SYNTHESIS AND CHARACTERIZATION OF NOVEL π-CONJUGATED SMALL MOLECULES AND POLYMERS WITH HYDROGEN BONDING

&

PREPARATION OF 2D SINGLE CRYSTALS FOR ORGANIC FIELD-EFFECT TRANSISTORS

A Thesis

Presented to

The Graduate Faculty of The University of Akron

In Partial Fulfillment

Of the Requirements for the Degree

Master of Science

Ruonan Deng

May, 2017
SYNTHESIS AND CHARACTERIZATION OF NOVEL π-CONJUGATED SMALL MOLECULES AND POLYMERS WITH HYDROGEN BONDING

&

PREPARATION OF 2D SINGLE CRYSTALS FOR ORGANIC FIELD-EFFECT TRANSISTORS

Ruonan Deng

Thesis

Approved:  

Accepted:  

Advisor  
Dr. Yu Zhu  

Dean of the College  
Dr. Eric J. Amis  

Faculty Reader  
Dr. Steven S.C. Chuang  

Dean of the Graduate School  
Dr. Chand Midha  

Department Chair  
Dr. Coleen Pugh  

Date
ABSTRACT

Two $\pi$–conjugated polymers containing isoindigo or 3,3-(ethane-1, 2-diylidene)bis(indolin-2-one) (EBI) units with latent hydrogen-bonding on the main chain were synthesized and characterized. The designed polymers use thermal liable t-Boc groups as side chains on the backbone and can be easily dissolved in common organic solvent. Further thermal treatment of the polymers at around 180 °C can convert the polymers into strong hydrogen-bonded materials. The effect of formation of intermolecular hydrogen bonding networks on the polymer film properties including the UV/Vis absorption and electrochemical properties are studied.

In the second part of this work, 2D organic single crystals of three conjugated small molecules, di-tert-butyl 1,4-dioxo-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-2,5(1H,4H)-dicarboxylate (DPPBoc), isoindigo, and cyclized DPP were successfully prepared by either solution epitaxial growth, mechanical exfoliation, or physical vapor deposition methods for organic field-effect transistor (OFET) applications. A thickness that less than 100 nm can be achieved for the obtained 2D crystals.
ACKNOWLEDGEMENTS

Every stage of my experiment was under the guidance of Dr. Yu Zhu and Dr. Haichang. I would like to show my deepest gratitude to my advisor Dr. Yu Zhu, a respectable scholar, and Haichang for their patience and instruction. Thanks for the FT-IR measurement of Hailiang Jin. Also thanks for the kind help of all my colleagues, especially Mr. Xiang Li, Mr. Kun Yang and Mr. Jiyang Jin. Finally, I am thankful for Dr. Steven S.C. Chuang spending his valuable time on my thesis.
TABLE OF CONTENTS

| LIST OF TABLES                              | vii |
| LIST OF FIGURES                            | viii |
| LIST OF SCHEMES                           | x   |

CHAPTER

PART 1 SYNTHESIS AND CHARACTERIZATION OF NOVEL π-CONJUGATED SMALL MOLECULES AND POLYMERS WITH HYDROGEN BONDING

I. INTRODUCTION

1.1 Organic Field-Effect Transistors (OFETs) .......................... 1
1.2 Organic Semiconducting Materials7 .............................. 5
1.3 Hydrogen-bonded Semiconducting Materials12-21 .............. 7

II. EXPERIMENT

2.1 Materials ................................................................. 10
2.2 Instrumentation ......................................................... 10
2.3 Synthesis ....................................................................... 12

III. RESULTS AND DISCUSSION

3.1 Materials Synthesis ..................................................... 17
3.2 Thermal properties ...................................................... 19
3.3 FTO IR spectroscopy ..................................................... 20
3.4 Optical Properties ....................................................... 22
3.5 Electrochemical Properties ............................................ 24
3.6 OFET Performance ....................................................... 25
PART 2 PREPARATION OF 2D SINGLE CRYSTALS FOR ORGANIC FIELD-EFFECT TRANSISTORS

I. INTRODUCTION ................................................................. 28
II. MATERIALS AND APPARATUS ........................................... 30
III. GROWTH PROCESS AND RESULTS ................................. 31
IV. CONCLUSION ...................................................................... 36

BIBLIOGRAPHY ........................................................................ 37


LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Optical and electrochemical properties of the pristine and annealed P1 and P2 films.</td>
<td>25</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>1.</td>
<td>Typical structure of OFET device with different configuration. (A) Bottom-gate/bottom-contact, (B) bottom-gate/top-contact, (C) top-gate/top-contact, and (D) top-gate/bottom contact.</td>
</tr>
<tr>
<td>2.</td>
<td>Typical characteristic output and transfer curves in the characterization of OFET devices. The boundary between linear and saturation was labeled in the output curves.</td>
</tr>
<tr>
<td>3.</td>
<td>Representative p-type (1, 2) and n-type (3, 4) conjugated small molecules (1, 2) and polymers (2, 4).</td>
</tr>
<tr>
<td>4.</td>
<td>Hydrogen-bonded pigment-like molecules which have been reported with excellent FET properties. The charge mobility of these two molecules-based devices can be as high as 1.5 cm²/V•S and 0.2 cm²/V•S for epindolidione and quinacridone, respectively.</td>
</tr>
<tr>
<td>5.</td>
<td>The molecular structure of isoindigo (left) and EBI (right) units.</td>
</tr>
<tr>
<td>6.</td>
<td>The molecular structure of the designed isoindigo-Boc and EBI-Boc based polymers (P1, P2). Both polymers can be converted into hydrogen-bonded materials after remove the Boc group using thermal treatment.</td>
</tr>
<tr>
<td>7.</td>
<td>¹H NMR spectrum of isoindigo-Boc in CDCl₃.</td>
</tr>
<tr>
<td>8.</td>
<td>¹H NMR spectrum of EBI-Boc molecule in CDCl₃.</td>
</tr>
<tr>
<td>9.</td>
<td>¹H NMR spectrum of P1 polymer in CDCl₃.</td>
</tr>
<tr>
<td>10.</td>
<td>¹H NMR spectrum of P2 polymer in CDCl₃.</td>
</tr>
<tr>
<td>11.</td>
<td>TGA curves of monomers (isoindigo-Boc, EBI-Boc) and polymers (P1, P2). The heating rate was 10°C/min with nitrogen protection.</td>
</tr>
<tr>
<td>12.</td>
<td>FTIR spectra of the Boc-protected monomers and polymers: (a) P1, (b) isoindigo-Boc, (c) P2, (d) EBI-Boc.</td>
</tr>
<tr>
<td>13.</td>
<td>UV/vis absorption spectra of monomers (isoindigo-Boc, EBI-Boc) and polymers (P1, P2) in solution (dichloromethane), thin film (5mg/ml in dichloromethane spin-coated on glass) and thin film-after annealing (treatment of the thin film in the argon filed glove-box under 200 oC for 5 min).</td>
</tr>
</tbody>
</table>
15. Cyclic voltammograms of the pristine (P1, P2) and thermal annealed (P1’, P2’) polymer thin films on ITO-coated glass substrates. Solution: 0.1 M TBAPF₆-acetonitrile. Potential calculated versus ferrocene. Scan rate: 100 mV s⁻¹; T=25°C. P1’ and P2’ were obtained through thermal treatment of P1 and P2 inside of argon filled glove box with 200°C for 2 min.

