SYNTHESIS OF A FULLERENE ACCEPTOR WITH VISIBLE ABSORPTION
FOR POLYMER SOLAR CELLS

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SYNTHESIS OF A FULLERENE ACCEPTOR WITH VISIBLE ABSORPTION
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Thesis

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ABSTRACT

As the global energy need is soaring in recent years, limited fossil energy cannot satisfy our need, and it will be exhausted within the next century. Therefore, we must develop alternative energy resources. Solar energy is considered to be one of the most attractive resources to address the growing global energy need for a clean, abundant and renewable source. A polymer solar cell (PSC) is a device, which can convert solar energy into electric energy. A polymer solar cell often needs an active layer called bulk heterojunction (BHJ), which consists of a donor material and acceptor material. Recently, many efforts have made to develop donor materials, but not many breakthroughs have been made in the acceptor materials. The most widely used acceptor material is [6, 6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM). However, it does not have strong absorption in visible range. Almost no contribution of the current is from the light absorbed by the acceptor. The goal of this research was to develop a novel fullerene material, which has some absorption in visible range. Molecules with conjugate dyes linked to the fullerene have been designed and synthesized. The acceptors are expected contribute to light harvesting. The conjugated materials have been characterized based on their structures, using \(^1\)H and \(^{13}\)C NMR and MS. UV-vis absorption spectra showed the better absorption in the visible range in comparison with PC₆₁BM. The device performance will be characterized in the future.
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CHAPTER I

INTRODUCTION

1.1 Solar Cell

A solar cell is a device that converts the solar energy directly into electricity. In the past few years, the price of fossil fuels has been increasing. Research and development efforts in alternative forms of power focus on finding alternate energy sources to replace or lessen the use of fossil fuels. Among the new type of energies, solar energy is considered to be one of the most attractive ways to address growing global energy needs because it is a clean, abundant, and renewable resource. Silicon-based solar cells take the main market because they represent the most mature solar cell technology which has high power conversion efficiency (PCE) of more than 25%. However, the large-scale solar commercial development of silicon-based solar cells is limited due to the relatively high cost and pollution. Alternatively, organic photovoltaic solar cells have been rapidly developing as one of the most promising candidates for low-cost solar cells, owing to the possibility of fabricating large-area and flexible solar cells by solution processing, which is much cheaper than silicon-based solar cells.

1.2 Inorganic Solar Cells

In the past thirty years, inorganic solar cells (single crystal, amorphous Si) have taken up a large market share. The PCE has reached 25%, which means silicon-based solar cells can be put into mass production. For the organic solar cell, the PCE is
much lower than the inorganic solar cell, basically below 10%.[6][7][8][9] There are two main reasons why the PCE of OSCs is low. First, the inorganic semiconductors usually have 3D crystal lattice. As a result, the material has individual LUMOs and HOMOs. While, the molecular interaction in organic solar cell materials is relatively low. Due to the weak interaction, it is difficult for organic semiconductors to form a 3D crystal lattice. [18] This results in LUMOs and HOMOs which cannot form a covalent band and valance band. Charges can only be transported by hopping instead of being transported within a band. The charge carrier mobility becomes lower. The second reason is that the exciton binding energy of organic materials is larger than inorganic material. In the inorganic semiconductor, a separated electron and hole are formed after absorbing light. While in organic solar cells, an exciton (an electron accompanying a hole) is formed instead of a separated electron and hole. Strong electric field is needed to dissociate the exciton. However, the price of inorganic solar cells is quite expensive.

1.3 Organic Solar Cells (OSCs)

OSCs are solar cells that use small organic molecules or polymer material. It is a newly developed technique following the silicon-based solar cells.

1.3.1 A Brief History of OSCs

In 1986, Tang fabricated the first two-layer organic photovoltaic cell. The PCE was about 1%. It was a breakthrough in the history of organic solar cells because the charge generation efficiency is relatively independent of the bias voltage and the fill factor value reached 0.65.[10] Organic solar cells started to develop during the 1990’s. In the year of 1991, Hiramoto made the first dye/dye bulk heterojuction(BHJ) photovoltaic (PV) by co-sublimation.[11] After that, Sariciftici made a breakthrough of
the bulk polymer heterojunction PV in 1992. The research group found that the spectral response of the film with C$_{60}$ is significantly enhanced due to the enhancement in the photo generation efficiency.

1.3.2 Structure

![Figure 1 Architecture of Bulk Heterojunction OSCs](image)

The organic solar cells apply solution processing layer by layer. As shown in figure 1, the BHJ PV device has a sandwich structure. The first layer is glass, which plays the role as a base layer. Indium tin oxide (ITO) is used for the anode and aluminum is used for the cathode. Poly [3, 4- (ethylenedioxy) thiophere]-poly (styrenesulfonate) (PEDOT: PSS) are used as the hole- conducting layer. The active layer, which is the most important layer, is right above the PEDOT: PSS layer. Bulk heterojunction donor and acceptor are blended in this layer. The composition and morphology of active layer will influence the efficiency of the solar cell. Therefore, scientists are trying to develop better active layer based on the working principle of organic solar cell.
1.3.3 Working Principle

Figure 2 Working Principles of Heterojunction OSCs\textsuperscript{[18]}

The mainstream PSC devices adopt the concept of a BHJ, where an active layer contains a p-type donor and an n-type acceptor, forming an interpenetrating nanoscale network. A semiconductor contains excess holes it is called "p-type", and when it contains excess free electrons it is known as "n-type". The electron flow of heterojunction solar cell is shown in figure 2. The donor material absorbs sunlight and an exciton is created, which is a bounded electron and hole pair. The exciton diffuses to the donor – acceptor interface, and dissociates into a hole and an electron. The electron is transferred to and collected by the cathode. The hole is transferred and collected by the anode. Then, the electric current forms.\textsuperscript{[19]}

