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Molecular Design of New Small Molecules and Polymers: Synthesis, Characterization and Application in Organic Solar Cells

Liu Xinli

A thesis submitted in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

Principal Supervisor: Professor WONG Wai Yeung, Raymond

Hong Kong Baptist University

September 2013
Declaration

I hereby declare that this thesis represents my own work (except for some data which were obtained from the collaborators) which has been done after registration for the degree of PhD at Hong Kong Baptist University, and has not been previously included in a thesis, dissertation submitted to this or other institution for a degree, diploma or other qualification.

Signature: ____________________________

Date: September 2013
Abstract

The molecular design, synthesis, spectroscopic and photophysical characterization of a new series of organic small molecules and transition metal-containing polymers incorporating different π-conjugated chromophores are discussed. The applications of some of these compounds in bulk heterojunction (BHJ) organic solar cells are also outlined.

Chapter 1 contains a brief overview on the background of organic solar cells, their structures and performance in solution-processed organic BHJ devices.

Chapter 2 presents the synthetic methodology and characterization of a series of new dipyrrin-based materials and their application in organic solar cells. In this section, four metal-based metallopolymers for organic solar cells have been designed, synthesized and two of them have been fabricated for BHJ organic solar cells. Through the alternation of different metal ions and boron element in the same dipyrrin framework, a series of dipyrrin-based metal complexes and BODIPY-containing compounds have been synthesized. Electrochemical analysis and DFT calculations proved that M4 with BODIPY-based structure is more efficient in optimizing the HOMO-LUMO energy level which further increases the $V_{oc}$ value.

A full account of the preparation, characterization, photophysical and thermal
properties of a new series of benzo[1,2-b:4,5-b']dithiophene (BDT), cyclopenta[2,1-b:3,4-b']dithiophene (CPT) and triphenylamine (TPA) centered small molecules are presented in chapters 3, 4 and 5, respectively. Different acceptor-donor-acceptor (A-D-A) based materials were prepared and employed in organic solar cells in order enhance the power conversion efficiency (PCE) of the devices. Some of the materials have been found to show higher PCEs of up to 3.91%. Given the excellent solution-processability as well as performance advantage, this work provides us a feasible strategy to develop low-cost and high PCE materials in solar cell applications, which would help small molecular organic solar cells to reach a level of practical applications.

In chapter 6, four low-bandgap Pt-containing polymers were synthesized and characterized by a variety of techniques. Among them, the largest $\lambda_{\text{onset}}$ of 699 nm in solution and $\lambda_{\text{onset}}$ of 736 nm in the thin film of P6 were observed and the corresponding energy gap $E_g$ was estimated to be 1.77 eV and 1.68 eV, respectively. After evaluating these oxidation and reduction potentials, P6 also showed the smallest band gap of 1.65 eV with the corresponding HOMO and LUMO energy levels of -5.17 eV and -3.52 eV, respectively. Also, the molecular weights of these polymers were examined by the GPC method. The highest $M_n$ of 24.0 kDa and $M_w$ of 50.4 kDa with the PDI of 2.10 were observed in P8.
Chapter 7 and 8 present the concluding remarks and the experimental details of the work described in Chapters 2-6.
Acknowledgements

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supporting during my course of study, to my wife for her love and personal support and to my daughter for her trust.
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<tr>
<td>M</td>
<td>Transition metal</td>
</tr>
<tr>
<td>Ar</td>
<td>Aryl</td>
</tr>
<tr>
<td>'Bu</td>
<td>tert-Butyl</td>
</tr>
<tr>
<td>&quot;Bu</td>
<td>n-Butyl</td>
</tr>
<tr>
<td>Et</td>
<td>Ethyl</td>
</tr>
<tr>
<td>OMe</td>
<td>Methoxy</td>
</tr>
<tr>
<td>Ph</td>
<td>Phenyl</td>
</tr>
<tr>
<td>R</td>
<td>Alkyl</td>
</tr>
<tr>
<td>TMS</td>
<td>Trimethylsilyl</td>
</tr>
<tr>
<td>X</td>
<td>Halogen</td>
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<tr>
<td>AcOH</td>
<td>Acetic acid</td>
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<tr>
<td>CHCl₃</td>
<td>Chloroform</td>
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<tr>
<td>CH₂Cl₂</td>
<td>Dichloromethane</td>
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<tr>
<td>CO</td>
<td>Carbonyl</td>
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<tr>
<td>DMF</td>
<td>N,N-Dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>Et₂O</td>
<td>Diethyl ether</td>
</tr>
<tr>
<td>EtOH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>NBS</td>
<td>N-Bromosuccinimide</td>
</tr>
<tr>
<td>NEt₃</td>
<td>Triethylamine</td>
</tr>
<tr>
<td>'Pr₂NH</td>
<td>Diisopropylamine</td>
</tr>
<tr>
<td>PCBM</td>
<td>[6,6]-Phenyl C₆₁ butyric acid methyl ether</td>
</tr>
<tr>
<td>P3HT</td>
<td>Poly(3-hexylthiphene)</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
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<td>---------</td>
<td>------------</td>
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<tr>
<td>$E_g$</td>
<td>Energy gap</td>
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<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>ppm</td>
<td>Part per million</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>h</td>
<td>Hour</td>
</tr>
<tr>
<td>s</td>
<td>Singlet</td>
</tr>
<tr>
<td>d</td>
<td>Doublet</td>
</tr>
<tr>
<td>dd</td>
<td>Doublet of doublet</td>
</tr>
<tr>
<td>t</td>
<td>Triplet</td>
</tr>
<tr>
<td>m</td>
<td>Multiplet</td>
</tr>
<tr>
<td>br</td>
<td>Broad</td>
</tr>
<tr>
<td>MALDI-TOF</td>
<td>Matrix-assisted laser desorption/ionization</td>
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<tr>
<td>TDDFT</td>
<td>Time-dependent density functional theory</td>
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<tr>
<td>$M^+$</td>
<td>Molecular ion</td>
</tr>
<tr>
<td>$m/z$</td>
<td>Mass to charge ratio</td>
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<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
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<td>GPC</td>
<td>Gel permeation chromatography</td>
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<td>PL</td>
<td>Photoluminescence</td>
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<tr>
<td>UV/Vis</td>
<td>Ultraviolet-visible</td>
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<tr>
<td>BHJ</td>
<td>Bulk heterojunction</td>
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<tr>
<td>OLEDs</td>
<td>Organic light-emitting diodes</td>
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<tr>
<td>OPV</td>
<td>Organic photovoltaic</td>
</tr>
<tr>
<td>PSCs</td>
<td>Polymer solar cells</td>
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<tr>
<td>MLCT</td>
<td>Metal-to-ligand charge transfer</td>
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<tr>
<td>ca.</td>
<td>Calculated</td>
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<tr>
<td>$S_0$</td>
<td>Singlet ground state</td>
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<td>$S_1$</td>
<td>Singlet excited state</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
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<tr>
<td>$T_1$</td>
<td>Triplet excited state</td>
</tr>
<tr>
<td>DP</td>
<td>Degree of polymerization</td>
</tr>
<tr>
<td>PDI</td>
<td>Polydispersity index</td>
</tr>
<tr>
<td>$M_n$</td>
<td>Number-average molecular weight</td>
</tr>
<tr>
<td>$M_w$</td>
<td>Weight-average molecular weight</td>
</tr>
<tr>
<td>a.u.</td>
<td>Arbitrary unit</td>
</tr>
<tr>
<td>eV</td>
<td>Electron volt</td>
</tr>
<tr>
<td>r.t.</td>
<td>Room temperature</td>
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<tr>
<td>$V_{oc}$</td>
<td>Open-circuit voltage</td>
</tr>
<tr>
<td>$J_{sc}$</td>
<td>Short-circuit current density</td>
</tr>
<tr>
<td>$FF$</td>
<td>Fill factor</td>
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<tr>
<td>PCE</td>
<td>Power conversion efficiency</td>
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**Symbols**

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<tr>
<td>$^\circ$C</td>
<td>Degree Celsius</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Wavenumber in cm$^{-1}$</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Chemical shift</td>
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<tr>
<td>$\Phi_p$</td>
<td>Phosphorescence quantum yield</td>
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<tr>
<td>$\lambda$</td>
<td>Wavelength</td>
</tr>
<tr>
<td>$\lambda_{abs}$</td>
<td>Absorption wavelength</td>
</tr>
<tr>
<td>$\lambda_{em}$</td>
<td>Emission wavelength</td>
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<tr>
<td>$\varepsilon$</td>
<td>Molar absorptivity/molar extinction coefficient</td>
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Chapter 1 Introduction

1.1 Organic Solar Cells

1.1.1 Background

The predictable exhaustion of common energy sources like fossil fuels and coals is an urgent problem which needs to be solved by human beings. Moreover, the increasing pressure generated by environmental concerns and climate change is becoming more serious. Now, for rational handling of these problems, people need to develop renewable energies, such as solar energy and wind energy, which have many advantages and may supply the energy needs. For efficiently exploiting solar energy, a solar cell technique, which is based on organic/inorganic semiconductors harvesting sunlight energy directly into electricity, has been extensively developed. As sun light can be engaged as an unfailing energy source, a significant development of solar cells is becoming more important to solve the energy problems. Among them, organic semiconductors’ applications emerged in 1970s when Tang et al. invented the first OLED. Now, OLEDs have been applied in commercial area, such as small OLED displays, because of their unique properties like flexibility and simple fabrication technology. Other than OLEDs, the working principle of solar cells is opposite. The basic principle of solar cells is absorption light to produce electrical energy based on
organic/inorganic semiconductors. With the inorganic solar cell technology facing cost bottlenecks for large area applications, the chance of using simple and cheap fabrication process in organic solar cells for is higher. Moreover, there are a lot of advantages of organic solar cells such as flexibility, lightweight and simple device techniques with low environmental impact. A lot of new applications such as portable solar panels may result from these advantages of organic solar cells. The basic working principles of organic solar cells are described below.

1.1.2 Overview of Organic Semiconductors

After the first silicon cell was found by Russell Ohl in 1941, a solar cell technique goes through a rapid development in the past two decades. Now, the highest efficiency of about 40.8% has been reported by the scientists at the U.S. Department of Energy’s National Renewable Energy Laboratory (NREL) in 2008. At present, silicon solar cells cover more than 85% photovoltaic market, but the high cost limits its applications. More and more vigorous discovery now is coming from organic solar cells, accompanied with their attractive features like low-cost, light-weight and flexibility etc. in 1906 and in 1913, Pochettino and Volmer have respectively researched the first organic compound: anthracene molecule. The suitable organic molecules for application in organic solar cells typically contain conjugated π-bond
backbone. Opposite to the giant covalent structure of inorganic materials, the organic molecules normally interacted with each other by weak van der Waals force. For this reason, the organic semiconductors normally show unique flexibility, light weight and low sublimation point properties, which will make the processing course easy in commercial fabrications.