16. TFT characteristics of P1 and P1’ based devices

17. Chemical structure of rubrene and a device fabricated based on rubrene single crystal (top view)

18. Chemical structures of the conjugated small molecules used in this work

19. Steps to grow 2D layered single crystals of organic conjugated materials by solution epitaxial growth method (left) and the 2D single crystal of DPPBoc obtained from this method as observed under optical microscope (right)

20. (a-b) The example of mechanical exfoliation by peeling off the graphite into graphene. (c-e) The isoindigo single crystals were observed by optical microscope (d) and tested by AFM (c and e)

21 (a) and (b) are the images of DPP and cyclizedDPP crystal grew by PVD method observed by the optical microscope, respectively
# LIST OF SCHEMES

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Synthesis route for isoindigo-Boc molecules</td>
<td>12</td>
</tr>
<tr>
<td>2. Synthesis route of EBI-Boc molecules</td>
<td>13</td>
</tr>
<tr>
<td>3. Synthesis of the designed polymers P1 and P2</td>
<td>14</td>
</tr>
</tbody>
</table>
PART 1
SYNTHESIS AND CHARACTERIZATION OF NOVEL \( \pi \)-CONJUGATED SMALL MOLECULES AND POLYMERS WITH HYDROGEN BONDING

CHAPTER I
INTRODUCTION

1.1 Organic Field-Effect Transistors (OFETs)

Since the first discovery of conductive polymers in 1970\textsuperscript{th}, organic \( \pi \)-conjugated semiconducting materials have attracted more and more attentions due to their promising applications in the printing electronics.\textsuperscript{1-3} Compare to the conventional silicon-based inorganic electronic materials, organic semiconductors (mainly conjugated polymers and conjugated small molecules or oligomers) have many advantages such as their organic synthetic versatility, low-temperature solution-processability, light-weighting, high flexibility, and so on.\textsuperscript{4} Due to those advantages, organic semiconductors have been extensively studied in the past several decades as the active materials in many electronic applications such as organic light-emitting diodes (OLEDs), organic solar cells (OSCs), organic field-effect transistors (OFETs), sensors, and so on.\textsuperscript{5-7}

Among the various organic materials based electronic devices, organic field-effect transistors (OFETs) is a type of electronic device that using organic semiconducting materials as active materials to amplify and/or switch electrical signals.\textsuperscript{8} With similar
function as the metal-oxide-semiconductor field-effect transistors (MOSFET), OFETs represent a critical building block for the next-generation of printable organic circuits, which could be utilized in many applications including curved flexible displays, electronic papers, and radio frequency identification (RFID) tags.\textsuperscript{9} Other than the practical applications, OFETs also can be used to study the theoretical mechanism of charge carrier transport in the organic semiconductor matrix and provide an insight to the structure-properties relationships of organic semiconducting systems.\textsuperscript{7}

The typical structures of OFET devices are shown in Figure 1.\textsuperscript{10} It is a three-terminal device that contains source, drain and gate electrodes. An insulating layer or called dielectric materials was sandwiched by the active organic semiconductor layer and gate electrode to form a structure similar to a capacitor. Depending on deposition sequences of electrodes, semiconducting materials, and/or dielectric materials in the device fabrication process, four different device configurations can be typically achieved: (A) Bottom-gate/bottom-contact, (B) bottom-gate/top-contact, (C) top-gate/top-contact, and (D) top-gate/bottom contact. We can see the detailed device structures of four configurations in Figure 1.
Figure 1. Typical configuration of OFET device with different configuration. (A) Bottom-gate/bottom-contact, (B) bottom-gate/top-contact, (C) top-gate/top-contact, and (D) top-gate/bottom contact.  