1.3.4 Figures of Merit

Typical current-voltage curves of OSCs are shown in figure 3. There are four major parameters. Short circuit current ($J_{SC}$) is defined as the current of the solar cell device when no reverse bias is applied. Open circuit voltage ($V_{OC}$) is defined as the device voltage when no current flows through the cell. Fill factor (FF) is defined as the ratio between maximum power point of the device and $J_{SC} \times V_{OC}$. Power Conversion Efficiency (PCE) is defined as the ratio between the output electrical
energy versus the input solar energy. The maximum output electrical energy is equal to $J_{SC} \times V_{OC} \times FF$.

$$PCE = \frac{J_{SC} \times V_{OC} \times FF}{P_{in}} \quad (1)$$

Among all of the parameters, PCE is the most important because it indicates the ability of the solar cell to convert solar energy to electrical energy. According what we discussed, three main approaches can be applied to improve PCE. Larger $J_{SC}$, larger $V_{OC}$ or larger fill factor will all improve higher PCE. Therefore, how to enhance $J_{SC}$, $V_{OC}$ or fill factor become an initial question for scientists.

Figure 3 Current-Voltage Curves of OSCs

1.3.4.1 High $J_{SC}$

High $J_{SC}$ can contribute to high PCE. Three strategies can be used to create a higher circuit current.

The first method is creating a new molecule with higher absorption. Absorbing more light energy will give a higher value of $J_{SC}$. When the band gap is low, the absorption spectrum range can better match the solar spectrum, which has a highest
emission wavelength around 700nm. In 2013, Yang Yang’s group in UCLA reported that a low band gap polymer (bandgap< 1.4eV), poly [2,7-(5,5-bis-(3,7-dimethyloctyl)-5H-dithieno[3,2-b:2’,3’-d]pyran)-alt-4,7-(5,6-difluoro-2,1,3-benzothiadiazole)] with a bandgap of 1.38eV. The absorption spectrum showed that the new molecule better much the solar spectrum. As a result, the device made from the new molecule performed well. The PCE can reach10.6% from the literature.

The other way is to make a higher charge mobility. The efficiency of charge transportation will be higher than before. In 2007, S. R. Marder developed a molecule with the charge motility as high as 1.3×10^{-2} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}. Device measurement showed that the material to be a promising material for all-polymer solar cells.

Third, a good pathway of charge is important, too. If the electron and hole cannot be separated efficiently, there will be a higher chance of charge recombination. In 2012, Dr. Guillermo C. Bazan and Dr. Alan J. Heeger publish a paper in Nature materials, reporting that a crystalline small molecule force the fullerene to form percolated pathways to the electrode. Therefore, the solution-processed solar cell reached 6.7% PCE.

1.3.4.2 High $V_{OC}$

The energy level of alignment donor and acceptor in OSCs is shown in figure 4. To obtain high $V_{OC}$, a suitable energy level of donor and acceptor is needed. $V_{OC}$ is proportional to $\Delta E_2$ (the energy gap between the highest occupied molecular orbital (HOMO) of donor material and the lowest unoccupied molecular orbital (LUMO) of acceptor material). That is to say, both a lower HOMO of the donor and a higher LUMO of the acceptor will contribute to a higher $V_{OC}$. However, a problem arises when the HOMO of the donor becomes low. The optical band gap becomes bigger when the HOMO of the donor is lowered. It goes against the previous objective,
which aims to lower the band gap so that the absorption light can better match the solar cell. Hence, only to lower the HOMO of the donor is not enough to improve $V_{OC}$. Another solution for improving $V_{OC}$ is to enhance the LUMO of the acceptor. This method is acceptable because it will not influence the band gap. However, it has an influence on the dissociation of the exciton. The energy offset is defined as $\Delta E_1$ (the energy difference between LUMOs of the donor and the acceptor).\textsuperscript{25} A large energy offset is good for the exciton to dissociate. Therefore, if the LUMO of the acceptor is set to be higher, the energy offset is lower than before. As a result, it is more difficult for dissociation. Usually, $\Delta E_1$ should be larger than 0.3 eV.\textsuperscript{26}

![Figure 4 Energy Level of Donor and Acceptor in OSCs][18]

Taking the entire factor into consideration, it is not enough just to consider lowering the HOMO of the donor and higher the LUMO of the acceptor. Opposite result will introduced when the HOMO of the donor becomes lower and the LUMO of the acceptor becomes higher. That is to say, a compromised energy level should be found.
1.4 Donor of OSCs

Much work has been done towards donor material. Basically, there are three
generation donor materials in the development history. The first generation is
represented by poly (p-phenylene vinylene) (PPV), which is shown in figure 5A. PPV
has a conjugated structure consisting of alternating single and double bonds within
polymer chain. In 1990, Burroughes et al. discovered the electroluminescence in a
PPV.\textsuperscript{[27][28]} PPV are conjugated polymers whose behavior being associated with the p
molecular orbitals delocalized along the polymer chain. The Second generation donor
is represented by P3HT, as shown in figure 5B. P3HT has thiophene unit structure in
backbone instead of benzene ring. The thiophene ring performs better electron
donating properties than benzene ring.\textsuperscript{[29]} The latest generation is called Donor-
Acceptor (D-A) copolymer, which means a donor material contents both donor and
acceptor molecule moieties. By designing molecules in this way, it is easy to tune the
energy level of donor material. For example, the molecule DTDCTB shown in figure
5C has both electron withdrawing and electron donating moieties.
1.5 Acceptor of OSCs

![Different Acceptor Molecules](image)

**Figure 6 Different Acceptor Molecules**

1.5.1 Conventional Acceptor

Much work has been done towards donor material. But much less work has been done for acceptor. Up to now, the most widely used acceptor is Phenyl-C$_{61}$-butyric acid methyl ester (PC$_{61}$BM, also PCBM) (shown in figure 6, left).