The frontier molecular orbital theory, found by Kenichi Fukui, is very helpful for understanding the conduction properties of semiconductors. The HOMO is the acronym of highest occupied molecular orbital, and the LUMO is the acronym of lowest unoccupied molecular orbital. HOMO and LUMO are referred to as frontier orbitals in the semiconductor area. The energy difference between the HOMO and LUMO is termed an energy gap (or band gap).\textsuperscript{[3, 4]} Organic semiconductors are composed by organic molecules linked with $\pi$-conjugated bonds which run through the length of the molecular backbone. The C atom in the backbone has one bond to each of its neighbors and one bond forming a double bond. Except for the formed $\sigma$-orbital using $sp^2$ hybridized orbital on carbon, the electron remaining on p-orbital of C atom would like to form a delocalized electronic cloud, as well as to form the $\pi$-bonded molecular orbital. The quasi-one-dimensional architecture for the conjugated organic semiconductors will be formed by this bond structure. Different bonding structure can be formed depending on the different electron overlap-function
of conjugated C atoms. At last, the C atom still has one bond available for attachment (except for one σ-bond and one π-bond), and some functional groups may link to the conjugated molecule by virtue of this available bond for improving the molecular properties.[5-11]

1.1.3 Operational Principles of Organic Solar Cells

Organic solar cells have undergone fast developments in recent years. Meanwhile, the properties like excellent film-forming capability, broad absorbance, higher mobility and proper HOMO-LUMO energy levels are required for ideal organic solar cell.[12-13] In view of these requirements above, a fundamental mechanism of organic solar cell operation should be understood firstly.

Four important processes are identified in understanding the operational principles of organic solar cells:

1) Exciton generation by absorption of photon

2) Excited state diffusion and dissociation

3) Charge transport

4) Charge collection at electrodes

Figure 1.1 illustrates the working mechanism of how the light energy transformed
to the electricity energy.[14-21]

1.1.3.1 Exciton Generation by Absorption of Sunlight

The first step is exciton generation. An electron of the organic semiconductor would be jumped into the molecular LUMO from HOMO after absorbing sun energy.[22] But due to a strong Coulomb interaction between electron and hole, these electron and hole still are binded tighter with an energy of 0.1-1.4 eV between them. People called this pair of electron and hole an exciton. After photo-excitation, the driving force becomes more important for efficient charge generation, which means the thermodynamic and kinetic energy must be favorable for stabilization of the electron-hole pair. The overall energy driving force for effective transfer of electron from the donor’s LUMO to acceptor’s LUMO is in direct proportion to the difference between the donor LUMO energy value and the acceptor LUMO energy value.[23, 24]
This step determines the number of utilization efficiency of absorbed photons in sunlight. The lack of absorption of these photons in active layer of solar cells is the most important problem for getting high energy conversion efficiency of solar cells.

The surface of the Earth’s solar photon flux distribution is shown in Figure 1.2. In order to harvest more sunlight energy, the absorption spectrum of the active layer material should match with the solar energy spectrum as much as possible. According
to the distribution spectrum, most of the photon flux is located at around 700 nm. It means the absorption peak position of the active layer should be preferably at around 700 nm, and the absorption bands should be able to cover the entire visible region.

**Figure 1.2** Photon flux from the sun (AM1.5) as a function of wavelength.

### 1.1.3.2 Exciton Diffusion and Exciton Dissociation

There are still two steps for generating electricity, one step is exciton diffusion; another step is exciton dissociation. During the period of exciton diffusion and dissociation, the possibility of exciton radiative recombination exists. In that case, molecular luminescence will be occurred at a timescale of ~ 1 ns. Resolved by Tang et al, who found that by using two different materials (donor material and acceptor material), the generated exciton would be able to survive and then migrate to the interface of donor and acceptor, and the process is called exciton diffusion.[25] For
exciton dissociation to happen, the band alignment between donor and acceptor materials (Fig. 1.1) should be placed adjacent to each other. After that, the exciton would be separated to electron (which flows into the acceptor’s LUMO) and hole (which stays in the donor’s LUMO). The exciton junction between donor and acceptor is named heterojunction. Now, fullerene and its derivatives are mostly chosen for acceptor materials, because these materials possess a lot of intrinsic advantages. The great advantage of fullerene is its lower LUMO energy level than LUMO energy level of common donors, which is favorable for accepting electrons from excited donor. However, the diffusion length of exciton is limited by self recombination. For achieving higher dissociation efficiency, the distance between the generated exciton and the interface of donor and acceptor should be shorter. Otherwise, the chance of exciton recombination will be increased. Hence, the thin active layer is profitable for phase separation. However, the low absorbance efficiency is a minus effect using thin active layer. To overcome this disadvantage, a large interfacial area for better exciton diffusion and dissociation is adopted through bulk heterojunction technology.

1.1.3.3 Charge Transport

After exciton diffusion and dissociation, the geminate pairs will be generated (the electron and hole are still bound by Coulomb-interaction, even though they are in
different materials now). Driven by the forces of drift and diffusion currents, the
geminate pairs may be transported. The electron will be carried to cathode at last and
the hole will be transported to anode. There is a need for a build-in electric field
which is created by the difference of high work function anode and low work function
cathode (different electrodes will form different potential gradient). This internal
electric field will overcome the Coulomb-interaction to dissociate the final geminate
pairs that would determine the open circuit voltage ($V_{oc}$) of the solar cells. Along the
potential gradient, the carrier moved in line with the drift current. The drift current is
comparatively insensitive to the electric field.

In practical photovoltaic mode (PV mode), the organic active layer is placed
between cathode and anode which have largely different work functions. Charge
separation occurs in the organic active layer. Figure 1.3 shows the typical PV mode
of solar cell.

![Figure 1.3 Typical PV mode of a solar cell](image)
1.1.3.4 Charge Collection at Electrodes

In the last step, the charge will be collected into electrode after the charge arrives at the interface between active layer and electrode. The potential barrier at the active layer/electrode interfaces is the main factor which will affect the efficiency of charge collection at electrodes. Improved charge collection efficiency can be achieved by adjusting the electrode materials on the electrode surface or improving the preparation process of devices.

In conclusion, based on the classic photovoltaic material devices, the main factors causing a lower energy conversion efficiency of these devices are two-fold: the materials absorption spectrum does not match with the solar spectrum and the carrier mobility of material is low.

1.1.3.5 Summary of the Operation

The overall operation of OSCs discussed above is illuminated in Figure 1.4. The four key steps are: (1) Exciton generation by absorption of sun energy; (2) Exciton diffusion; (3) Exciton dissociation and formation of geminate pairs; (4) Charge transport and collection at electrode. The external quantum efficiency (EQE), so called incident photon to current conversion efficiency (IPCE), is the percentage of
the number of charge carriers eventually collected at the electrodes divided by the photons given by outside. EQE is also defined by these four steps, which are represented by $\eta_A$, $\eta_{\text{diff}}$, $\eta_{\text{diss}}$ and $\eta_C$, respectively.

**Figure 1.4** Organic solar cell processes.

\[
\text{EQE} = \frac{\text{electrons/sec}}{\text{photons/sec}} = \frac{\text{current/(charge of 1 electron)}}{\text{(total power of light)/(energy of one photon)}}
\]

\[
\eta_{\text{EQE}} = \eta_A \times \eta_{\text{IQE}} = \eta_A \times \eta_{\text{diff}} \times \eta_{\text{diss}} \times \eta_C
\]

$\eta_A$: Photon absorbed;

$\eta_{\text{diff}}$: Exciton diffusion;

$\eta_{\text{diss}}$: Exciton dissociation;

$\eta_C$: Charge collection;

$\eta_{\text{IQE}}$: Internal Quantum Efficiency;

Normally, the insufficient sunlight absorption by inadequate band gap or by a thin active layer may decrease the value of photon absorbed ($\eta_A$). Both of exciton recombination of their reciprocal quenching-reaction at electrodes and restricted phase
separation in active layer will lower the EQE value.

1.1.4 Basic Working Principles of Organic Solar Cells

Figure 1.5 shows the equivalent circuit diagram of the ideal solar cells. As shown, the photo-generated current is represented by $I_L$ under a constant current source $G$, and $I_L$ is proportional to the incident flux. The diode behavior of organic solar cell is represented by diode characteristics. $I_D$ means the organic-diode reversed saturation current density. But in actual situation, there is always a certain value of the series resistance $R_s$ and parallel resistance $R_{sh}$, caused by the presence of an ohmic electrode and a semiconductor’s thin film, respectively. $R_s$ is constituted by contact resistances, and is connected with loads in series. The parallel connected resistance $R_{sh}$ comes from a leakage of solar cell itself. $R_{sh}$ makes a photocurrent partly split when flowing through the load.

![Figure 1.5](image.png)

**Figure 1.5** (a) The equivalent circuit of solar cells (b) $J$-$V$ curves of solar cells.

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The output characteristics of organic solar cells are generally expressed by the current-voltage (J-V) curve (Figure 1.6 b). The main parameters that characterized organic solar cell performance are:

1. Open-circuit voltage: $V_{oc}$

Open circuit voltage ($V_{oc}$) is defined as the maximum output voltage of an organic solar cell when no current flows through a solar cell. For bilayer or bulk heterojunction solar cells, research studies have demonstrated that the $V_{oc}$ is strongly related to the energy difference between the LUMO energy level of the acceptor and the HOMO energy level of the donor. However, in practical case, $V_{oc}$ is affected by many factors like work function variation in different electrode materials, different ratio of donor/acceptor and various interface situations, etc. Thus, for achieving higher $V_{oc}$ and then for yielding higher PCE value of organic solar cells, a thorough investigation both on materials chemistry and materials physics is necessary.

2. Short circuit current: $J_{sc}$

Short circuit current ($J_{sc}$) is defined as the maximum output current in organic solar cell when external applied voltage is zero, which is purely based on photo generated charge carriers. The unit area short circuit current is represented by short circuit current density, whose unit is mA/cm$^2$ or A/cm$^2$. The short circuit current is limited by various factors like: light absorption capability, light-induced exciton
generation and transport, the morphology of active layer and active layer/electrode interface structure, etc. All factors improving the material unit absorption intensity, effective separation of exciton and increasing the mobility of charge carriers are very crucial for enhancing the short circuit current.