The operation principle of OFET device is similar to that of conventional FET based on inorganic semiconductors. Depending on applying the gate voltage or not, the device can be switched between the ‘on’ and ‘off’ states. When the gate voltage is not applied, the device is in ‘off’ state and there will be no charge carrier existed in the semiconductor layer. In this state, the semiconductor material behaviors like insulating materials and the source-drain current will be near zero. However, when a bias is applied onto the gate electrode, charge carriers will accumulate at the interface between the semiconductor and dielectric materials to form a conduction channel. Then source-drain current will be increased dramatically and the device is transformed into ‘on’ state.
The characterization of OFET devices is usually based on two curves: the output curve and transfer curve (shown in Figure 2). In both curves, the on and off states can be observed depending on the gate voltage and the formation of conduction channel or not. Based on these two curves, the important parameters to evaluate the device performance such as the charge mobility and on/off ratio can be calculated. The charge mobility evaluates the of charge carrier drift velocity per unit of electric field in the semiconducting layer when the device is in the on state. On/off ratio is defined by the difference of currents of the device at ‘ON’ and ‘OFF’ states. Another parameter is the threshold voltage that indicates the gate voltage from which the conduction channel starts to form. Specifically, the charge mobility of the semiconductors in the devices can be extracted from two regimes: (1) the linear regime, where the current changes as a parabola and the performance follows equation below:

\[ I_{DS} = \frac{W}{L} \times \mu C_1 (V_{GS} - V_{TH}) \times V_{DS} \]

and (2) the saturation regime where the source-drain current is irrelevance of source-drain voltage and the mobility is given by equation

\[ I_{DS} = \frac{W}{2L} \times \mu C_1 (V_{GS} - V_{TH})^2, \]

where L is the channel length (length between of the source and drain electrodes that parallel to the current flows), W is the channel width (length of the channel in the direction that perpendicular to the current flows in the transistor) and C is the capacitance of the insulating materials.
As mentioned above, π-conjugated polymers and conjugated small molecules are the two classes of organic semiconductors. Each class of materials has their own pros and cons. Polymers usually have better solution processability and mechanical flexibility due to their higher molecular weight. The charge transport can be preceded in both interchains and intrachains. However, the polydispersity of polymer’s molecular weight may result to a variation of device performance due to the batch-to-batch difference. Conjugated small molecules are easier to purify and thus give high crystalline films. Single crystal-based devices are also available for small molecules.

Figure 2. Typical characteristic output and transfer curves in the characterization of OFET devices. The boundary between linear and saturation was labeled in the output curves.

1.2 Organic Semiconducting Materials

As mentioned above, π-conjugated polymers and conjugated small molecules are the two classes of organic semiconductors. Each class of materials has their own pros and cons. Polymers usually have better solution processability and mechanical flexibility due to their higher molecular weight. The charge transport can be preceded in both interchains and intrachains. However, the polydispersity of polymer’s molecular weight may result to a variation of device performance due to the batch-to-batch difference. Conjugated small molecules are easier to purify and thus give high crystalline films. Single crystal-based devices are also available for small molecules.
Depending on the type of charge carrier generated in OFET devices, organic semiconductors can be divided into n- and p-type materials.\textsuperscript{7,11} For p-type semiconductors, the major charge carrier is negatively charged electron while that for n-type semiconductors is positively charged hole. In Figure 3, several representative p-type and n-type conjugated small molecules and polymers are shown.

To develop a good organic semiconductor, there are many aspects need to be considered. First, the materials should also be environmental stable enough in the devices states when voltage was applied in order to have real application potential. Then, the (macro)molecules should have an idea molecular structure with good coplanarity and energy levels which endow the materials good intrinsic electronic properties. Moreover, the intermolecular packing of the semiconducting materials needs to have maximum intermolecular interactions and \( \pi \)-stacking overlap in order to obtain a smooth intermolecular charge transfer process.

Figure 3. Representative p-type (1, 2) and n-type (3, 4) conjugated small molecules (1, 2) and polymers (2, 4).\textsuperscript{7}
1.3 Hydrogen-bonded Semiconducting Materials\textsuperscript{12-21}

Although great potential have been given, the performances of OFETs are still suffered from their low charge mobility when compared to the inorganic silicon-based devices. One major reason for that is the weak van der Waals interactions existed in the organic semiconducting materials when their film was deposited from the organic solution. These weak interactions usually give a disordered molecular packing in the films and limit the efficient charge transport between the material domains.\textsuperscript{8}

Introducing stronger interactions such as hydrogen-bonding is one strategy reported in the literature to enhance the orientation and packing of molecules in the solid state in order to achieve a high device performance. Many pigment-like molecules with strong intermolecular hydrogen bonding networks such as quinacridone, epindolidione, and diketopyrrolopyrroles (DPP) have been studied in the OFET applications and show very good FET performances. Figure 4 shows the structure of two hydrogen-bonded conjugated small molecules which exhibited excellent FET properties.

![Figure 4. Hydrogen-bonded pigment-like molecules which have been reported with excellent FET properties. The charge mobility of these two molecules-based devices can be as high as 1.5 cm\textsuperscript{2}/V\textcdot S and 0.2 cm\textsuperscript{2}/V\textcdot S for epindolidione and quinacridone, respectively.\textsuperscript{15}](image-url)
Although the molecular packing and orientation may be enhanced by the strong 
hydrogen-bonding interactions, the solution processability of these materials will become 
low since their solubility is dramatically decreased due to the strong intermolecular 
interactions. Using thermal-labile protection group such as the tert-butoxyl carbony (Boc) 
group block the hydrogen-bonding site of the molecules is one way to solve this problem. 
The Boc functionalized molecules can be readily dissolved in common organic solvents 
due to the absence of strong hydrogen bonding interactions, indicating the materials is 
still solution-processable. After remove the Boc group, the free hydrogen-bonding sites 
will be released and the intermolecular hydrogen-bonding networks will be activated.

![Molecular structure of isoindigo (left) and EBI (right) units.](image)

Figure 5. The molecular structure of isoindigo (left) and EBI (right) units.

Here we designed two Boc group functionalized conjugated polymers with latent 
hydrogen bonding on the backbone (see Figure 6). The polymers are based on two 
hydrogen-bonding sites containing structure: isoindigo and 3,3-(ethane-1,2-
diyldiene)bis(6-bromoindolin-2-one) (EBI). Isoindigo is one of the indigoid natural 
organic dyes widely discovered in the nature. EBI has a similar structure to isoindigo but 
with an extended π-conjugation due to the additional propene unit in the middle of two
oxindole rings in the structure. The molecular structures of these two conjugated units are shown in Figure 5. Previous works have proved these two structure-based semiconducting materials have huge potential in the FET application. However, to the best of our knowledge, those studies for the isoindigo and EBI-based polymers are all focused on the normal alkyl chain functionalized materials and the FET properties of hydrogen-bonded isoindigo/EBI based polymers are still lacked. It is necessary to explore the effect of the formation of intermolecular hydrogen-bondings on the physiochemical, molecular packing and charge transport properties of those isoindigo and EBI based materials.