PCBM was prepared by Hummelen and Wudlin in 1995. It is widely used because it has three important advantages. First, it offers the advantage of good solubility in organic solvents such as chloroform, chlorobenzene, dichlorobenzene. That is to say, PCBM can be used in solution processing, which is cheap and convenient. Second, it has higher electron mobility, which is important because all the mechanisms in polymer solar cells are based on the electron mobility. Additionally, PCBM has higher electron affinity. Since PCBM is an acceptor, electron withdrawing is important. However, two weak points including weak absorption in the visible region and a low LUMO energy level limit the better performance of PCBM. Weak absorption in the visible region limits its contribution to light harvesting in the PV conversion. The low LUMO energy level of the acceptor material results in lower $V_{OC}$ of the PSCs, since the $V_{OC}$ is proportional to the difference between the LUMO
energy level of the acceptor and the HOMO energy level of the donor. As a result, the PCE of the OSCs based on poly (3-hexylthiophene) (P3HT), PCBM is usually 2-4%, which is far away from satisfactory. \cite{18}

1.5.2 Newly Designed Novel Acceptors

Recently, scientists and researchers are trying hard to find novel acceptors to replace PCBM. The acceptors are expected to have better performance.

1.5.2.1 Acceptor 1

In 2011, Mikroyannidis and his colleagues synthesized a simple yet effective acceptor F for OSCs (shown in figure 6, middle). Compared the new molecule with PCBM, it has many advantages. First, the novel molecule F has a higher LUMO energy level than PCBM, which is 0.25eV higher than PCBM. Also, the molecule is more soluble in common organic solvents than PCBM. The reason is that F has increased organic moiety. Third, F shows stronger and wider light absorption than PCBM, especially in the range of 250-290 nm. Therefore, OSCs based P3HT and F shows a higher PCE than the conventional one, which is about 4.23\%. \cite{15}

1.5.2.2 Acceptor 2

Also in 2011, Mikroyannidis published another paper reporting that his newly designed acceptor (shown in figure 6, right). Combined with P3HT, the device has a PCE of 5.32% when A is casted from subsequent thermal annealing. \cite{30} Three reasons can explain the higher PCE. First, the novel molecule F has a higher LUMO energy level than PCBM, which is 0.15eV higher than PCBM. Second, the increment of J_{SC} contributes a lot to higher PCE. The increment of crystallinity of film plays an important role in the hole mobility. Third, PSCs made from A have a broader light absorption spectrum.
1.6 Molecular Design

Last year, we have synthesized C$_{60}$PhFFDCV (shown in figure 7A) and it showed better light absorption than PCBM. However, the absorption within the visible light is still far from satisfaction. Therefore, to obtain higher conversion efficiency, a new molecule (shown in figure 7B) was designed based on the principles of getting high PCE.

![Figure 7 The Novel Molecules](image)

The new molecule is expected to have a better performance than any precious. The conjugated structure is expected to ensure a suitable energy level and higher charge mobility. The C$_{60}$ alkyl ball has a strong ability of accepting electrons, which is important for an acceptor material. The introduction of the alkyl chain is expected to increase the solubility of the molecule. The DTDPP moiety is also electron withdrawing group and has low-lying LUMO energy level. Also, DTDPP is a dye which has a good visible light absorption. As reported, copolymers containing DTDPP and other moieties, for example, bithiophene , the charge transport properties are high of both hole and electron, 0.1cm$^2$/(V·s) and 0.09cm$^2$/(V·s)$^{[31]}$, respectively. Most importantly, the PCEs can reach 2.3-3%. $^{[32]}$ $^{[33]}$
CHAPTER II

EXPERIMENTAL

2.1 Materials

In this section, the chemicals and equipment will be introduced. All the materials were bought from Aldrich or Sigma.

2.1.1 Chemicals

Reactants:

Fluorine (Aldrich, 98%), bromine (Aldrich, 98%), 1-bromohexane (Aldrich, 98%), bis(pinacolato) dinoron (Sigma, 98%), tetrakis (triphenylphosphine) palladium (Pd(PPh$_3$)$_4$) (Aldrich), C$_{60}$ (Sigma), thiophene-2-carbonitrile (Sigma, 98%), 1-bromodecane (Sigma, 98%), N-Bromosuccinimide (NBS) (Aldrich, 98%).

Solvents:

Chloroform, dichloromethane (CH$_2$Cl$_2$), dimethyl sulfoxide (DMSO), dimethylformamide (DMF), tetrahydrofuran (THF), ethyl acetate (EA), 2-methyl-2-butanol, ethanol, hexane, toluene, methanol.

Inorganic Chemicals:

Sodium hydroxide (NaOH) (Sigma-Aldrich, ≥98.0%), tetrabutyl ammonium bromide (Sigma-Aldrich, ≥98.0%), potassium acetate (AcOK) (Sigma-Aldrich, ≥99.0%), potassium carbonate (K$_2$CO$_3$) (Sigma-Aldrich, ≥99.0%), manganese dioxide (MnO$_2$) (Sigma-Aldrich, ≥99.99%), acetic acid (HAc) (Sigma-Aldrich, ≥99.7%) Potassium tert-butoxide (t-BuOK) (Sigma-Aldrich, ≥99.0%).
Others:

Distilled water, liquid nitrogen, silica gel column, N\textsubscript{2}.

2.1.2 Equipment

Ice bath, oil bath, two-necked flask (500mL), dropping funnel (100mL), Büchner funnel, Büchner flask, round-bottomed reaction flask (250mL), Erlenmeyer flask (250mL), separatory funnel (500mL), schlenk flask (100mL), stir bars, pipettes.