3. Fill factor: FF

Fill factor is a ratio of areas in the J-V curve (deep shade/light shade, Figure 1.5 (b)) and the equation is shown below:

\[ FF = \frac{J_{\text{max}} \cdot V_{\text{max}}}{J_{\text{sc}} \cdot V_{\text{oc}}} = \frac{P_{\text{max}}}{J_{\text{sc}} \cdot V_{\text{oc}}} \]

In this formula, \( V_{\text{max}} \) (the maximum output voltage) and \( J_{\text{max}} \) (the maximum output current) correspond to the maximum output power \( P_{\text{max}} \). FF is the ratio within rectangular area (\( P_{\text{max}} = V_{\text{max}} \cdot J_{\text{max}} \)) and outer rectangular area (\( V_{\text{oc}} \cdot J_{\text{sc}} \)) in Figure 1.5. FF depends on the number of carriers which are able to reach the electrode when the bias increases to nearly \( V_{\text{oc}} \) while the build-in electric field is weakened. In fact, there is a competition between carriers transport and recombination. The product of charge carrier lifetime \( \tau \), mobility \( \mu \) and internal electric field \( E \) determines the carrier drift distance \( d \) in unit electric field intensity (\( d = \tau \cdot \mu \cdot E \), and the \( \tau \cdot \mu \) should be as large as possible). In addition, the series resistance \( R_s \) has a great influence on FF in which, generally \( R_s \) is required as small as possible. At last, the parallel resistance \( R_{sh} \) should be large enough to limit an adverse influence like short circuits or current leakage in
solar cell device.

4. Power conversion efficiency: PCE

Power conversion efficiency (PCE) represents the efficiency of how much incident light can be converted to electricity. The formula is given below:

$$PCE = \frac{P_{\text{max}}}{P_{\text{light}}} \times 100\% = \frac{J_{\text{max}} \times V_{\text{max}}}{P_{\text{light}}} \times 100\% = \frac{J_{\text{sc}} \times V_{\text{oc}} \times FF}{P_{\text{light}}}$$

$P_{\text{light}}$ is the light intensity incident on the device.

5. Incident photon to electron conversion efficiency: IPCE

Incident photon to electron conversion efficiency (IPCE) is a percentage of incident photons in a given wavelength divided by the charges that are finally carried to an external circuit. It is equivalent to external quantum efficiency $(EQE)$

$$IPCE (\text{EQE}) = \frac{N_{\text{charge}}}{N_{\text{photon}}} = \frac{1240 \times J_{\text{sc}}}{\lambda \times P_{\text{light}}}$$

where $N_{\text{charge}}$ is the number of photon induced charge carriers; $N_{\text{photon}}$ is the number of incident photons; $\lambda$ is the wavelength of incident light; $P_{\text{light}}$ is the power of incident light. Enlarging the external quantum efficiency may be achieved by improving the material absorption efficiency, enhancing the capability of exciton diffusion and transport, and enhancing carriers collection efficiency.
1.1.5 Solar Cell Architectures

Organic photovoltaic cell, as a typical sandwich structure, is composed by conductive glass (ITO)/ photoactive layer/ metal electrodes. Depending on the active layer structure, organic solar cells can be divided into monolayer solar cells, bilayer solar cells, bulk heterojunction solar cells and tandem solar cells. Device structures are shown in Figure 1.6. At present, the widespread used structure of organic solar cells is the bulk heterojunction architecture.

Figure 1.6 Structure of organic solar cell devices: (a) single-layer cells, (b) double-layer cells, (c) bulk heterojunction solar cells and (d) tandem solar cells.
1.1.5.1 Bulk Heterojunction Solar Cells

In the mid 1990s, one of the most important breakthroughs in organic solar cell technology is the bulk heterojunction (BHJ) solar cell structure (Figure 1.7 c). This concept is a landmark of organic solar cells. As bilayer solar cells have significant drawbacks like insufficient contact between donor and acceptor materials and short exciton diffusion length, bulk heterojunction solar cell technique has been discovered. The typical method of BHJ firstly includes spin-coating the solutions which contain donor material and acceptor material (normally is PCBM) together onto a substrate, followed by vaporization of the solution (sometimes with thermal co-deposition method). The donor and acceptor materials will form a nanoscale network film on the substrate, called active layer film. This method can largely enhance materials interconnection, as a result, the normal phase separation distance is among 10-20 nm, which is favorable for exciton diffusion. Moreover, using this structure device, carrier generation may distribute throughout the whole active layer. Inherently, in the active layer, the continuous channel on the connection interface to electrodes may be constructed, and the generated carriers can transfer to the electrode to give rise to the photovoltaic effect. At last, the separated electrons and holes are transported along conjugated polymer and PCBM interpenetrating network toward the respective contacts for collection. Using this kind of structure, PCE over 7% in organic solar
cells can be achieved now. Moreover, the solution processing method of BHJ is simple, low-cost and suitable for large area fabrication.

1.1.5.2 Tandem Solar Cells

To increase the absorption intensity and absorption range in the active layer of organic solar cells, tandem solar cell technique, which uses series/parallel connection linking several cells, has been developed now (Figure 1.6(d)).[27] Solar cells stacking in series may achieve both of higher $V_{oc}$ and broad absorption range at the same time, because different layers may cover different absorption regions. For example, tandem solar cell P3HT:PCBM/ZnPc:C$_{60}$ showed higher $V_{oc}$ and larger absorption range compared with the original solar cell. Normally people use ZnO/PEDOT:PSS as the interlayer in tandem solar cells. The parallel cells can also enhance the efficiency, because the sum $J_{sc}$ of full current outputs by two parallel cells will be obtained. The tandem solar cell technique is an effective way to achieve higher PCE, and also it is a frontier domain in organic solar cells. Since Blom’s group first reported the preparation of tandem solar cells by spin-coating technique, the efficiency of tandem solar cells is over 10% to date.
1.2 BHJ Solar Cells Based on Polymer-Fullerene Composite

There is an important way to improve energy conversion efficiency of polymer solar cells by adjusting the conjugated polymer’s structure. Conjugated polymer materials with excellent performance normally possess the following properties: broad and strong absorption in visible region (high absorption capability); high hole mobility (still maintaining a high hole mobility after being blended with fullerene); good solubility, well film-forming properties and excellent thermal stability. Up till now, a few kind of conjugated polymers have been extensively investigated as donor materials in BHJ solar cells. They include polythiophene materials, donor-acceptor copolymers, Pt-containing conjugated polymers and organic small molecules.

1.2.1 Polythiophene and Its Derivatives

The most representative conjugated polymer deeply investigated as photovoltaic donor materials is P3HT. Because of its high structural regularity, good hole mobility, relative thick active layer as the optimal thickness (~200 nm), it is favorable for roller printing or ink-jek printing, etc. low cost technology which can realize large scale application. In 2003, for the first time, Chirase et al. used P3HT as a donor material in BHJ organic solar cells. Using P3HT as donor and PCBM as acceptor in a device
structure of ITO/(PEDOT:PSS)/(P3HT:PCBM)/Al, the energy conversion efficiency of 0.2% ($V_{oc} = 0.48$ V, $J_{sc} = 1.28$ mA/cm$^2$, FF = 0.31) was obtained. After that, by controlling the active layer growth rate from solution to solid state, a PCE over 5% based on P3HT as donor has been reported in 2005, by virtue of optimized temperature and time in annealing process.$^{[29, 39]}$ It was the highest efficiency value of organic solar cells at that time. The improvement of PCE based on P3HT is mainly due to thermal annealing, which can make P3HT to show better crystallinity, more regular arrangement, red-shifted absorption band and improved hole mobility. These advantages after thermal annealing will enhance both of material short circuit current and fill factor. Although P3HT has shown good photovoltaic performance, its maximum absorption peak appears only at about 550 nm accompanied by an absorption edge at 650 nm. The insufficient harvesting of sunlight restricts P3HT for improving its performance. Moreover, the higher HOMO level of P3HT makes the $V_{oc}$ in P3HT/PCBM device to lower to around 0.6 V, which further limited its development.

Scheme 1.1 lists the structures of P3HT and its derivatives. The highest PCE of 3~4% for P3HT derivatives has not met the demand for commercialization yet.
Scheme 1.1 Polythiophene derivatives for OSCs.

1.2.2 Donor-Acceptor Copolymers

In recent years, donor-acceptor (D-A) architectural polymers with narrow band gap and broad absorption properties have been extensively investigated. In these polymers, the polymer backbone consisted of alternating electron donating group and electron accepting group. This D-A structure will induce easier transfer of charge within the whole molecular backbone. In this way, the energy gap of polymer will be
reduced and the corresponding absorption spectrum will be bathochromically shifted.

In addition to favorable charge transfer, the alternating D-A structure has other advantages as follows: (1) Continuous aromatic ring structure will make the polymer backbone more planar, which is favorable for improving the degree of \( \pi \)-electron delocalization. (2) Alternately arranged single and double bond along the molecular backbone can also reduce the relative band gap. (3) Alternating D-A structure can reduce the difference in the length of a single bond and a double bond, which can also reduce the energy gap. Among the reported narrow band gap materials, cyclopentadithiophene, benzodithiophene, etc. have been extensively researched as electron donor units, while benzothiadiazole, quinoxaline, etc. have been widely investigated as electron acceptor units. The detailed characters of them will be discussed below.