Figure 6. The molecular structure of the designed isoindigo-Boc and EBI-Boc based polymers (P1, P2). Both polymers can be converted into hydrogen-bonded materials after remove the Boc group using thermal treatment.
CHAPTER II

EXPERIMENT

2.1 Materials

9,9-dihexylfluorene-2,7-diboronic acid, bis(1,3-propanediol)ester, 4-dimethylamino-pyridine (DMAP), di-tert-butyl dicarbonate, Pd(PPh3)4, NaHCO₃, K₂CO₃ and the solvents were obtained from Sigma-Aldrich. Anhydrous tetrahydrofuran (THF) was distilled over sodium and freshly used. All the reaction were carried out under N₂ protection.

2.2 Instrumentation

All thermal annealing processing were done in a hot plate under 200 °C inside of argon-filled glove box. ¹H-NMR spectra were recorded using a Mercury 300 spectrometer. UV/Vis absorption spectra were obtained using a Hewlett Packard Model 8453 UV/Vis spectrophotometer. Molecular weights of polymers were determined upon gel permeation chromatography (GPC, Waters 1515 HPLC) equipped with Styragel columns. All measurements were carried out in tetrahydrofuran at 45 °C. Cyclic voltammograms were measured using an electrochemical analyzer from CH Instruments (CHI 608E). Thin films of the two polymers were coated on ITO plates using spin-cast method and then tested in acetonitrile solvent that containing 0.1 M tetrabutylammonium.
hexafluorophosphate salt (TBAPF₆) as electrolyte. Platinum wires were used as reference and counter electrodes. The voltage data were calculated for the standard calomel electrode (SCE). Scan rate: 100 mV s⁻¹; temperature: 20 °C. The thermal gravimetric analysis (TGA) was performed under nitrogen atmosphere (20 ml/ min) using a TA Instrument Model Q500 at a heating rate of 10 °C/min (TGA). Infrared spectra were obtained on Nicolet-6700 FTIR spectrometer by casting films on KBr plates from solution. The heating rate was 20 °C/min. The polymer films were deposited by spin-coating polymer solution in chloroform (8 mg L⁻¹) and thermal annealing at 200 °C. Bottom-gate, top-contact thin-film filed-effect transistors was fabricated to evaluate the polymer semiconductors. An n-doped Si wafer with 300 nm SiO₂ was used as the substrate, where the conductive n-Si layer was used as gate electrode (G) and the SiO₂ as the dielectric (Ci, capacitance of 10 nF cm⁻²). After cleaning the substrate with DI water and acetone, the source (S) and drain (D) electrode pairs were deposited on the surface using gold (50 nm) through a shadow mask. P1 and P2 solution in chloroform (5 mg/ml) were then spin-coated on the top to finish the device fabrication process. The device was treatment upon thermal annealing in argon-filled glove box at 50 °C for 0.5 h and 200 °C for 5 min before the TFT device test, respectively. A channel length (L) of 30 µm and width (W) of 1 mm was employed for the devices. The devices were characterized in vacuum using a Hewlett Packard 4155A semiconductor analyzer. The field-effect mobility was calculated using Eq 1 based on the linear regime of the transfer characteristic curves:

$$\mu = \frac{L}{W \cdot C_i \cdot V_{SD}} \frac{\partial I_{SD}}{\partial V_G}$$  \hspace{1cm} (Eq 1)

where L and W are the channel length and width, and Ci is the capacitance per unit area of the gate dielectric.
2.3 Synthesis

![Chemical structure diagram](image)


**6,6’-Dibromoisoindigo (isoindigo).** In a 100 ml bottom, 6-bromoisatin (1.06 g, 4.72 mmol) and 6-bromooxindole (1 g, 4.72 mmol) were suspended in AcOH (30 ml), then conc. HCl (0.2 ml) was added. The mixture was heated to 117°C to reflux for 24 h. The mixture was allowed to cool to room temperature and filtered. The crude solid product was washed with water, EtOH and AcOEt. After drying, it yielded brown product (1.8 g, yield: 90 %). 1H-NMR (300 MHz, d6-DMSO) δ ppm: 10.05 (s, 2 H), 8.96–8.99 (d, 2 H), 7.15–7.18 (m, 2 H), 6.97–7.00 (d, 2 H).

**Isoindigo-Boc.** In a Schlenk flask, isoindigo (1.25 g, 3 mmol), and DMAP (0.76 g, 6.3 mmol) were dissolved in anhydrous THF (35 ml) at room temperature under nitrogen protection. Di-tert-butyl dicaronate (1.69g, 9 mmol) in anhydrous THF (4 ml) was added in one portion, and then allowed the reaction overnight. The major part of THF was removed by rotary evaporator. The remained mixture was dropped into 5 % NaHCO₃ solution. The forming precipitates were filtered off and washed with water, then redissolved in CH₂Cl₂ and washed three times with water. The organic layer was dried over anhydrous magnesium sulfate and the solvent removed at reduced pressure. The crude product purified by column chromatography on silica gel with hexane : DCM = 1 : 2 as eluent to yield isoindigo-Boc (1.62 g, 87%). 1H-NMR (300 MHz, d1-CDCl₃) δ ppm:
8.83–8.86 (d, 2 H), 8.07–7.08 (d, 2 H), 7.30–7.33 (m, 2 H), 1.67 (s, 18 H). 13C NMR: δ ppm: 165.27, 148.32, 141.92, 131.71, 130.15, 127.73, 127.24, 120.44, 117.83, 85.45, 28.09.