2. 2 Synthesis

The synthetic rout will be introduced step by step. In total, there are nine steps for the whole molecular synthesis.
2.2.1 Synthesis of DTDPP

A mixture of t-BuOK (8.20 g, 73.1 mmol) and 2-thiophenecarbonitile (4.00 g, 36.6 mmol) was dissolved in 2-methyl-2-butanol (30 mL) in a round bottomed flask.
At 90 °C, a solution of diethyl succinate (2.90 g, 16.6 mmol) in 2-methyl-2-butanol (15mL) was added dropwise into the flask. The mixture was stirred at 90 °C for 20 h.

After cooled to 50 °C, methanol (20mL) and glacial acetic acid (20 mL) was added. The mixture was stirred for another 30 min before being filtered. The filter cake was washed by large amount of water and then methanol, and then the solid was dried by vacuum to give DTDPP as a dark brown solid (2.20, 7.32 mmol).

The yield of the reaction was 44%.

\[ ^1 \text{H NMR (300 MHz, DMSO): } \delta \text{ (ppm) 11.25 (s, 2H), 8.21–8.20 (d, 2H), 7.97–7.95 (d, 2H), 7.31–7.29 (t, 2H).} \]

\[ ^{13} \text{C NMR (75 MHz, DMSO): } \delta \text{ (ppm) 162.13, 136.67, 133.14, 131.78, 131.31, 129.21, 109.08. MALDI–TOF mass m/z: [M+H]^+ \text{ calcd. for C}_{14}\text{H}_9\text{N}_2\text{O}_2\text{S}_2, 301.0; \text{ found, 301.0.}} \]

2.2.2 Synthesis of C\textsubscript{10}DTDPP

\[
\begin{align*}
\text{DTDPP (2.00 g, 6.66 mmol) was dissolved in DMF (60 mL), and then K}_2\text{CO}_3 (3.50 g, 25.4 mmol) and a small amount of 18-crown-6 was added. The reaction mixture was heated at 110 °C for 1 h. A solution of 1-bromodecane (5.50 g, 22.6 mmol) in DMF (30mL) was added dropwise. The dark red mixture was maintained at 110 °C overnight.}
\end{align*}
\]

\[
\begin{align*}
\text{After cooled to ambient temperature, CH}_2\text{Cl}_2 (300 mL) and water (200 mL) was added, and the layers were separated. The organic layer was then washed by water (3 \times 100 mL). The organic layer was dried by anhydrous Na}_2\text{SO}_4. \text{ The pure product was}
\end{align*}
\]
obtained through silica gel column chromatography (CH\textsubscript{2}Cl\textsubscript{2}:hexane = 2:1) as a dark red solid (1.99 g, 3.43 mmol).

The yield of the reaction was 52%.

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm) 8.93–8.92 (d, 2H), 7.64–7.63 (d, 2H), 7.30–7.27 (t, 2H), 4.10–4.04 (t, 4H), 1.80–1.70 (m, 4H), 1.46–1.26 (m, 28H), 0.90–0.86 (t, 6H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm) 161.29, 139.95, 135.24, 130.62, 129.73, 120.56, 107.61, 42.19, 31.85, 29.92, 29.49, 29.26, 29.21, 26.84, 22.65, 14.10. MALDI–TOF mass m/z: [M+H]\textsuperscript{+} calcd. for C\textsubscript{34}H\textsubscript{49}N\textsubscript{2}O\textsubscript{2}S\textsubscript{2}, 581.3; found, 581.3.

2.2.3 Synthesis of C\textsubscript{10}DTDPP-Br

\begin{center}
\includegraphics[width=0.8\textwidth]{figure11.png}
\end{center}

Figure 11 Synthetic Route of C\textsubscript{10}DTDPP-Br

C\textsubscript{10}DTDPP (200 mg, 0.34 mmol) was dissolved in CHCl\textsubscript{3} (20 mL). N-bromosuccinimide (NBS, 54 mg, 0.30 mmol) was added to the solution in ice/water bath. After stirred for 1 h, saturated Na\textsubscript{2}SO\textsubscript{3} solution (10 mL) was added, and then the mixture was stirred for another 15 min.

The organic layer was separated and concentrated. The residue was purified through a silica gel column to give a dark red solid (126 mg, 0.19 mmol).

The yield of the reaction was 63%.

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm) 8.94–8.93 (d, 1H), 8.68–8.66 (d, 1H), 7.66–7.64 (d, 1H), 7.30–7.23 (m, 2H), 4.09–3.97 (m, 4H), 1.80–1.68 (m, 4H), 1.46–1.27 (m, 28H), 0.90–0.86 (t, 6H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm) 161.25, 161.09, 140.43, 138.52, 135.48, 135.04, 131.63, 131.22, 130.89, 129.71, 128.64,
2.2.4 Synthesis of 2, 7-Dibromofluorene

\[ \text{Fluorene (20.00g, 0.12mol), chloroform (100mL) and a stir bar were added into a two-necked flask (500mL). One neck was equipped with rubber plug, while the other one was equipped with a dropping funnel (100mL), which was loaded with bromine (38.55g, 0.24mol). The rubber plug was equipped with a syringe needle to keep the pressure in the flask the same with the barometric pressure. The flask was put in ice bath, avoiding light. The bromine was added dropwise. After adding all the bromine, ice bath was removed. The solution was stirred at room temperature for 24h. The crude product was filtered and washed with chloroform (70mL). Then, the product crystallized from chloroform as the reaction proceeded.} \]

The product was filtered by Büchner funnel and washed with chloroform three times. After this, the product was crystallized from chloroform. The product (29.62g, 0.09mol) was white crystal.

The yield of the reaction was 76%.