1.2.2.1 Cyclopenta[2,1-b:3,4-b']dithiophene (CPT) Based Conjugated Polymers

In 2006, Mühlbacher group reported a D-A copolymer PCPDT-BT, which was based on cyclopenta[2,1-b:3,4-b']dithiophene (CPT) as donor unit and benzothiadiazole (BT) as acceptor unit (Scheme 1.2). The HOMO and LUMO energy levels of this copolymer were -5.30 eV and -3.57 eV, respectively. The other properties of PCPDT-BT were electrochemical energy gap \( E_g^{EC} \) of 1.73 eV, \( E_g^{opt} \) of
1.40 eV, solid-film absorption at 775 nm, absorption edge at 890 nm and hole mobility $\mu$ of $2 \times 10^{-2}$ cm$^2$/Vs.$^{[40]}$ The optimized device based on PCPDT-BT was a $J_{sc}$ of 11 mA/cm$^2$, $V_{oc}$ of 0.65 V, FF of 47% and PCE of 3.2%. A same material researched by Zhu et al. was also published, with the reported PCE of 3.5%.$^{[41]}$ After that, Heeger group presented a new result based on PCPT-BT material. Using alkyl dithiol as the additive, the material morphology was optimized, and nearly doubled device performance was achieved ($V_{oc}$ of 0.65 V, $J_{sc}$ of 16.2 mA/cm$^2$, FF of 55% and PCE of 5.5%).$^{[42]}$ Recently, Ding group reported a D-A copolymer PCPT-TTz based on CPT as donor unit and tetrazine as acceptor unit, higher PCE of 5.4% was obtained.$^{[43]}$ Through changing the bridged C atom to Si atom in CPT unit, dithienosilole (DTS) unit was synthesized for the donor material. Hou’s group researched a D-A copolymer PDTS-BT with DTS donor unit and BT acceptor unit. The PCE of 5.1% was obtained. $^{[44]}$ Using similar DTS unit with two n-dodecane chain linked to Si atom for increasing material solubility, Bazan’s group reported a new copolymer PDTS-BT (R= n-C$_{12}$H$_{25}$). A PCE of 5.9% was achieved, compared with the PCE of 2.7% based on polymer PCPT-BT (R= n-C$_{12}$H$_{25}$) with no silicon-replaced CPT unit.$^{[45]}$ Except for silicon-replaced CPT unit, a dithienopyrrole (DTP) unit with nitrogen-replaced central bridged C atom normally shows more electron-rich property than CPT unit. When DTP was used as the donor group, this
electron-rich property may enhance relative donor-acceptor orbital overlap and lower the energy gap. As a result, polymer PDTP-BT shows a smaller band gap of 1.45 eV, however, due to the lower $V_{oc}$ of 0.54 V, a PCE of 2.8% was achieved.\textsuperscript{[46]} Using CPT as the donor unit and diketopyrrolopyrrole (DPP) as the acceptor group, Janssen et al. synthesized a copolymer PCPT-DPP, with smaller band gap of 1.39 eV and PCE of 1.7%. Li et al. reported a copolymer PDTS-TTz based on dithienosilole (DTS) as donor unit and thiazolothiazole (TTz) as acceptor unit. Due to the rigid and coplanar properties of TTz unit, the backbone planarity and $\pi$-$\pi$ stacking property were increased. The hole mobility of $7.8 \times 10^{-2} \text{ cm}^2/\text{Vs}$ was achieved and a $V_{oc}$ of 0.73 V, $J_{sc}$ of 11.25 mA/cm$^2$, FF of 71.6%, PCE of 5.88% were obtained based on PDTSTTZ/PC$_{71}$BM blend.\textsuperscript{[47]}

![PCPT-BT](image1.png)

![PCPT-TTz](image2.png)
Yang’s group also reported a series of silicon containing polymers named PDTS-DTBT. Through adjusting an alkyl chain length on DTS unit, the effect on the photovoltaic performance was investigated. The best PCE of 3.43% was received by using n-dodecyl as the alkyl chain.\textsuperscript{[48]} Using DTS as the donor unit which copolymerized with thieno[3,4-c]pyrrole-4,6-dione (TPD) acceptor unit, Chu’s group prepared the polymer PDTS-TPD. With narrow energy gap of 1.73 eV and lower HOMO energy level of -5.57 eV, a higher PCE of 7.3% was shown after being

\textbf{Scheme 1.2} D-A copolymers with CPT derivatives as donor unit.
1.2.2.2 Benzo[1,2-b:4,5-b′]dithiophene (BDT) Based Conjugated Polymers

Benzo[1,2-b:4,5-b′]dithiophene (BDT) molecule was applied in the field effect transistor field because of its easy forming regulation and good stability in air environment. The BDT unit is also a good electron donating group with easily purified advantage. Application of BDT unit into OSC field is a huge advancement for the OSC development (Scheme 1.3, Table 1.1). In 2009, Yu et al. researched a new narrow band-gap polymer PTB1, which was composed by thieno[3,4-b]thiophene (TT) unit as acceptor unit and BDT as donor unit. The performance based on PTB1/PC$_{71}$BM (1:1.2) was a PCE of 5.30% with $J_{sc}$ of 15.0 mA/cm$^2$. Then this research group synthesized a series of copolymers based on BDT and TT units. Through changing the substituent alkyl groups both on BDT and TT units, the corresponding photoelectric properties were relatively influenced. Among them, a hole mobility of PTB3 and PTB4 were increased to 7.1 cm$^2$/Vs and 7.7 cm$^2$/Vs, respectively. After adding 3.0% DIO for improving the polymer morphology, both higher PCE of 5.85% and 5.9% were achieved based on PTB3 and PTB4, respectively. Recently, PCE over 7% was reported based on this kind of polymer. These results demonstrated that the BDT-containing polymers have an
extensive potential for OSC application.\textsuperscript{[52]} On the other hand, Hou et al. reported a PBDT-TT\textsubscript{C} and PBDT-TT\textsubscript{CF} with PCE of 6.58\% and 6.77\%, respectively.\textsuperscript{[53, 54]} Then, Huo et al. reported a copolymer of PBDT-DTBT, which was based on BDT as donor unit and di-2-thienyl-2,1,3-benzothiadiazole (DTBT) as acceptor unit. A PCE of 5.66\% with \( V_{oc} \) of 0.92 V was obtained in the BHJ device.\textsuperscript{[55]} Zou’s group reported a copolymer of PBDT-TPD based on BDT as donor unit and thieno[3,4-\text{c}]-4,6-dione as acceptor unit. A large area photovoltaic cell of 1 cm\(^2\) has been fabricated based on this copolymer with a higher PCE of 5.5\% being reported.\textsuperscript{[56]} Frechet et al. have changed the alkyl chain at thieno[3,4-\text{c}]-4,6-dione (TPD) unit to obtain three polymers PBDT-TPD-P1, PBDT-TPD-P2 and PBDT-TPD-P3. A PCE of 6.8\% was achieved by using two n-octane groups as the alkyl chains.\textsuperscript{[57]} Li et al. reported two polymers PBDT-V and PBDT-BTZ based on BDT unit. In the PC\textsubscript{71}BM blended BHJ device, a PCE of 2.63\% and 3.82\% were obtained based on PBDT-V and PBDT-BTZ, respectively.\textsuperscript{[58, 59]} You et al. reported copolymers of PBnDT-TAZ and PBnDT-DTffBT, which use BDT as donor moiety and benzotriazole (TAZ) or fluoro-dithienyl-benzothiadiazole (DTffBT) as acceptor unit.\textsuperscript{[60, 61]} The HOMO and LUMO energy level of PBnDT-TAZ were -5.36 V and -3.05 V, respectively. A higher PCE of 7.10\% was achieved with a \( J_{sc} \) of 12.45 mA/cm\(^2\) and FF of 72.2\% in its BHJ device. Interestingly, this kind of materials possessed a higher hole mobility of
1×10⁻³ cm²/Vs, which is similar to P3HT (1×10⁻³ cm²/Vs). As a result, when the thickness of the active layer reached up to 1000 nm, the PCE based on PBnDT-TAZ was still maintained at 6.06%. The advantages of these kinds of materials were very beneficial for large area fabrication like ink-jek printing or roller printing etc. An extraordinary performance based on PBnBT-DTffBT/PCBM was obtained with PCE up to 7.20%. In conclusion, most of the materials based on BDT as donor unit have shown a great performance (>5%) and excellent potential in organic solar cells.
Scheme 1.3 D-A copolymers with benzodithiophene as donor unit.

Table 1.1 Energy levels and photovoltaic properties of some chosen polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$E_{\text{HOMO}}$ (eV)</th>
<th>$E_{\text{LUMO}}$ (eV)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
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<tbody>
<tr>
<td>PTB1</td>
<td>-4.90</td>
<td>-3.20</td>
<td>0.56</td>
<td>15.0</td>
<td>63.3</td>
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<td>PTB2</td>
<td>-4.94</td>
<td>-3.22</td>
<td>0.60</td>
<td>12.8</td>
<td>66.3</td>
<td>5.10</td>
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<tr>
<td>PTB3</td>
<td>-5.04</td>
<td>-3.29</td>
<td>0.72</td>
<td>13.9</td>
<td>58.5</td>
<td>5.85</td>
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<tr>
<td>PTB4</td>
<td>-5.12</td>
<td>-3.31</td>
<td>0.74</td>
<td>13.0</td>
<td>61.4</td>
<td>5.90</td>
</tr>
<tr>
<td>PTB5</td>
<td>-5.01</td>
<td>-3.24</td>
<td>0.66</td>
<td>10.7</td>
<td>58.0</td>
<td>4.10</td>
</tr>
<tr>
<td>PTB6</td>
<td>-5.01</td>
<td>-3.17</td>
<td>0.62</td>
<td>7.74</td>
<td>47.0</td>
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<tr>
<td>PTB7</td>
<td>-5.15</td>
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<td>14.5</td>
<td>68.9</td>
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<tr>
<td>PBDT-TPD</td>
<td>-5.01</td>
<td>-3.24</td>
<td>0.62</td>
<td>13.2</td>
<td>63.0</td>
<td>5.15</td>
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## 1.2.3 Metal-Containing Conjugated Polymers

Metal-containing conjugated polymers, as another kind of promising candidate for BHJ organic solar cells, have been broadly investigated in the past decade. Scheme 1.4 shows some examples of platinum metallopolyyne which are applied in organic solar cells. Also, a great stability of these polymers in air or moisture conditions gives a promising case of using these materials into practical application. Meanwhile, these metallopolyyne polymers can be easily prepared from the reaction of diethynyl precursors with platinum-chloride complexes by Sonogashira reaction. This is an alternative strategy for the synthesis of new type materials for organic solar cells.\textsuperscript{[62-64]}