3,3’-(ethane-1,2-diylidene)bis(6-bromo-1-pyropionylindolin-2-one) (1). In a 100 ml round-bottom flask, 6-bromoisatin (6.4 g, 28.4 mmol) was suspended in propionic anhydride (24 ml). Then pyridine (8 ml) was added in the mixture and heated to 116 oC with refluxing. The solution was changed from clear to dark powder suspended after 0.5 h. After cooling, the dark red powder was filtered, washed with acetone, ether and chloroform. The dark insoluble red powder product (1.65 g, yield: 21 %) was used for the next step without further purification.

3,3-(ethane-1,2-diylidene)bis(6-bromoindolin-2-one) (EBI-1). In a 100 ml round-bottom flask, 1 (1 g, 1.8 mmol) was suspended in ethanol (27 ml) with potassium hydroxide (0.2 g, 3.59 mmol) for 0.5 h. After cooling down, the dark solid was filtered, washed with acetone, ether, ethanol, dilute hydrochloric acid and water. The red solid product was obtained (0.51 g, yield: 64 %). 1H-NMR (300 MHz, d6-DMSO) δ ppm:
10.71–10.78 (d, 2 H), 8.61–8.65 (d, 0.8 H), 7.95–8.11 (m, 2.5 H), 6.96–7.19 (d, 4.8 H).

(NMR spectrum is complicate because of the existence of different isomers).

**EBI-Boc.** In a flask, EBI-1 (0.44 g, 1 mmol), and DMAP (0.27 g, 2.2 mmol) were dissolved in anhydrous THF (10 ml) at room temperature under nitrogen protection. Di-tert-butyl dicarbonate (0.57 g, 3 mmol) in anhydrous THF (2 ml) was added in one portion, and then allowed the reaction overnight. The major part of THF was removed by rotary evaporator and the remained mixture was washed with 5 % NaHCO₃ solution. By extracted with DCM solvent, the organic layer was dried over anhydrous Na₂SO₄ and the solvent removed using rotary evaporator. The raw product was then purified by column chromatography on silica gel with hexane : DCM = 1 : 2 as eluent to yield EBI-Boc (0.57 g, 90%). H-NMR (300 MHz, d1-CDCl₃) δ ppm: 8.89 (s, 2 H), 8.08 (s, 2 H), 7.51–7.54 (d, 2 H), 7.31–7.34 (d, 2 H), 1.68 (s, 18 H). 13C NMR: δ ppm: 164.59, 148.83, 140.41, 129.44, 129.11, 127.59, 125.34, 122.21, 121.98, 118.83, 85.01, 28.09.

Scheme 3. Synthesis of the designed polymers P1 and P2.
Poly(isoindigo-Boc-n-hexylfluorene) (P1). Isoindigo-Boc (0.12 g, 0.20 mmol), 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (0.10 g, 0.20 mmol, 1.00 eq) and Pd(PPh$_3$)$_4$ (11 mg, 0.01 mmol) were dissolved in toluene (4 ml) and degassed with nitrogen for 10 min. Then a degassed solution of Na$_2$CO$_3$ (0.08 g, 0.7 mmol) in DI-water (2 ml) was added. After stirring at 90 °C for 7 hours, the purple reaction mixture was cooled down and diluted with 50 mL DCM. After washed with brine (2×50 ml) and water (50 ml), the organic phase was dried with MgSO$_4$ and filtered with Celite to evaporate the solvent. The obtained materials were dissolved in minimum amount of DCM again and re-precipitated in methanol to give a purple solid. Soxhlet extraction with methanol and n-hexane was then carried out to remove the oligomers and impurities, giving final P1 powders (0.11 g, yield: 64 %). Molecular weight (GPC, THF): Mw = 21.4 KDa, Mn = 8.9 KDa, PD = 2.4. $^1$H-NMR (300 MHz, d$_1$-CHCl$_3$) δ ppm: 9.04–9.19 (m, 2 H), 8.87–8.92 (m, 2 H), 8.10–8.37 (m, 2 H), 7.51–8.37 (br, 6 H), 1.96–2.23 (br, 4 H), 1.67–1.75 (m, 18 H), 1.08–1.25 (br, 16 H), 0.74–0.83 (br, 6 H).

Poly(EBI-Boc-n-hexylfluorene) (P2). The synthesis followed the same procedure as described for P1 except that the monomer isoindigo-Boc was replaced by EBI-Boc. Mw = 21.4 KDa, Mn = 8.9 KDa, PD = 2.4. $^1$H-NMR (300 MHz, d$_1$-CHCl$_3$) δ ppm: 9.04 (s, 2 H), 8.10–8.34 (m, 2 H), 8.10–8.34 (m, 4 H), 7.53–8.83 (br, 6 H), 7.28–8.42 (br, 2 H), 2.08 (s, 4 H), 1.68–1.75 (s, 18 H), 1.08–1.25 (br, 16 H), 0.77 (s, 6 H).

P1’ and P2’: P1’ and P2’ were obtained upon thermal annealing P1 and P2 at 200 °C inside of Ar-filled glove box, respectively.
CHAPTER III

RESULTS AND DISCUSSION

3.1 Materials Synthesis

The t-Boc group protected isoindigo and EBI small molecules were synthesized as shown in Scheme 1 and Scheme 2. Isoindigo and EBI pigment molecules were synthesized first and then reacted with bicarbonate compound to give the two small molecules. Figure 7 and 8 showed the $^1\text{H}$ NMR spectrum of isoindigo-Boc and EBI-Boc small molecules in the deuterated chloroform. Each peak in the spectrums can be assigned to the protons in the molecular structure with expected integration area, indicating the successful synthesis of the designed molecules. Based on these two monomers and another commercialized monomers (9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester, Sigma-Aldrich, 99%), the isoindigo and EBI based polymers were synthesized using palladium-catalyzed Suzuki coupling reaction (P1 for isoindigo-based polymer, P2 for EBI-based polymer). The $^1\text{H}$ NMR spectrums of these two polymers were showed in Figure 9 and Figure 10.
Figure 7. $^1$H NMR spectrum of isoindigo-Boc in CDCl$_3$.