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) (ppm) 7.67–7.68 (s, 2H), 7.59–7.62 (d, 2H), 7.49–7.53 (d, 2H), 3.87 (s, 2H). \(^{13}\)C NMR (300 MHz, CDCl\(_3\)): \(\delta\) (ppm) 144.74, 139.65, 130.10, 128.25, 121.13, 120.91, 36.52.

2.2.5 Synthesis of 9, 9-Dihexyl-2, 7-Dibromofluorene
18

Figure 13 Synthetic Route of 9, 9-Dihexyl-2, 7-dibromofluorene

Sodium hydroxide (16.00g) was dissolved in distilled water (32g), obtaining 50% aqueous sodium hydroxide. 2, 7-Dibromofluorene (6.48g, 20mmol), tetrabutyl ammonium bromide (0.80g, 2.5mmol) were dissolved in DMSO (44mL). The solution was added into a 250mL flask together with a stir bar. Then, aqueous sodium hydroxide was added to the flask. The flask was put in the oil bath for 10 minutes at 60 °C. After heat equilibrium, 1-bromohexane (8.25g, 55mmol) was added. The reaction system contained two phases, oil phase and water phase. The color of the oil phase changed from pink to red and finally purple. The mixture reacted for 8h.

After the reaction, the mixture was extracted with EA (100mL) in 500mL separatory funnel and washed by distilled water three times. The upper solution was poured into an Erlenmeyer flask. Sodium sulfate anhydrous (about 5g) was added to dry the solution. The solution was evaporated by rotary evaporator. The crude product was crystallized from absolute ethanol and yellowish powder was obtained. The powder was purified by silica gel column chromatography (hexane). A white powder (7.91g, 16.1mmol) was obtained. [34]

The yield of this reaction was 80 %.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ (ppm) 7.51–7.54 (d, 2H), 7.47 (d, 2H), 7.44 (s, 2H), 1.89–1.95 (m, 4H), 1.04–1.17 (m, 12H), 0.76–0.81 (t, 6H), 0.54–0.59 (m, 4H).

2.2.6 Synthesis of FB
2-Bromo-9-fluorenone (1.34g, 5.18 mmol), AcOK (5.08g, 51.8 mmol), anhydrous THF (90mL) and a stir bar were added to a 250mL Schlenk flask. Then, the solution was put into liquid nitrogen to cool down. Bis (pinacolato) diboron (1.71g, 6.73 mmol) and \((\text{Pd}(\text{PPh}_3)_4)(0.240g, 0.208 \text{mmol})\) were added at low temperature. The mixture was degased by Freeze-Pump-Thaw method three times on the vacuum line. After getting rid of majority of the air, the reaction took place at the temperature of 80 °C, 24h. The mixture turned yellow around 3h.

The crude product was filtered to get rid of AcOK and separated by silica gel column chromatography (CH_2Cl_2). The solvent was evaporated by rotary evaporator and the product turned out to be yellow powder (1.41g, 4.60 mmol).

The yield of this reaction was 83%.

\(^1\text{H NMR}\) (300 MHz, CDCl_3): δ (ppm) 8.31 (s, 1H), 7.94–7.97 (d, 1H), 7.67–7.69 (d, 1H), 7.55–7.58 (d, 1H), 7.53 (s, 1H), 7.48–7.50 (d, 1H), 1.37 (s, 12H). \(^{13}\text{C NMR}\) (300 MHz, CDCl_3): δ (ppm) 193.73, 146.87, 144.18, 141.42, 134.53, 134.46, 133.33, 130.46, 129.44, 124.21, 120.64, 119.58, 84.09, 24.85.

2.2.7 Synthesis of FFBr
2,2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)fluoren-9-one (0.306g, 1.00mmol), 9,9-Dihexyl-2, 7-dibromofluorene (3.44g, 7.00mmol), K$_2$CO$_3$ (1.38g, 10mmol), THF (30mL), distilled water (15mL) and a stir bar were added to a 100mL schlenk flask. Then, the solution was put into liquid nitrogen to cool down. Then, Pd(PPh$_3$)$_4$ (0.068g, 0.06mmol) was added in low temperature. The mixture was degased for three times on the vacuum line. After getting rid of the air, the reaction took place at the temperature of 80 ℃, overnight.

The crude product was separated by silica gel column chromatography (hexane: CH$_2$Cl$_2$=3:1). The solvent was evaporated by rotary evaporator and the product turned out to be orange powder (468mg, 0.79mmol).

The yield of this reaction was 79%.

$^1$H NMR (300 MHz, CDCl$_3$): δ (ppm) 7.99 (s, 1H), 7.70–7.81 (m, 3H), 7.47–7.63 (m, 8H), 7.31–7.35 (t, 1H), 1.93–2.09 (m, 4H), 1.08–1.27 (m, 12H), 0.76–0.87 (t, 6H), 0.87–0.89 (m, 4H). $^{13}$C NMR (300 MHz, CDCl$_3$): δ (ppm) 193.74, 153.21, 151.22, 144.23, 143.05, 142.42, 139.93, 139.51, 139.00, 134.86, 134.74, 134.42, 133.08, 130.02, 128.92, 126.18, 125.80, 124.34, 122.80, 121.26, 121.13, 120.96, 120.61, 120.31, 120.14, 55.56, 40.25, 31.41, 29.56, 23.71, 22.51, 13.93.

2.2.8 Synthesis of FF-C$_{10}$DTDPP

![Diagram of FF-C$_{10}$DTDPP synthesis]

Figure 16 Synthetic Route of FF-C$_{10}$DTDPP
FFB (140 mg, 0.22 mmol), C10DTDPP-Br (145 mg, 0.22 mmol), K2CO3 (300 mg, 2.20 mmol) and Pd(PPh3)4 (13 mg, 0.01 mmol) was added in a schlenk flask. CHCl3 (15 mL), EtOH (3 mL) and water (10 mL) was added as mixed solvent. The reaction mixture was degased three times, and it was heated at 80 °C for 24 h. After cooled to ambient temperature, it was dilute with CHCl3 (100 mL) and washed by water (3 × 50 mL). The organic layer was dried by anhydrous Na2SO4.