<table>
<thead>
<tr>
<th>Polymer</th>
<th>E0 (V)</th>
<th>E1 (V)</th>
<th>E2 (V)</th>
<th>E3 (V)</th>
<th>E4 (V)</th>
<th>E5 (V)</th>
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</thead>
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<td>PBDT-TTe</td>
<td>-5.12</td>
<td>-3.35</td>
<td>0.70</td>
<td>14.7</td>
<td>64.1</td>
<td>6.58</td>
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<tr>
<td>PBDT-TTeF</td>
<td>-5.22</td>
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<td>15.2</td>
<td>66.9</td>
<td>7.73</td>
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<tr>
<td>PBDT-V</td>
<td>-5.16</td>
<td>-2.82</td>
<td>0.71</td>
<td>6.46</td>
<td>57.0</td>
<td>2.63</td>
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<tr>
<td>PBDT-DTBT</td>
<td>-5.31</td>
<td>-3.44</td>
<td>0.92</td>
<td>10.70</td>
<td>57.5</td>
<td>5.66</td>
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<tr>
<td>PBDT-DTf BT</td>
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<td>-3.33</td>
<td>0.91</td>
<td>12.91</td>
<td>61.2</td>
<td>7.20</td>
</tr>
<tr>
<td>PBDT-TAZ</td>
<td>-5.36</td>
<td>-3.05</td>
<td>0.79</td>
<td>12.45</td>
<td>72.2</td>
<td>7.10</td>
</tr>
<tr>
<td>PBDT-BTz</td>
<td>-5.15</td>
<td>-2.95</td>
<td>0.86</td>
<td>7.84</td>
<td>57.0</td>
<td>3.82</td>
</tr>
</tbody>
</table>
A series of soluble platinum metallopolynes MP6-M10 were reported by Wong et al. The MP6/PCBM based device showed a PCE of 4.9%, $V_{oc}$ of 0.82 V, $J_{sc}$ of 15.4 mA/cm$^2$ and FF of 0.39.$^{[65]}$ On the other hand, metallopolynes M7-M10 with different number of thiophene unit have been synthesized. Among them, MP10 with most thiophene substituent groups represented the highest PCE value of 2.5%, accompanied with a $V_{oc}$ of 0.88 V, $J_{sc}$ of 6.5 mA/cm$^2$ and FF of 0.44. Then Jen et al.
reported another metallopolyyne polymer MP11. After blended with PC71BM, a $V_{oc}$ of 0.79 V, $J_{sc}$ of 9.61 mA/cm$^2$, FF of 0.49 and PCE of 3.7% were obtained.$^{[66]}$

1.2.4 Small Molecules for Organic Solar Cells

Organic small molecule semiconductors become a promising candidate for bulk heterojunction solar cells because of their advantages over their polymeric counterparts such as well defined molecular structure, definite molecular weight, and high purity without batch to batch variations. In recent years, a great deal of effort has been dedicated to develop this class of materials, for example, dendritic oligothiophenes,$^{[67-69]}$ star- or X-shaped molecules,$^{[70-74]}$ linear analogs with donor–acceptor–donor (D–A–D) structures, fused polycyclic arene, and other organic dyes (Scheme 1.5).
1.3 Scope of the Thesis

It is important in solar cell field that a discovery of new suitable materials can be discovered for challenging traditional conjugated polymers. Now, a lot of works are focused on developing suitable organic small molecules through tailoring their structures as well as modifying their energy levels. As a member of organic semiconducting materials, organic small molecular semiconductors with their unique advantages have represented a great potential in organic solar cell application. Compared with polymer materials, the characters of small molecule semiconductors
including well‐defined molecular structure, well reproducible synthetic route and no batch to batch variations attract people to pay a great amount of effort on developing these materials. A series of small molecular semiconductors like oligothiophenes, acenes, fused polycycles, push‐pull chromophores, dikctopyrrolopyrrole and related dyes have been investigated as n‐type materials in OSCs. The fast progress has been generated by this effort and the PCE value based on this class of material is growing fast. To date, the highest PCE of 7.38% has been reported by Chen’s group using benzo[1,2-b:4,5-b']dithiophene‐centered oligothiophene unit as a n‐type material for bulk heterojunction organic solar cells.

Based on these discussions above and new functional materials design, this thesis is more focused on the synthesis and application of designed organic materials (including small molecules and polymers) in organic solar cells. The general structures of each kind of materials will be discussed in details in this thesis (Schemes 1.6-1.9).

**Scheme 1.6** Diagram for dipyrrin based polymers and small molecules.
Scheme 1.7 Diagram for CPT and BDT based small molecules.

Scheme 1.8 Diagram for TPA based small molecules.

Scheme 1.9 Diagram for new metallopolyyne materials.
References:


Today 2007, 10, 28.


Chapter 2 Synthesis and Characterization of Dipyrrin-Based Small Molecules and Polymers for Solution-Processed Organic Solar Cells

2.1 Introduction

It is well known that energy is one of the most important factors which will crucially influence the human beings and other living creatures. At present, the common available energy sources over the world are mainly fossil fuels energy and coal energy. However, as an environmental deterioration and a stockpile shortage in fossil fuels and coals, people have to turn their attention to develop renewable energy sources such as wind energy, hydraulic energy, geothermal energy and solar energy, etc. because they have a great potential that may be considered as available candidates for largely replacing the present energy sources. Among them, the solar energy is one of the most acceptable materials for renewable energy sources.\(^{[1-4]}\) As for the rational exploitation of the solar energy, organic solar cells (OSCs), with a lot of advantages like low-cost, light weight, and large-area fabrication on flexible substrates, have been developed quickly in the past years.\(^{[5-9]}\) As a member of OSC materials, organic small molecules with their unique advantages have presented a wide variety in organic photovoltaic materials. Compared to organic polymeric materials, organic small
molecular materials own advantages like well-defined molecular structure, synthetically high reproducibility and no batch to batch variations, etc. A series of small molecular semiconductors like oligothiophenes, acenes and fused polycycles, push-pull chromophores, diketopyrrolopyrroles and their dyes have been intensively investigated as photovoltaic materials for OSCs.[10, 11] An average of PCE over 4% has been achieved recently by using these small molecular materials.[12-14] The highest PCE of 8.01% to date was reported by Bazan’s group using small molecule p-DTS(FBTTh₂)₂ as n-type material for solution-processed bulk heterojunction (BHJ) solar cells.[15] Among the numerous n-type materials, triphenylamine (TPA) has been extensively studied owing to its low oxidation potential, reversible redox behavior and good film-forming properties. Materials with TPA segments as the electron donor have shown long lived charge excited state and good hole-transporting ability. In addition, trigonal geometry of triarylamine prevents the formation of aggregates at the semiconductor surface. By using the TPA fragment as electron-rich donor (D) to link with electron-deficient acceptor (A) can facilitate electron delocalization and form D-A structure materials which is a very powerful strategy in designing OSC materials with low band gaps and at the same time facilitate intramolecular charge transfer (ICT) from donor to acceptor. On the other hand, one of the most common acceptor units for OSCs is 2,1,3-benzothiadiazole (BT) because of its strong electron-accepting ability.
and easy accessibility. Moreover, the formation of hydrogen bonds between nitrogen atoms in thiadiazole with adjacent units would lead to more planar backbone and facilitate photoinduced charge transfer. With these fine characteristics, many polymers and small molecules with a BT acceptor unit performed good photovoltaic properties with light absorption over a wide wavelength region.\footnote{16} The best OSC performance of BT-containing copolymer Si-PCPDTBT showed a band gap of 1.37 eV which gave a PCE over 5.9\% and short circuit current density ($J_{sc}$) of 17.3 mA/cm$^2$. While star-shaped small molecule S(TPA-BT-HTT) containing BT unit exhibited a band gap of 1.9 eV that achieved a $J_{sc}$ of 9.51 mA/cm$^2$ and PCE of 4.3\% in its bulk heterojunction (BHJ) device.\footnote{17} Besides, in a large amount of capable candidates for small molecular OSCs, a family of boron dipyrromethene (BODIPY) is found to be useful in this area. It is an important class of fluorescent dyes with facile synthesis and purification steps, outstanding stabilities, redox activity, and ease of modification by different functional group to tune the desired optical features.\footnote{18-28} Recently, dipyrrin based BODIPY dyes shows a PCE as high as 4.7\%, with band gap of 1.42 eV and $J_{sc}$ of 14.2 mA/cm$^2$.\footnote{29} As a BODIPY analogue, dipyrrin ligands and their relative metal-containing complexes (like zinc, copper, iron and nickel, etc.) are normally applied in building supramolecular structures,\footnote{30} coordination polymers,\footnote{31} or constructing organic frameworks.\footnote{32} However, the photochemical properties of
bis(dipyrrinato)-metal complexes have rarely been studied, as there are only a few reports concerning fluorescence properties of this class complexes. The construction of light-harvesting materials by using the dipyrrin-metal complexes is very interesting and may have good potential in organic solar cell application.\textsuperscript{[33-39]}

In this section, we synthesized and characterized a series of new TPA-BT modified dipyrrin compounds bearing boron or metal ions [Ni(II), Zn(II), Pd(II)] and investigated their photophysical, electrochemical and photovoltaic properties. The strategy presented here is to use TPA unit as donor and BT unit as acceptor to construct an effective D-A configuration for tailoring the relative molecular energy levels and to promote the appearance of an intermolecular charge transfer (ICT) in their resulting compounds. We believe that after coupling dipyrrin-metal part or BODIPY part through the \textit{meso} position of the dipyrrin with the D-A structure, the whole molecule can form a cross-conjugated disposition relative to the linear conjugated sequence in the D-A moiety. Our effort aimed to investigate the different capability of these molecules as n-type materials used in BHJ devices, which has been rarely investigated so far. The general structures of this type compounds are shown in Figure 2.1.
2.2 Dipyrrin-Based Metallopolymers for Organic Solar Cells

2.2.1 Synthesis

Generally, the methods for preparing dipyrrin-based metallopolymers P1-P4 are outlined in Schemes 2.1 and 2.2. For P1 and P2, by using triphenylamine as the starting material, acylation by two-fold equivalents of POCl₃ reagent led to L1-Aldehyde. Then, it reacted with excess pyrrole to prepare L1-Dipyrrmethane. The required precursor L1 was synthesized through oxidation of L1-dipyrrmethanes by two-fold equivalents of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). At last,
P1 and P2 were achieved by reacting L1 with the corresponding metal salt under base conditions. The synthetic pathways of P1 and P2 are shown in Scheme 2.1.

Scheme 2.1 Synthetic pathways of P1 and P2.

The synthetic pathways of P3 and P4 are shown in Scheme 2.2. 4-(Bis(4-bromophenyl)amino)benzonitrile was coupled with thiophen-2-yl-2-boronic acid via Suzuki coupling reactions to obtain 4-(bis(4-thiophen-2-yl)phenyl)amino)-benzonitrile. Then, the corresponding dithiophene-containing compound was acylated by two-fold equivalents of POCl₃. After subsequent acid-catalyzed condensation reaction with pyrrole, L2-dipyrrromethane was obtained. The precursor L2 was synthesized by oxidation reaction of this dipyrrromethane with two-fold
equivalents of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Finally, P3 and P4 were achieved through L2 by reaction with the corresponding metal salt under base conditions. Compared with P1 and P2, P3 and P4 with two additional π-conjugated thiophene units may show different physical properties.

Scheme 2.2 Synthetic pathways of P3 and P4.

2.2.2 $^1$H and $^{13}$C NMR Spectroscopy of P1-P4

All of the corresponding ligands and platinum metallopolymers were fully
characterized by common spectroscopic techniques. Because of a poor solubility of nickel metallopolymers, limited characterizations of them were presented.