Figure 8. $^1$H NMR spectrum of EBI-Boc molecule in CDCl$_3$.

Figure 9. $^1$H NMR spectrum of P1 polymer.
3.2 Thermal properties

The thermal behavior of Boc-protected small molecules and polymers was studied by thermogravimetric analysis (TGA) technique. As shown in Figure 11, two obvious weight loss processes for all the four samples were observed. The first weight loss stage for all the four conjugated materials occurred between 150~200°C, which should originate from the decomposition of t-Boc group at high temperature. The observed weight loss percentages of four materials (isoindogo-Boc, EBI-Boc, P1, and P2) are 30.9%, 31.4%, 20.7% and 25.1%, respectively, which agrees very well to the theoretical calculated weight loss percentages of t-Boc removal for those four (macro)molecules. For the second weight loss stages, the occurrence of these processes all started above 300 °C. This indicated the excellent thermal stability of these materials after remove the Boc group.

Figure 10. $^1$H NMR spectrum of P2 polymer.
Figure 11. TGA curves of monomers (isoindigo-Boc, EBI-Boc) and polymers (P1, P2). The heating rate was 10 °C/min with nitrogen protection.

3.3 FT-IR Spectroscopy.

To further prove the successful deprotection of t-Boc group in the monomers and polymers, kinetic Fourier transform infrared (FT-IR) spectroscopy of the four materials was carried out to monitor the evolution of functionalities in the (macro)molecules at different temperature. For P1 and isoindigo-Boc, as shown in Figure 12 (a) and (b), it is easily found that there are two peaks at 1782 cm\(^{-1}\) (C=O) and 1050 cm\(^{-1}\) (C-H) were disappeared when the temperature was increased to around 180°C. Clearly, the elimination of these two peaks is due to the decomposition of t-Boc groups at increased temperature. In addition, in the region of 3100–3450 cm\(^{-1}\), a new broad absorption band was formed as the temperature was raised up. This can be ascribed to formation of intermolecular hydrogen bonding after the t-Boc was removed and free N-H bonds were
released. For P2 and EBI-Boc, similar peak disappearance and generation induced by the removal of Boc group can be observed as shown in Figure 12 (c) and (d). Interestingly, when comparing the broad absorption band around 3200 cm\(^{-1}\) of two monomers and polymers, it can be observed that the bands for monomers are much larger than that of the polymers. This indicates the hydrogen-bonding in small molecules is much stronger than that in the polymer films after the Boc group was decomposed. Obviously, this is very reasonable because that, in the polymer films the formation of hydrogen bonding is much difficult due to the long polymer chain entanglement. Although free N-H bonds were generated, the low mobility of the rigid polymer chains will keep the polymer chains away without formation of hydrogen bonding.

![FTIR spectra](image)

**Figure 12.** FTIR spectra of the Boc-protected monomers and polymers: (a) P1, (b) isoindigo-Boc, (c) P2, (d), EBI-Boc.
3.4 Optical Properties.

The UV/Vis optical absorption of the two monomers and corresponded polymers are recorded in solution, pristine films and annealed film states to study the effect of Boc removal and hydrogen-bonding formation on their optical absorption properties. For isoindigo-Boc small molecules, absorption peaks of spin-casted thin films have a red shift when compared with that in the solution state. This is ascribed to the closer packing of (macro)molecules in solid state than that in solution state. After annealing at 200 °C for 5 min, the absorption peak of isoindigo films became broader and red-shifted. This is due to the formation of H-bonds which will enhance the interaction between different molecules and results a better efficient conjugation. For both of the P1 and P2 films after thermal treatment, the onset absorption wavelength showed a red shift compared with the pristine thin film, which is in accordance with the isoindigo-Boc small molecules for the more ordered molecular packing.

For EBI small molecules, same red shift was observed for the solid film when compare to the solution absorption. However, for the annealed films, an unexpected slightly hypochromic shift was observed compared to the pristine films.
Figure 13. UV/vis absorption spectra of monomers (isoindigo-Boc, EBI-Boc) and polymers (P1, P2) in solution (dichloromethane), thin film (5mg/ml in dichloromethane spin-coated on glass) and thin film-after annealing (treatment of the thin film in the argon filled glove-box under 200 °C for 5 min).

Figure 14. Single crystal structures of EBI-Boc and EBI small molecules.
To explain the blue shift of the annealed EBI films, the single crystal structure of both the EBI-Boc and EBI molecules were studied. As shown in Figure 14, EBI-Boc showed a 2D brickwall packing motif while the hydrogen-bonded EBI single crystal exhibited a herribone packing motif. In the brickwall packed EBI-Boc crystals, a nearly 50% π electron cloud overlap is occurred between each adjacent molecules along the π-π stacking direction. On the other hand, for the herribone packed EBI crystal, only edge-to-face overlap can be observed and no face-to-face π electron cloud overlap is existed.4 Clearly, after removing the Boc group, the overall π-π stacking is largely decreased, which can be explained as the reason for the blue shift for the EBI small molecules after formation of hydrogen-bonding.

3.5 Electrochemical Properties.
The electrochemical properties of the synthesized polymers before and after thermal treatment were investigated by cyclic voltammetry (CV) measurements. CVs were recorded in 0.1 M solution of TBAPF6/acetonitrile versus the potential of the SCE, which was calibrated by the ferrocene-ferrocenium (Fc/Fc+) redox couple in the same solvent. CV curves are shown in Figure 15. Based on the oxidation/reduction onset potential, the HOMO/LUMO energy levels were calculated using the equation that LUMO = HOMO + \( E_{\text{g opt}} \). All the calculated HOMO, LUMO, and bandgap data is summarized in Table 1. As illustrated in Figure 15 and Table 1, bandgaps of polymers after annealing are smaller than that of the polymers before annealing. The oxidation onset potential for the annealed polymer films are also decreased when compared to the pristine films.
Figure 15. Cyclic voltammograms of the pristine (P1, P2) and thermal annealed (P1’, P2’) polymer thin films on ITO-coated glass substrates. Solution: 0.1 M TBAPF₆-acetonitrile. Potential calculated versus ferrocene. Scan rate: 100 mV s⁻¹; T=25 °C. P1’ and P2’ were obtained through thermal treatment of P1 and P2 inside of argon filled glove box with 200 °C for 2 min.