The organic layer was concentrated, and the residue was purified through silica gel column chromatography (CH2Cl2: hexane = 2:1) to give a dark purple solid (150 mg, 0.14 mmol).

The yield of the reaction was 64%.

1H NMR (300 MHz, CDCl3): δ (ppm) 9.02–9.01 (d, 1H), 8.95–8.93 (d, 1H), 8.01 (s, 1H), 7.83–7.50 (m, 12H), 7.35–7.28 (m, 3H), 4.19–4.08 (m, 4H), 2.12–2.09 (m, 4H), 1.89–1.73 (m, 4H), 1.50–1.28 (m, 28H), 1.17–1.06 (m, 12H), 0.91–0.86 (m, 6H), 0.79–0.71 (m, 10H). 13C NMR (75 MHz, CDCl3): δ (ppm) 193.89, 161.45, 161.24, 152.14, 152.00, 150.78, 144.32, 143.15, 142.52, 141.62, 140.21, 139.92, 139.39, 139.18, 136.85, 135.05, 134.93, 134.83, 134.49, 133.19, 132.08, 130.41, 129.90, 129.00, 128.56, 128.44, 125.90, 125.45, 124.49, 124.43, 122.93, 121.08, 120.69, 120.48, 120.41, 120.38, 120.28, 107.97, 107.78, 55.52, 42.27, 40.36, 31.87, 31.45, 30.01, 29.98, 29.62, 29.58, 29.56, 29.52, 29.50, 29.30, 29.27, 29.25, 26.93, 26.88, 23.82, 22.65, 22.53, 14.08, 13.95. MALDI–TOF mass m/z: [M+H]+ calcd. for C72H87N2O3S2, 1091.6; found, 1091.6.

2.2.9 Synthesis of C60FF-C10DTDPP
FF-C\textsubscript{10}DTDPP(120 mg, 0.11 mmol) was dissolved in CHCl\textsubscript{3} (5 mL) and THF (10 mL). p-Toluenesulfonylhydrazide (40 mg, 0.22 mmol) and two drops of glacial acetic acid was added. The solution was heated reflux for 8 h. After cooled to ambient temperature, the solvent was removed by vacuum. The residue was dissolved in pyridine (15 mL), followed by the addition of sodium methoxide (12 mg, 0.22 mmol). The suspension solution was stirred at ambient temperature for 3 h before added into a degased C\textsubscript{60} (80 mg, 0.11 mmol) solution in toluene (100 mL) under nitrogen atomosphere. The reaction mixture was stirred at 90 °C for 24 h. The solvent was removed by a rotary evaporator, and the residue was purified through silica gel column chromatography (toluene: hexane = 5:1) to give a dark purple solid (38 mg, 0.02 mmol) in 18% yield. $^1$H NMR (300 MHz, CDCl\textsubscript{3}): $\delta$ (ppm) 9.28 (s, 1H), 9.03–9.02 (d, 1H), 8.95–8.94 (d, 1H), 8.84–8.81 (d, 1H), 8.14–8.08 (m, 2H), 7.98–7.95 (d, 1H), 7.85–7.50 (m, 10H), 7.31–7.28 (t, 1H), 4.18–4.07 (m, 4H), 2.11–2.05 (t, 4H), 1.88–1.73 (m, 4H), 1.50–1.27 (m, 28H), 1.12–1.02 (m, 12H), 0.91–0.85 (m, 6H), 0.75–0.71 (m, 10H). $^{13}$C NMR (75 MHz, CDCl\textsubscript{3}): $\delta$ (ppm) 161.41, 161.19, 152.15, 152.05, 150.82, 147.86, 147.50, 145.52, 145.36, 145.28, 145.24, 144.77, 144.73,
144.69, 144.67, 144.64, 144.59, 144.48, 143.87, 143.40, 143.34, 143.32, 143.30, 143.16, 143.09, 142.53, 142.19, 142.14, 141.74, 141.30, 141.20, 140.95, 140.78, 140.72, 140.34, 140.06, 139.91, 139.85, 139.35, 139.31, 139.10, 136.93, 135.09, 131.91, 130.45, 129.86, 128.83, 128.58, 128.36, 127.75, 127.36, 126.08, 125.46, 125.16, 124.46, 124.06, 121.37, 120.56, 120.46, 120.44, 120.30, 120.27, 107.92, 107.73, 78.43, 55.44, 46.67, 42.25, 40.56, 31.87, 31.60, 30.01, 29.83, 29.56, 29.53, 29.52, 29.30, 29.29, 29.26, 26.92, 26.89, 24.00, 22.66, 14.16, 14.13, 14.09. MALDI–TOF mass m/z: M⁺ calcd. for C₁₃₂H₈₆N₂O₂S₂, 1794.6; found, 1794.7.
3.1 Discussion of Molecular Design

The molecule can be divided into three parts. \( \text{C}_{60} \) and Fluorene can increase conjugation. Alkyl chain- part can increase solubility. DTDPP has a strong electron withdrawing property.

3.1.1 \( \text{C}_{60} \) and Fluorene-- Increase Conjugation

\( \text{C}_{60} \) and fluorene were designed to increase conjugation. \[^{[18]}\] Conjugation along the backbone forms extended electron states which determine energy levels. Also it has processing advantages. \( \text{C}_{60} \) are easily dissolved in toluene and 1, 2-Dichlorobenzene (ODCB).