$^1$H and $^{13}$C NMR analyses clearly demonstrated a well-defined structure for each of the compounds. $^1$H NMR resonances stemming from the protons of the organic moieties were observed. The $^{13}$C NMR spectral data give precise information about the regiochemical structure of the compounds (Figures 2.2, 2.3, 2.4 and 2.5). The proton signals of triphenylamine are located on the downfield regions (around 7.20 ppm). The significant signal at 9.89 is assigned to the CHO proton in L2-Aldehyde (Figure 2.3). The distinct signals located at 6.47 ppm are the characteristic proton signals of dipyrrins in L2 (Figure 2.4).

![Figure 2.2 $^1$H NMR spectrum of L2-Thiophene in CDCl$_3$.](image)
Figure 2.3 $^1$H NMR spectrum of L2-Aldehyde in CDCl$_3$.

Figure 2.4 $^1$H NMR spectrum of L2 in CDCl$_3$. 
2.2.3 Optical Absorption Spectroscopy

The optical absorption spectra of P1 and P3 were investigated in CH$_2$Cl$_2$ solution at room temperature. Figure 2.6 shows the absorption spectra of L1, L2, P1 and P3. Generally, the bands at around 250-400 nm of all compounds can be ascribed to the $\pi$ - $\pi^*$ transition of the molecular backbone. Compared with P1 and L1, the similar bands located at around 250-350 nm suggest that the $\pi$ - $\pi^*$ transition of molecular backbone does not change after metallopolymerization. On the other hand, the bonds located at around 350-600 nm of P1 and L1 are significantly different and the red shift of 69 nm was observed in P1 compared with L1. We believe that the

Figure 2.5 $^{13}$C NMR spectrum of L2 in CDCl$_3$. 

---

Figure 2.6 Optical absorption spectra of L1, L2, P1 and P3.
metal-to-ligand charge-transfer (MLCT) in P1 is the main reason for the red shift of the absorption bands. Similar situation happened in P3 and L2, and the red shift of 73 nm in P3 as compared with L2 is caused by the analogous MLCT transition in P3.

![Normalized absorption spectra of L1, L2, P1 and P3 in CH2Cl2.](image)

**Figure 2.6** Normalized absorption spectra of L1, L2, P1 and P3 in CH2Cl2.

### 2.2.4 Photovoltaic Performance

The device structure was ITO/poly(3,4-ethylene-dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS)/polymer:PCBM blend/Al. Indium tin oxide (ITO) glass substrates (10 Ω per square) were cleaned by sonication in toluene, acetone, ethanol, and deionized water, dried in an oven, and then cleaned with UV ozone for 300 s.
Received PEDOT:PSS solution was passed through the 0.45 μm filter and spin-coated on patterned ITO substrates at 5000 rpm for 3 min, followed by baking in N₂ at 150 °C for 15 min. The compound:PCBM (1:3 ~ 1:5) in the active layer was prepared by spin-coating the dichlorobenzene solution at 800 rpm (or 1000 rpm) for 2 min. The substrates were dried at room temperature under low vacuum (vacuum oven) for 1 h and then stored under high vacuum (10⁻⁵-10⁻⁶ Torr) overnight. An Al electrode (100 nm) was evaporated through a shadow mask to define the active area of the devices (2 mm² circle). All the fabrication procedures (except drying, PEDOT:PSS annealing, and Al deposition) and cell characterization were performed in air. Power conversion efficiency was determined from J-V curve measurement (using a Keithley 2400 sourcemeter) under white light illumination (at 100 mW/cm²). For white light efficiency measurements, an Oriel 66002 solar light simulator with an AM 1.5 filter was used. The light intensity was measured by a Molectron Power Max 500D laser power meter. For the measurement of the external quantum efficiency, different wavelengths were selected with an Oriel Cornerstone 74000 monochromator, while the photocurrent was measured with a Keithley 2400 sourcemeter. The light intensity was measured with a Newport 1830-C optical power meter equipped with 818-UV detector probe.

The solar cells were fabricated by using the metal-based polymers mentioned in
this section as donor material and PCBM as electron acceptor material. Relevant data are summarized in Table 2.1. The hole collection electrode consisted of ITO with a spin-coated poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate), while Al served as the electron collecting electrode.

### Table 2.1 Solar cell performance of the devices

<table>
<thead>
<tr>
<th>donor</th>
<th>d (nm)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>PCE (%)</th>
<th>FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>65</td>
<td>0.53</td>
<td>0.36</td>
<td>0.049</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>0.61</td>
<td>0.95</td>
<td>0.15</td>
<td>0.26</td>
</tr>
<tr>
<td>P3</td>
<td>60</td>
<td>0.52</td>
<td>0.55</td>
<td>0.084</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>0.44</td>
<td>0.44</td>
<td>0.055</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Atomic force microscopy (AFM) was used to characterize the blends of P3/PCBM with a ratio of 1:4, as shown in Figure 2.7. The figure indicated that the P3/PCBM blended film is not smooth enough and some kind of phase separation was observed. The undesirable morphology in P3/PCBM blended film will lower the PCE value.
Figure 2.7 $J-V$ curves of P3/PCBM blend and the corresponding AFM image of P3/PCBM in 1:4 blend film.

2.3 Dipyrrin-Based Small Molecules for Organic Solar Cells

2.3.1 Synthesis

The building of D-A structural block by combing electron-deficient 2,1,3-benzothiadiazole (BT) unit as acceptor with various donor materials has been extensively investigated in BHJ organic solar cells. BT and its derivatives are also categorized as electron-transport materials, and have been widely introduced into various polymers to tailor the energy levels and fine tune the absorption band over the entire visible region.\cite{40, 41} Now we designed and prepared a series of new small molecules which feature effective D-A segment linked with functional dipyrrins
directly. The aggregative properties will be expected. For building the D-A segment, electron-rich triphenylamine unit was used as the donor material and electron-deficient 2,1,3-benzothiadiazole unit was employed as the acceptor. More importantly, functional dipyrrin segment was composed of dipyrrin complexed with metal ions or disubstituted boron atom. Scheme 2.3 shows the chemical structures and synthetic strategies of the key ligand (L3). Firstly, 2,7-dibromo-2,1,3-benzothiadiazole (BT) was coupled with triphenylamine-boronic acid under palladium catalyzed Suzuki coupling reaction conditions to get L3-Br, which then underwent another coupling reaction between L3-Br and 5-formylthiophen-2-yl-2-boronic acid to yield L3-Aldehyde. Treatment of L3-Aldehyde with excess pyrrole in the presence of trifluoroacetic acid gave L3-dipyrromethane. Finally, oxidation of L3-dipyrromethane to L3 was conveniently performed by using DDQ as the oxidizing reagent. Metal-containing compounds M1-M3 were obtained by using L3 to react with different metal acetate salt in a THF/NEt₃ mixture solution (Scheme 2.4). A one-pot synthesis of BODIPY M4 was used by the oxidation of L3-dipyrromethane with DDQ followed by reacting it with BF₃/OEt₂ solution directly (Scheme 2.5). These final compounds were purified by chromatography on neutral aluminum oxide, and fully characterized by UV/Vis and H, C and F NMR spectroscopy, respectively.
All reactions were carried out under nitrogen atmosphere. All reagents and chemicals, except pyrrole which was distilled before use, were purchased from commercial sources and used without further purification. The metal acetate salts were purchased from Fluka and used as received. Other chemicals were purchased from Sigma-Aldrich or Alfa Aesar. Tetrahydrofuran (THF) was dried over Na/benzophenone ketyl and freshly distilled prior to use. Separation and purification of products were achieved by column chromatography on silica gel or preparative thin-layer chromatography (TLC) on glass plates (20 cm × 20 cm), pre-coated with Merck Kieselgel 60 GF254. All the purifications were carried out in air using laboratory grade solvents as eluents.
Scheme 2.3 Synthetic pathways of L3.
Scheme 2.4 Synthetic pathways to prepare metal-based small molecules M1-M3.

Scheme 2.5 Synthetic pathways of M4.

2.3.2 Spectroscopic Characterization of M1-M4

The high resolution (HR) MALDI-TOF (matrix-assisted laser
desorption/ionization time-of-flight) spectra were obtained by a Autoflex Bruker MALDI-TOF mass spectrometer. NMR spectra were measured in deuteriated solvents as the lock and reference on a Bruker AV 400 MHz FT-NMR spectrometer, with $^1$H, and $^{13}$C NMR chemical shifts quoted relative to Me$_4$Si standard. Electronic absorption spectra were obtained with a Hewlett Packard 8453 spectrometer. The photoluminescence (PL) spectra were measured in dichloromethane with a PTI Fluorescence Master Series QM1 spectrophotometer. The cyclic voltammetry measurements were performed with a conventional three-electrode configuration consist of a glassy carbon working electrode, Pt-wires auxiliary electrode and Ag/AgCl as reference electrode. All the CV measurements was performed in deoxygenated MeCN, with 0.1 M [Bu$_4$N][PF$_6$] supporting electrolyte.

2.3.2.1 $^1$H and $^{13}$C NMR Spectroscopy

The proton signals of triphenylamine are on the downfield region (around 7.20 ppm) and the proton signals of 2,1,3-benzothiadiazole are on the downfield region (around 8.0 ppm). The peak located at 6.48 ppm is a characteristic proton signal of dipyrrin group (Figure 2.9). The corresponding $^1$H NMR and $^{13}$C NMR spectra of ligands and final molecules are shown in Figures 2.8-2.13, respectively.
Figure 2.8 $^1$H NMR spectrum of L3-Aldehyde in CDCl$_3$.

Figure 2.9 $^1$H NMR spectrum of L3 in CDCl$_3$. 
Figure 2.10 $^1$H NMR spectrum of M2 in CDCl$_3$.

Figure 2.11 $^{13}$C NMR spectrum of M2 in CDCl$_3$. 
Figure 2.12 $^1$H NMR spectrum of M4 in CDCl$_3$. 
**2.3.3 Photophysical Properties of M1-M4**

To investigate the potential of newly synthesized BODIPY and dipyrrin-based metal complexes in OSCs, their absorption and emission spectra were recorded in CH$_2$Cl$_2$. Their UV and PL spectra are illustrated in Figures 2.14-2.15 and their corresponding photophysical data are summarized in Table 2.2. L3 and its relative compounds M1-M4 present main absorption bands in the range of 370–650 nm. These absorption bands can probably be assigned to the ICT transitions. The absorption peaks of the metal-containing compounds showed slight red-shifts (by about 30–40 nm) in the lowest energy absorption peak with enhanced absorption.
coefficients as compared to L3. Among them, zinc-containing compound M2 exhibited the farthest red shift which is located at 496 nm with the highest molar extinction coefficient \( (9.32 \times 10^4 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}) \). Compared with other metal-containing complexes M1-M3, the absorption peak of BODIPY-containing compound M4 was further red-shifted and centered at 514 nm, accompanied by a decrease of the absorption intensity. Incorporation of the BODIPY group into TPA-BT part alternates the effective conjugation in M4 and results in a decrease of LUMO energy level. According to the DFT calculations, the lowest-energy transition in M4 corresponds to a TPA→BT-BODIPY intramolecular charge transfer, while the energy transfer in M1 was due to TPA→BT. As a result, the band gap of M4 was smaller than M1 by about 0.27 eV.