Table 1. Optical and electrochemical properties of the pristine and annealed P1 and P2 films.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>λ_{abs, max} [nm]</th>
<th>Oxidation</th>
<th>Reduction</th>
<th>E_{opt}^{c}</th>
<th>E_{cc}^{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In DCM In thin film</td>
<td>onset[V]</td>
<td>HOMO [eV]</td>
<td>LUMO [eV]</td>
<td>[eV]</td>
</tr>
<tr>
<td>P1</td>
<td>559</td>
<td>558</td>
<td>0.61/–5.41</td>
<td>–1.01/–3.79</td>
<td>1.81/1.61</td>
</tr>
<tr>
<td>P1’</td>
<td>--</td>
<td>558</td>
<td>0.33/–5.13</td>
<td>–1.23/–3.57</td>
<td>1.73/1.56</td>
</tr>
<tr>
<td>P2</td>
<td>538</td>
<td>546</td>
<td>0.69/–5.49</td>
<td>–1.25/–3.55</td>
<td>1.91/1.94</td>
</tr>
<tr>
<td>P2’</td>
<td>--</td>
<td>551</td>
<td>0.66/–5.46</td>
<td>–1.14/–3.66</td>
<td>1.85/1.80</td>
</tr>
</tbody>
</table>

3.6 OFET Performance

To investigate the effects of hydrogen-bonding formation on the charge transport properties of two polymers, OFET devices of both polymers were fabricated
in the bottom gate, top contact configuration, with the simple Si/SiO$_2$/Au/polymers architecture. The FET behavior of both polymers before and after thermal annealing at 180°C for 30 min was tested. All polymer devices showed p-type properties. Figure 16 showed the transfer characterization curves of the P1 based OFET devices before (left) and after (right) removing the side chains by thermal treatment. The hole mobility of P1 can be calculated from these curves to be 1.8 * $10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$ with a current On/Off ratio of 1 * $10^4$, by sweeping the gate voltage ($V_G$) from -100 V to 20 V under a source-drain voltage ($V_{SD}$) was 50 V. In contrast, the thermal annealed devices of P1 (named P1’) showed a hole mobility 8.7 * $10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ under the same condition. Compared to the pristine devices, a two magnitude (480 times) of charge mobility were obtained. For P2 based transistors, no FET behavior was observed before thermal anneal and only with the formation of hydrogen-bonding networks in the materials, a hole mobility of 4.18*10$^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ can be observed. The enhanced hole mobilities of two polymers before and after annealing suggest that the removal of t-Boc group and the formation of hydrogen-bonding would increase the interaction and the $\pi$-stacking of polymers and results in a better performance.

Figure 16. TFT characteristics of P1 and P1’based devices.
In summary, two \( \pi \)-conjugated small molecules and polymers based on isoindigo and EBI were synthesized and characterized. All the small molecules and polymers contain a thermal liable t-Boc group which can be removed by thermal anneal at 180\(^\circ\)C as proved by TGA and FT-IR results. After the Boc group was removed, intermolecular hydrogen-bonding networks can be formed in the materials. The effect of this hydrogen-bonding formation on the optical absorption, electrochemical properties, and the charge mobility properties of the polymers are investigated. A 480 times increase of hole mobility is showed for P1 and for P2 only the hydrogen-bonded films after thermal treatment showed FET behaviors. These results proved the possibility of using hydrogen-bonding for the improvement of charge transport properties of organic semiconducting materials.
PART 2

PREPARATION OF 2D SINGLE CRYSTALS FOR ORGANIC FIELD-EFFECT TRANSISTORS

CHAPTER I

INTRODUCTION

The determination of accurate structure-relationship of organic semiconducting materials in the organic field-effect transistor applications is a very challenging topic in today’s organic electronic field. Various parameters such as the structural changes resulted varied molecular packing and complicated film morphology that typically showed in thin film of these materials can have huge impact on the final observed device performance. These issues become more severe when it comes to the conjugated polymer systems in which the conformation disordered is prevail and their morphology is easily to be changed depending on the device fabrication conditions, substrate nature, etc. Consequently, property structure-device performance correlation is usually not available by only direct comparisons of measured mobilities between devices prepared from different labs and this for sure provide no benefit for high performance OFET materials design. Their charge mobility is also not very low due to the lack of highly ordered packing between molecules (for example, the totally disordered conjugated polymers usually give a low charge mobility in the range of $10^{-6}$ to $10^{-4}$ cm$^2$/V•s).
However, for organic single crystals, due to their lack of defect, impurities, and grain boundaries, the materials provided an excellent platform to study the intrinsic charge transport property as well as the structure-properties relationship of organic semiconductors.\textsuperscript{25-27} The close and regular packing of molecules in the single crystal also can facilitate the efficient charge hopping between adjacent molecules and give very high charge mobilities in the OFET devices. Therefore, single crystal based OFET devices have been extensively studied in the past several decades and many of them show extremely high charge mobilities. For example, the single crystal based FET devices of rubrene showed a hole mobility of 15-40 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} which is already comparable to the amorphous silicon based inorganic FET devices (Figure 17).\textsuperscript{28}

![Figure 17. Chemical structure of rubrene and a device fabricated based on rubrene single crystal (top view).\textsuperscript{25,28}](image)

In the fabrication of single crystal based OFET devices, the source and drain electrodes are usually deposited by thermal evaporation or electron-beam evaporation method by which a thickness in the range of tens of nanometers is usually adopted. Therefore, in order to have an adequate contact between the organic crystal piece and the electrode pad, a thickness for organic single crystals that is comparable to the electrode thickness is highly desired. In this sense, 2D thin-layered organic single crystals which have a large length and width but relative small height provide a good choice for the purpose. In this part of work, efforts on the exploring of 2D single crystals based several conjugated small molecules including DPPBoc, isoindigo, DPP, and cyclized DPP are discussed.
CHAPTER II

MATERIALS AND APPARATUS

All the materials including DPPBoc, isoindigo, DPP, and the cyclized DPP were synthesized according to the procedures in literatures. All the solvents were obtained from Sigma-Aldrich. Four conjugated small molecules are listed below.