3.1.2 Alkyl Chain--Increase Solubility

A good solubility is vital for an acceptor molecule in OSCs because solution processing can be applied to donor material. Apart from the processability issue, good solubility also plays an important role in crystallinity, which will determine the performance. The degree of solubility is determined by various structure factors, including the chain length of the aliphatic groups, the polarity of the attached substituents, backbone rigidity. To increase the solubility of the molecule, the branched alkyl chains are more effective than their straight-chain counterparts.\[^{[18]}\]
Therefore, the structure in the middle, which contains fluorene and alky chains, is designed to increase the solubility of the molecule.[35]

3.1.3 DTDPP--Strong Electron Withdrawing Property

There are two reasons that can be used to explain why DTDPP functionality was chosen to be part of the molecule. First, as an acceptor material, attracting electrons is very important because the electrons, dissociated from exciton, will be transported to acceptor part. The DTDPP group has high electron affinity and electron-transport property due to the electron-withdrawing effect.[36][37] Second, it is known from the literature that cyano group had a low-lying LUMO so that it can play the role as an electron acceptor.[38][39]

3.2 Discussion of Suzuki Reaction Mechanism

![Figure 18 Reaction Mechanism of the Suzuki Reaction](image)

In a Suzuki reaction[40][41], palladium (Pd) (0) plays the role of catalyst. Pd (0) is easy to oxidize in the open air. Therefore, getting rid of the oxygen before the reaction
is necessary. First, palladium takes oxidation addition reaction with the halide 2 to form the organopalladium species 3. Then, the base reacts with 3 to give intermediate 4. Also, the other reactant 2 reacts with base and gives intermediate 6. Third, intermediate 4 and 6 react and give the organopalladium species 8. Reductive elimination of 8 and gives desired product 9, which successfully links reactants 2 and 5. At the same time, the palladium forms.

3.3 Result and Discussion of 2, 7-Dibromofluorene

Figure 19 \(^1\)H-NMR of 2, 7-Dibromofluorene

\(^1\)H-NMR of 2, 7-Dibromofluorene (Figure 19) shows that there are six aromatic hydrogen atoms and two aliphatic hydrogen atoms.
Figure 20 $^{13}$C-NMR of 2, 7-Dibromofluorene

$^{13}$C-NMR (Figure 20) shows that there 6 different aromatic carbon atoms and the one peak in aliphatic carbon area corresponds to the carbon in position 9.

The reaction to synthesize discussion of 2, 7-dibromofluorene is an exothermic reaction and gives off a lot of heat at the beginning of this reaction. Therefore, bromine was added drop wise and the reaction took place in ice bath in case of too many side reactions.

A relatively big stir bar or mechanical stirrer is needed was needed because the product was not easy to dissolve in chloroform.

A lot of product (nearly 2/3) was in the mother solution after the first recrystallization. Therefore, it is necessary to recrystallize the product in mother solution again to prevent wasting product.
3.4 Result and Discussion of 9, 9-Dihexyl-2, 7-Dibromofluorene

![Fig 21](image)

**Figure 21** $^1$H-NMR of 9, 9-Dihexyl-2, 7-Dibromofluorene

$^1$H-NMR (Figure 21) shows that there are six aromatic hydrogen atoms. There are more aliphatic hydrogen atoms, which corresponds to the successful linking of alkyl chains.

In order to give 2, 7-Dibromofluorene and NaOH enough time to react to get carbanion, which can react with 1-bromohexane. 1-bromohexane (8.252g) was added after heat equilibrium under stirring. As a result, the reaction is more efficient.
3.5 Result and Discussion of FB

Figure 22 $^1$H-NMR of FB

$^1$H-NMR (Figure 22) shows that there are 7 aromatic hydrogen atoms. The strong peak in aliphatic hydrogen atoms region represents successful linking of boronic ester.
Figure 23 $^{13}$C-NMR of FB

The strong peak in $^{13}$C-NMR (Figure 23) shows that there are 12 aliphatic carbon atoms, which corresponds to the $-\text{CH}_3$ structure. Also, the number of aromatic carbon is 12 and the peak in 193.73ppm corresponds to the carbon atom in the functional group C=O.

Anhydrous THF was used in this reaction. If water exists in the reaction system, the product will react with one of the raw material 2-Bromo-9-fluorenone. The side reaction is similar to the reaction of next step. AcOK is a relatively weak base. The usage of AcOK is another way to prevent the side reaction.

It is vital to separate the crude product as soon as possible when using the silica gel column chromatography. The longer time was used, the fewer products were obtained. The reason is that pH of silica gel is less than 7; the product is easy to degrade to in an acid environment. Therefore, the yield will go down if the product stays long in silica gel column.
3.6 Result and Discussion of FFBr

Figure 24 $^1$H-NMR of FFBr

$^1$H-NMR (Figure 24) shows that there are 13 aromatic hydrogen atoms. The similar peaks in aliphatic hydrogen atoms region with 9, 9-dihexyl-2, 7-dibromofluorene, represents successful linking of the two conjugated structure.
The $^{13}$C-NMR (Figure 25) shows that there are more aromatic carbon atoms in this molecule. Also, the disappearance of the strong peak of $–CH_3$ and the appearance of the seven aliphatic carbon atoms peak show the successful liking of the two conjugated structure.

This reaction is not as reactive as the reaction which gives FB. Therefore, $K_2CO_3$ is used instead of AcOK because $K_2CO_3$ is not as weak as AcOK. Also, distilled water is used to dissolve $K_2CO_3$ in order to get more bases involved in the reaction system. Since water is used, there is no need to use anhydrous THF.
3.7 Result and Discussion of DTDPP

![H-NMR of DTDPP](image1)

Figure 26 $^1$H-NMR of DTDPP

$^1$H-NMR of 2, 7-Dibromofluorene (Figure 26) shows that there are four aromatic hydrogen atoms.