![Normalized absorption spectra of M1, M2, M3 and M4 in CH2Cl2.](image)

**Figure 2.14** Normalized absorption spectra of M1, M2, M3 and M4 in CH2Cl2.
Figure 2.15 Normalized photoluminescence spectra of L3, M1, M2, M3 and M4 in CH$_2$Cl$_2$ at 293 K.

Table 2.2 Photophysical data for compounds L3 and M1-M4 in CH$_2$Cl$_2$ at 293 K.

<table>
<thead>
<tr>
<th></th>
<th>Absorption</th>
<th>Emission</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>$\varepsilon_{\text{max}}$ (10$^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$)</td>
</tr>
<tr>
<td>L3</td>
<td>464</td>
<td>2.77</td>
</tr>
<tr>
<td>M1</td>
<td>490</td>
<td>5.52</td>
</tr>
<tr>
<td>M2</td>
<td>496</td>
<td>9.32</td>
</tr>
<tr>
<td>M3</td>
<td>495</td>
<td>5.63</td>
</tr>
<tr>
<td>M4</td>
<td>514</td>
<td>2.94</td>
</tr>
</tbody>
</table>

[a] Quantum yields were measured with an excitation wavelength of 450 nm using Ir(ppy)$_3$ as the reference ($\Phi_F = 0.40$).
Except for the BODIPY based dipyrrin-compounds, dipyrrin species normally do not show any luminescence until the discovery of highly emissive dipyrrin-zinc (II) complex ($\Phi_F = 0.36$) reported by Lindsey and co-workers. The reason for obtaining such high emission was contributed to the rotation restriction of the meso-mesityl ring relative to the plane of the dipyrrin chromophore. To our surprise, without rotation restriction of the thienyl ring relative to the dipyrrin segment, compounds M1, M2, M3 and M4 still show photoluminescence in CH$_2$Cl$_2$ at 293 K (Figure 2.15). The similar emission quantum efficiencies in M1 and M3 may be caused by the similar decay process of electron from ICT excited state, which was dominant over the MLCT transition. The higher quantum yield in M2 than M1 and M3 may be attributed to the zinc (II) closed-shell d$^{10}$ electron configuration, which was likely to be important to avoid the non-radiative deactivation pathways from excited state. Hence, the $\Phi_F$ of M2 was larger than M1 and M3. Due to the intrinsic nature of BODIPY, M4 presented the highest $\Phi_F$ (0.47).

2.3.4 Electrochemical Properties

The electronic levels of an organic semiconductor are crucial for governing the overall photovoltaic performance. To evaluate the oxidation ($E_{ox}$) and reduction
potentials \( E_{\text{red}} \) of these conjugated molecules, cyclic voltammetry (CV) was performed on their thin films on glassy carbon electrode measured in 0.10 M [Bu4N][PF6] in acetonitrile with a Pt wire counter electrode and a Ag/AgCl reference electrode under N2 atmosphere at a scan rate of 50 mV/s. The cyclic voltammograms and a summary of the electrochemical data versus Ag/Ag+ are depicted in Figure 2.16 and Table 2.3, respectively. There are a quasi-reversible oxidation wave and a couple of quasi-reversible reduction peaks, observed for all the compounds under CV conditions. The quasi-reversible oxidation process is probably attributed to the triphenylamine group and the first quasi-reversible reduction process to the acceptor group. The identity of the metal center only cause a slight shift on the \( E_{\text{ox}} \) and \( E_{\text{red}} \).\(^{[46]}\)

The HOMO energy levels of M1, M2 and M3 are -5.25, -5.20, and -5.25 eV, respectively, while the corresponding LUMO energy levels are -3.51, -3.53 and -3.57 eV, respectively. The HOMO and LUMO energy levels of M1-M3 are approximately equal to that of L3 which indicated the exclusion of MLCT transitions within these complexes.\(^{[47]}\) Compound M4 was examined to have the lowest HOMO level of -5.33 eV among all the compounds due to the addition of electron accepting ability from BF2 unit which further stabilizes the HOMO as compared to the others. The difference between the LUMO energy levels of M1–M3 and PC71BM (-4.0 eV) is in the range of 0.14~0.49 eV, which is important for efficient electron transfer from the donor to
acceptor [25]. The lower HOMO energy level of the organic donor is also very important for obtaining higher $V_{oc}$ of the OPVs, because $V_{oc}$ is proportional to the difference between LUMO level of the acceptor and HOMO level of the donor used in the BHJ active layer. Therefore, M4 would potentially get a higher $V_{oc}$ value among all the compounds.
Figure 2.16 Cyclic voltammograms of L3, M1, M2, M3 and M4. Left: cathodic scan in 0.10 M Bu4NPF6/CH3CN, Right: anodic scan in 0.10 M Bu4NPF6/CH3CN; scan rate 100 mV/s; Y-axis (µA).

Table 2.3 Electrochemical properties of L3, M1, M2, M3 and M4.

<table>
<thead>
<tr>
<th></th>
<th>$E_{ox}$ (eV)</th>
<th>HOMO (eV)</th>
<th>$E_{red}$ (eV)</th>
<th>LUMO (eV)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L3</td>
<td>0.57</td>
<td>-5.30</td>
<td>-1.15</td>
<td>-3.58</td>
<td>1.72</td>
</tr>
<tr>
<td>M1</td>
<td>0.52</td>
<td>-5.25</td>
<td>-1.22</td>
<td>-3.51</td>
<td>1.74</td>
</tr>
<tr>
<td>M2</td>
<td>0.47</td>
<td>-5.20</td>
<td>-1.20</td>
<td>-3.53</td>
<td>1.67</td>
</tr>
<tr>
<td>M3</td>
<td>0.52</td>
<td>-5.25</td>
<td>-1.16</td>
<td>-3.57</td>
<td>1.68</td>
</tr>
<tr>
<td>M4</td>
<td>0.60</td>
<td>-5.33</td>
<td>-0.87</td>
<td>-3.86</td>
<td>1.47</td>
</tr>
</tbody>
</table>

a Onset oxidation and reduction potentials
b HOMO = -e($E_{ox} + 4.73$) (eV)
c LUMO = -e($E_{red} + 4.73$) (eV)
2.3.5 Theoretical Studies

To understand the optical and electrochemical properties of our compounds, we have modeled the electronic structure by density functional theory (DFT).\textsuperscript{[48,49]} The electronic distributions in the frontier molecular orbitals of the selected compounds are displayed in Figures 2.17 and 2.18. For complexes M1-M3, typically, the HOMOs of the compounds are generally contributed by the TPA unit and spread toward the BT unit and the LUMOs by the BT acceptor unit. From this, it is evident that the electronic excitation from HOMO to LUMO would result in the migration of charge from TPA segment to the acceptor, i.e. the dominated electronic transition from HOMO to LUMO in M1-M3 is ICT without the involvement of metal centers. Therefore, we observed that there is only slightly difference of electronic distributions for molecular orbitals contributing significantly to the prominent electronic excitations among M1-M3. Such behavior justifies the nearly identical absorption profiles of M1-M3. While in the case of M4, the majority of HOMO still remains in the TPA segment, however, the LUMO density resides on the BF\textsubscript{2} as well as the BT unit. Therefore, M4 shows more red shift in its absorption spectrum with respect to others and maintains a stronger ICT in full conjugation within the molecule.\textsuperscript{[50]} The more delocalization of M4 lowers the LUMO energy level and further decreases the
molecular band gap, which may provide a practical approach to optimize the molecular energy level.\textsuperscript{[51, 52]}

<table>
<thead>
<tr>
<th></th>
<th>M1</th>
<th>M4</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>LUMO+1</strong></td>
<td><img src="image1" alt="M1 LUMO+1" /></td>
<td><img src="image2" alt="M4 LUMO+1" /></td>
</tr>
<tr>
<td><strong>LUMO</strong></td>
<td><img src="image3" alt="M1 LUMO" /></td>
<td><img src="image4" alt="M4 LUMO" /></td>
</tr>
<tr>
<td><strong>HOMO</strong></td>
<td><img src="image5" alt="M1 HOMO" /></td>
<td><img src="image6" alt="M4 HOMO" /></td>
</tr>
<tr>
<td><strong>HOMO-1</strong></td>
<td><img src="image7" alt="M1 HOMO-1" /></td>
<td><img src="image8" alt="M4 HOMO-1" /></td>
</tr>
</tbody>
</table>

**Figure 2.17** DFT/B3LYP/6-31G gap orbital energy and topologies of M1 and M4
<table>
<thead>
<tr>
<th></th>
<th>M2</th>
<th>M3</th>
</tr>
</thead>
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<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>LUMO</td>
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</tr>
<tr>
<td>HOMO</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>HOMO-1</td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
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</tbody>
</table>

**Figure 2.18** DFT/B3LYP/6-31G gap orbital energy and topologies of M2 and M3

### 2.3.6 Performance of BHJ Organic Solar Cells

BHJ solar cells based on M1, M2, M3 and M4 were constructed in a typical configuration of ITO/PEDOT-PSS/active layer/Ca/Al and their photovoltaic...
properties were examined. The active layer comprises of 1:3 blend ratio of M1-M4:PC71BM. Since the thickness of active-layer had a significant influence on the performance of the photovoltaic devices, OSCs were optimized empirically by scrutinizing variation in the thickness of the active layer. The resulting open circuit voltage (\(V_{oc}\)), short circuit current (\(J_{sc}\)), fill factor (FF), and PCE values were determined from the current density-voltage \(J-V\) curves and all of the relevant solar cell parameters are summarized in Table 2.4. Figure 2.19 shows the \(J-V\) characteristics of the OSCs under AM 1.5G condition at 100 mW/cm\(^2\). From the \(J-V\) curves, the optimized active layer thickness for M1-M4 was 50, 45, 45, and 60 nm, respectively. Further increase of the thickness of the active layer results in lower \(J_{sc}\) and leads to a poor device performance. This may be attributed to the resistance and slow down of charge transport within the device as the thickness of active layer increases. Among all the compounds, M4 exhibited the best PCE contributed by the highest value of \(V_{oc}\) and \(J_{sc}\). The higher photoconversion efficiency observed in M4 is interesting as it possesses only slightly longer absorption wavelength but with small molar extinction coefficient in the series relative to the others. Probably, the more negative LUMO observed for M4 provides a platform to obtain higher \(V_{oc}\) since this value was determined by the difference between the HOMO energy of the donor and LUMO energy of the fullerene derivative in the BHJ solar cell. The higher \(J_{sc}\) of the device
based on M4 may plausibly be caused by the stronger ICT interaction. The PCE of M4 is 0.58% with $V_{oc}$ of 0.81 V, $J_{sc}$ of 3.03 mA/cm$^2$ and FF of 0.24. In addition, the overall efficiencies of other devices are mainly hindered by diminishing the value of $V_{oc}$ due to the mismatch of the HOMO of the compounds and LUMO level of PC$_{71}$BM. The best PCE values of M1-M3 are 0.15, 0.12 and 0.085%, respectively. Further works need to be done to optimize these devices.