![Chemical structures of the conjugated small molecules used in this work.](image)

Figure 18. Chemical structures of the conjugated small molecules used in this work.

Petri dishes, 5 mL vials are used for the solution epitaxial growth method; scotch tape, silicon wafer and the optical microscope were used for the mechanical exfoliation method; tube furnace, glass tube, ceramic boat, vacuum pump and the argon were used for the physical vapor deposition method.
CHAPTER III

GROWTH PROCESS AND RESULTS

**Solution Epitaxial Growth.** A Petri dish was first cleaned by sonicating acetone and isopropanol for 15 min, and then blown dry using a N₂ gas flow. 25 mL of de-ionized water was poured into the Petri dish. Solution of ThioDPP-Boc small molecules were dissolved into the dichloromethane with the concentrate was 1 mg/mL, which was dropped on the water surface. Then the solution extended fast on the water surface due to the surface tension difference between water and the solution surfaces. As strong π-π molecular interactions can be formed between the molecules of organic semiconductors, the aggregation of those molecules can be occurred to generate micrometer-sized 2D single crystals. Several hours later, another several drops of the same solution were dropped onto the water surface, inducing the epitaxial growth of small 2D single crystals based on previously formed seed crystals along the surface direction. In ideal conditions, 2D single crystal of organic semiconductors with sizes of millimeters or centimeters are expected to be obtained, which is beneficial for the convenient fabrication of single crystal-based FET devices. Solvent type and solution concentration are the major parameters to control the crystal growth process of organic semiconducting materials. A proper solvent and concentration of organic semiconductor solution can efficiently avoid
polycrystalline growth, which is essential for solution-epitaxial growth of uniform and high quality organic 2D single crystals. The process and the result are depicted in Fig. 18. We can see from the images under the optical microscope that the size of the crystals can reach up to several hundred micrometers, which is big enough for the OFET fabrication. Besides, multiple-layered structures were observed, as indicated by the contrast change in different region of the single crystal pieces.

Figure 19. Steps to grow 2D layered single crystals of organic conjugated materials by solution epitaxial growth method (left) and the 2D single crystal of DPPBoc obtained from this method as observed under optical microscope (right).
**Mechanical Exfoliation Method.**

Gently tap the isoindigo crystals onto a 2 inches piece of Scotch tape and then perpendicularly stick it to another piece of tape. Press the two pieces of tapes and then gently pull them apart. Re-adhere one of two pieces of tape (usually the top piece of tape) to another piece of new tape for gently pressing and pulling apart. Repeat these steps for several times until the “film” is dull red. The number of the repeated adhering and peeling cycles of the crystals on the Scotch tapes depend on the initial size and amount of crystals. After finishing the mechanical exfoliation steps, the obtained single crystal pieces are transferred to silicon wafer by adhering the sticky side of the bottom piece of tape to the silicon wafer surface. Then optical microscopy and AFM technique can be used to examine the overall size and thickness of the exfoliated single crystal pieces. Fig. 19 (a) depicted the exfoliation process of graphite into the few layer graphene in which a similar principle is used for the exfoliation of organic single crystals in current study. Figure (b) is the AFM images of mechanical exfoliated isoindigo crystal pieces using the exfoliation process as described above. We can see the thickness of the crystal was about 80 nm, and the overall size was around 10 µm. Although the overall size of the obtained crystal is still difficult for fabricating the OFET device (as the typical source-drain channel used in OFETs currently is in the range of tens of micrometers), these results suggested the feasibility of using mechanical exfoliation method to achieve thin film single crystals of organic semiconductors.
Physical Vapor Deposition Method (PVD). The materials were firstly needed to be purified by the tube furnace in the ceramic boat which was put into the glass tube. The glass tube was firstly evacuated by the pump until the pressure was about 10 mm/Hg and the argon was then flowed into the tube furnace with the flow speed was 10 mL/min to eliminate the influence of air, with the pressure was around 100 mm/Hg. The temperature was then raised to transform the materials from solid state into gas phase, deposited at the cooled zone carried by the flow gas for about 8 hours, which was 250 °C for sublimating DPP and 280 °C for cyclized DPP, respectively. The sublimation temperatures for different materials are about 100 °C lower than the final decomposition temperature tested by the TGA.
After sublimation at least 3 times, the materials can be used to grow the 2D single crystals by PVD. Followed by the argon flowed into the tube furnace with the speed was at 200-300 mL/min for about 1 h under room temperature, the materials was heated into gas phase, carried by the flow gas with the flow speed was about 15 mL/min and then deposited on the cooled substrate to grow the 2D single crystal. The temperature for DPP and cyclized DPP were 290 °C and 310 °C, respectively. The crystals of the two materials on the source-drain electrodes prepatterned on the silicon wafer were observed under the optical microscope in Fig. 21. Further OFET performances were characterized by other student, I will not discuss it here.

Figure. 21 (a) and (b) are the images of DPP and cyclizedDPP crystal grew by PVD method observed by the optical microscope, respectively.
CHAPTER IV

CONCLUSION

In this part of work, three methods including solution epitaxial growth, mechanical exfoliation and the physical vapor deposition were used to grow the 2D organic single crystals of conjugated small molecules. The sizes of the crystals obtained from solution epitaxial growth as well as the PVD can reach to several hundreds of micrometer to fabricate the OFET devices. Mechanical exfoliation method gave a very thin crystal layers (less than 100 nm) but with relative small size which make it difficult for device fabrication.