![C-NMR of DTDPP](image2)

Figure 27 $^{13}$C-NMR of DTDPP

$^{13}$C-NMR (Figure 27) shows that there 7 different aromatic carbon atoms.
Figure 28 Reaction Mechanism of DTDPP

Figure 28 shows us the reaction mechanism of the reaction of DTDPP. The negatively charged carbon atom in the middle of the diethyl succinate attacked the positively charged carbon atom in the carbonitrile group. The nitrogen atom will be negatively charged and it will attack the positively charged carbon atom which is linked to the double bond oxygen atom. The negatively charged ethyl oxide group will leave the molecule and the carbon on the newly born ring will attack the carbonitrile again the same mechanism will be repeated. Finally the DTDPP will form.
3.8 Result and Discussion of C$_{10}$DTDPP

$^1$H-NMR (Figure 29) shows that there are three kinds of aromatic hydrogen atoms. There are more aliphatic hydrogen atoms, which corresponds to the successful linking of alkyl chains.

Figure 29 $^1$H-NMR of C$_{10}$DTDPP

$^{13}$C-NMR (Figure 30) of C$_{10}$DTDPP
$^{13}$C-NMR (Figure 30) shows that there 7 different aromatic carbon atoms and aliphatic hydrogen carbons added.

3.9 Result and Discussion of $\text{C}_{10}\text{DTDPP-Br}$

![Chemical structures and NMR spectra](image)

Figure 31 $\text{C}_{10}\text{DTDPP-Br}_2$ and $\text{C}_{10}\text{DTDPP-Br}$

$^1$H-NMR (Figure 32) shows that there are 5 aromatic hydrogen atoms. The more peaks in aliphatic hydrogen atoms region represents successful linking of bromine atom.

$^1$H-NMR (Figure 32) shows that there are 5 aromatic hydrogen atoms. The more peaks in aliphatic hydrogen atoms region represents successful linking of bromine atom.
$^{13}$C-NMR of C$_{10}$DTDPP-Br

$^{13}$C-NMR (Figure 33) shows that there 7 different aromatic carbon atoms and aliphatic carbons added.

C$_{10}$DTDPP react with NBS and the fifth position of the thiophene ring will be replaced by bromine. In case of side reaction 2 Br. Basically there are three strategies to control the ratio between the two products. First, the ratio between C10DTDP and NBS is controlled to be 1:0.85. Secondly, NBS was added while stirring. Third, the reaction was taken place in ice bath. In this case, the yield of this step can be about 75%.
3.10 Result and Characterization of FF-C$_{10}$DTDPP

$^1$H-NMR (Figure 34) shows that there are 18 aromatic hydrogen atoms and 67 aliphatic hydrogens. The similar peaks in aliphatic hydrogen atoms region and aliphatic hydrogens region with C$_{10}$DTDPPBr and FFB, represents successful linking of the two conjugated structure.

Figure 34 $^1$H-NMR of FF-C$_{10}$DTDPP

$^1$H-NMR (Figure 34) shows that there are 18 aromatic hydrogen atoms and 67 aliphatic hydrogens. The similar peaks in aliphatic hydrogen atoms region and aliphatic hydrogens region with C$_{10}$DTDPPBr and FFB, represents successful linking of the two conjugated structure.

Figure 35 $^{13}$C-NMR of FF-C$_{10}$DTDPP
The $^{13}$C-NMR (Figure 35) shows that there are more aromatic carbon atoms and aliphatic carbon atoms in this molecule which indicates the successful linking of the two conjugated structure.

3.11 Result and Discussion of C$_{60}$FF-C$_{10}$DTDPP

Figure 36 $^1$H-NMR of C$_{60}$FF-C$_{10}$DTDPP

$^1$H-NMR (Figure 36) shows that there are 18 aromatic hydrogen atoms 68 aliphatic hydrogens.

Figure 37 $^{13}$C-NMR of C$_{60}$FF-C$_{10}$DTDPP

The $^{13}$-NMR (Figure 37) shows more peaks in the region of 120-160ppm, which represents successful linking with the structure of C$_{60}$. 
In conclusion, the designed molecule has been successfully synthesized and characterized. Absorption spectra of PCBM and $C_{60}$FFPhDCV and $C_{60}$FF-$C_{10}$DTDPP in both in film and solution have been obtained.

![Figure 38 UV–Vis Absorption Spectra of PCBM and $C_{60}$FFPhDCV in Film and Solution](image-url)
The absorption of C$_{60}$FFPhDCV was investigated in both dilute chloroform solution and thin film. From figure 38, it can be concluded that the novel acceptor has a better absorption in the visible region. Especially in the form of thin film, the absorption is even broader. That is to say, it has better ability to absorb solar energy, which will result in higher PCE.

Figure 39 UV–Vis Absorption Spectra of PCBM and C$_{60}$FF-C$_{10}$DTDPP in Film and Solution

The absorption of C$_{60}$FF-C$_{10}$DTDPP was investigated in both dilute chloroform solution and thin film. From figure 39, it can be concluded that the novel acceptor has a better absorption in the visible region. Especially in the form of thin film, the absorption is even broader. The reason is that, in dilute solution, the aim is to detect the absorption of one molecule. While in the form of thin film, the $\pi$-$\pi$ stacking among the conjugated structure exists, resulting in the red-shift of absorption.
Compared to C_{60}FFPhDCV, C_{60}FF-C_{10}DTDPP has a plateau in the visible region between 550nm - 600nm, that is to say, it has better ability to absorb solar energy, which will result in higher PCE.

In the future work, more detailed photophysical and electrochemical properties will be characterized, and the device performance will be tested.
REFERENCES


