentrated by rotary
evaporation to get the solid. Target 4c was isolated following flash chromatography (silica gel, 10% DCM/pentane) as light yellow solid in 90% yield. $^1$H NMR(400MHz, CDCl$_3$) $\delta$: 8.33(dd, 2H, J=1.0, 7.8Hz), 7.72 (dd, 2H, J=1.0, 7.2Hz), 7.50(dd, 2H, J=7.2, 7.8Hz), 0.32(s, 18H). $^{13}$C NMR(100MHz, CDCl$_3$) $\delta$: 133.12, 131.33, 126.02, 121.16, 102.79, 99.91, 0.06. GC-MS: m/z: 320(M+), 305(100%). mp: 105°C.

**Compound 4a**

![Chemical structure of 4a](image)

Compound 4a was prepared in fashion similar to compound 1, purified with flash chromatography (silica gel, chloroform) and received as a light yellow colored solid in 71.4% yield and was further purified by recrystallization from DCM/heptane. $^1$H NMR(400MHZ, CDCl$_3$) $\delta$: 8.50(dd, 2H, J=1.0, 8.4Hz), 8.08 (dd, 2H, J=1.0, 7.2Hz), 7.74 (dd, 2H, J=7.2, 8.4Hz). $^{19}$F NMR (376MHz, CDCl$_3$) $\delta$: -78.36 (s, 6F). GC-MS: m/z: 368(M+), 299(100%). mp:136-138°C.
Compound 4b was prepared in fashion similar to compound 1, purified with flash chromatography (silica gel, 15% DCM/pentane) and was further purified by placing under reduced pressure at 65 °C for 48 hours and received as a yellow colored solid in 66% yield and was further purified by recrystallization in DCM/heptanes. $^1$H NMR(400MHz, CDCl$_3$) $\delta$: 8.49 (dd, 2H, J=1.0, 7.8Hz), 8.08 (dd, 2H, J=1.0, 7.2Hz), 7.75 (dd, 2H, J=7.2, 7.7Hz). $^{19}$F NMR (376MHz, CDCl$_3$) $\delta$: -80.96 (t, 6F, J=8.6Hz), -119.56 (m, 4F), -126.53 (s, 4F) GC-MS: m/z: 568(M+), 399(100%). mp: 143-147°C.
Figure 4.1: $^1$H (top) and $^{19}$F (bottom) NMR (55°C, CDCl$_3$) spectra of compound 1. (*solvent, **CCl$_3$F, #H$_2$O, ^silicone grease)
Figure 4.2: $^1$H (top) and $^{19}$F (bottom) NMR (55°C, CDCl$_3$) spectra of compound 2. (*solvent, **CCl$_3$F, ^hexane, #H$_2$O)
Figure 4.3: $^1$H (top) and $^{19}$F (bottom) NMR (55°C, CDCl$_3$) spectra of compound 3a. (*solvent, **CCl$_3$F, #H$_2$O, ^silicone grease)
Figure 4.4: $^1$H (top) and $^{19}$F (bottom) NMR (55°C, CDCl$_3$) spectra of compound 3b. (*solvent, ^ heptane, **CCl$_3$F, #H$_2$O)
Figure 4.5: $^1$H (top) and $^{19}$F (bottom) NMR (55°C, CDCl$_3$) spectra of compound 4a. (*solvent, ^ heptane, ! DCM, **CCl$_3$F, #H$_2$O)
Figure 4.6: $^1$H (top) and $^{19}$F (bottom) NMR (55°C, CDCl$_3$) spectra of compound 4b. (*solvent, ^ heptane, **CCl$_3$F, #H$_2$O)
Figure 4.7: $^1$H (top) and $^{13}$C(bottom) NMR (29°C, CDCl$_3$) spectra of compound 4c (*solvent, ^ pentane, #H$_2$O)
Figure 4.8: $^1$H (top) and $^{13}$C(bottom) NMR (29°C, CDCl$_3$) spectra of compound 2d(*solvent, #H$_2$O, ^silicone grease)
Figure 4.9: Differential pulse voltammograms (vs Fe/Fe⁺) of compounds 1 to 4b. Conditions: 0.1M (n-Bu)₄PF₆ in DCM at ambient temperature; working electrode, Pt; counter electrode, Ag wire; reference electrode, Pt; scanning rate: 100mV/s.
Figure 4.10: GC traces (total ion count from GC-MS measurements) for compounds 1 to 4c.
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