![Figure 2.19 Current density versus voltage (J-V) characteristics of optimized devices made from M1-M4: PC$_{71}$BM.](image-url)
Table 2.4 Device performance of the BHJ devices based on M1-M4:PC71BM (1:3, w/w).

<table>
<thead>
<tr>
<th>donor</th>
<th>thickness (nm)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>PCE</th>
<th>FF</th>
</tr>
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<tr>
<td>M1</td>
<td>65</td>
<td>0.58</td>
<td>0.74</td>
<td>0.11</td>
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<tr>
<td></td>
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<td>0.25</td>
</tr>
<tr>
<td>M2</td>
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<td>0.54</td>
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<td>0.26</td>
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<tr>
<td></td>
<td>60</td>
<td>0.42</td>
<td>0.94</td>
<td>0.10</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>0.41</td>
<td>1.13</td>
<td>0.12</td>
<td>0.26</td>
</tr>
<tr>
<td>M3</td>
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<td>0.47</td>
<td>0.59</td>
<td>0.068</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.47</td>
<td>0.75</td>
<td>0.085</td>
<td>0.24</td>
</tr>
<tr>
<td>M4</td>
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<td>0.78</td>
<td>1.65</td>
<td>0.29</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>0.81</td>
<td>3.03</td>
<td>0.58</td>
<td>0.24</td>
</tr>
</tbody>
</table>

2.3.7 Conclusions

In this section, four metal-based metallopolymers for organic solar cells have been designed, synthesized and two of them have been fabricated for BHJ organic solar cells. However, even though P3 maintained more broad absorption band and smaller band gap compared with P1, the PCE of P1 was larger than P3. The overall light to electricity conversion efficiency of P1 was 0.15% with $V_{oc}$ of 0.61V, $J_{sc}$ of 0.95 mA/cm$^2$ and FF of 0.26 under AM 1.5 irradiation (100 mW/cm$^2$).
On the other hand, through the alternation of different metals ions and boron element in the same dipyrrin framework, a series of dipyrrin-based metal complexes and BODIPY-containing compounds have been synthesized. Their optical and electrochemical properties have been investigated. DFT calculations were also applied for further illustration of the structure property relationship. Electrochemical analysis and DFT calculations proved that M4 with BODIPY-based structure is more efficient to optimize the HOMO-LUMO energy level which further increases the $V_{oc}$ value. This modification may provide an idea that further modification of the structure of the BODIPY-based materials properly could be crucial for getting higher photovoltaic conversion efficiency. The overall light to electricity conversion efficiency of M4 was 0.58% with $V_{oc}$ of 0.81V, $J_{sc}$ of 3.03 mA/cm$^2$ and FF of 0.58 under AM 1.5 irradiation (100 mW/cm$^2$).

References:


363.


Chapter 3 Synthesis and Characterization of Benzo[1,2-b:4,5-b']dithiophene (BDT)-Based Small Molecules for Solution-Processed Organic Solar Cells

3.1 Introduction

3.1.1 BDT-Based Conjugated Polymers and Small Molecules

After continuous research works in recent years, the approach of obtaining low band gap materials by virtue of constructing donor-acceptor (D-A) structural molecules now has became one of the most successful methods in the BHJ organic solar cells.\(^\text{[1, 2]}\) The electron-rich unit, which is usually named donor, represents an electron donating group; the electron-deficient unit is normally called accepter.\(^\text{[3]}\) The intrinsic characters of D-A construction are beneficial for an intermolecular charge transfer (ICT) which will lower the molecular band gap. Moreover, the \(\pi\)-electrons are facilitated to delocalize along the D-A molecules because of the ICT that brings the molecules to have a more planar configuration. One distinctive feature of the D-A configuration is that the electronic distributions in the HOMO energy level are mostly located on the donor’s molecular orbital (and delocalized along the D-A structure) and the electronic distributions in LUMO energy level are mostly occupied on the
acceptor’s molecular orbitals.\textsuperscript{[4, 5]} This unique feature shows us a great possibility to tailor the energy levels and HOMO/LUMO energy levels through individually choosing donor units and acceptor units. In accordance with this strategy, plentiful organic materials have been synthesized and investigated.\textsuperscript{[6-10]} Among them, the most representative donor units include: fluorene unit, benzodithiophene (BDT) unit, cyclopentadithiophene (CPT) unit, triphenylamine (TPA) unit and so on.\textsuperscript{[11-20]} The most representative accepter units include: benzothiadiazole (BT) unit, dithienyl-benzothiadiazole (DTBT) unit, fluoro-benzothiadiazole (f-BT) unit, thiadiazolopyridine (PyT) unit and quinoxaline (Qx) unit.\textsuperscript{[21-32]} Through various successful organic D-A materials, we found that the BDT unit is one kind of donor units which can match very well with these accepter groups above. The corresponding examples of BDT-containing D-A materials are illustrated in Scheme 3.2. Impressively, all the PCE values based on these materials are over 5\%.\textsuperscript{[33-36]} The synthetic routes for BDT units are listed in Scheme 3.1.\textsuperscript{[35, 37-38]}
Scheme 3.1 Synthetic routes of three kinds of BDT units.

The benzo[1,2-\textit{b}:4,5-\textit{b'}]dithiophene-4,8-dione is a key intermediate to synthesize all three kinds of BDT units. Its synthetic routes are listed in Scheme 3.4. Starting from this dione intermediate, the BDT unit with different functional group such as alkoxyl, alkyl or thienyl group, have been synthesized (Scheme 3.1). Firstly, the alkoxyl-substituted BDT was synthesized by reducing the dione intermediate with zinc powder in sodium hydroxide aqueous solution. Then, the produced phenolic-sodium salt reacted with excess alkyl bromide under a catalytic amount of potassium iodide and TBAB (tetrabutylammonium bromide) to yield the alkoxyl substituted BDT. On the other hand, the alkyl-substituted BDT was synthesized by the reaction of dione-intermediate with alkynyl-lithium or alkynyl-magnesium bromide followed by in situ reaction with reductive reagent SnCl$_2$/HCl to obtain the unit. After
reduction of the alkynyl-BDT by Pd/C and H₂, the alkyl substituted-BDT was synthesized with a yield over 50%. At last, the thienyl-substituted BDT was readily prepared from the reaction of dione intermediate with thienyl-lithium, followed by reduction with SnCl₂/HCl reagent.

Scheme 3.2 Molecular structures of the polymer materials based on BDT unit with PCE over 5%.

Based on BDT unit as donor and di-2-thienyl-2,1,3-benzothiadiazole (DTBT) unit as acceptor, Huo et al. reported the D-A alternating copolymer PBDTDTBT. The lower HOMO energy level of -5.31 eV with \( V_{oc} \) of 0.92 V, band gap of 1.87 eV, a higher PCE of 5.66% was obtained in its BHJ devices.\cite{35} For further tailoring the
relative energy levels, You et al. replaced the BT unit by a more electron deficient thia diazolopyridine (PyT) unit. After copolymerization with BDT unit, the alternating D-A copolymer PBDTDTByT was made.\textsuperscript{[33]} As expected, this material showed more deeply HOMO energy level of -5.47 eV, with a band gap of 2.03 eV, $V_{oc}$ of 0.85 V, and PCE of 6.32\% was obtained in its BHJ device. Also, You et al. have investigated another copolymer PBDTDTffBT which uses fluorine substituted BT unit to replace the original BT unit for copolymerization with BDT unit.\textsuperscript{[34]} As we know, fluorine atom can play a crucial role in organic solar cells because of its unique features like stable oxidation, elevated resisitance to degradation, higher hydrophobicity, and larger effect on inter- and intra-molecularr interaction via C–F H, F S, and C–F πF interactions.\textsuperscript{[39-42]} As a result, the HOMO and LUMO energy level of PBDTDTffBT were -5.36 V and -3.05 V, respectively, and a higher PCE of 7.10\%, $J_{sc}$ of 12.45 mA/cm\(^2\) and FF of 72.2\% were achieved in its BHJ device. Meanwhile, this kind of material also possesses a higher hole mobility of 1×10\(^{-3}\) cm\(^2\)/Vs, which is similar to P3HT (1×10\(^{-3}\) cm\(^2\)/Vs). Interestingly, when the thickness of active layer of PBDTDTffBT/PCBM reached up to 1000 nm, the PCE was still maintained at 6.06\%. These advantages based on PBDTDTffBT material are very beneficial for applying in large area fabrication by ink-jek printing or roller printing. More recently, Chou et al. reported a copolymer PBDTDFQ which uses BDT unit as donor and fluorinated
The quinoxaline unit as acceptor. This polymer exhibited $V_{oc}$ of 0.76 V, $J_{sc}$ of 18.2 mA/cm$^2$, FF of 58.1% and excellent PCE of 8.0% in its optimized BHJ devices with an blend ratio of PBDTTFQ:PC$_{71}$BM (1:1, w/w).\textsuperscript{[36]} The excellent $J_{sc}$ value is attributed to the higher hole mobility and the better continuous interpenetration structures within the blend materials. The sufficient continuous interpenetration is very beneficial for exciton dissociation and charge transport. As we know, a lot of D-A structural materials based on BDT unit as donor have presented an excellent performance and their further commercialization will be expected.

Not only successful in constructing D-A copolymers, BDT unit is also predominant in building organic small molecules.\textsuperscript{[43]} In scheme 3.3, it exhibited a good example that BDT unit can improve the molecular performance in BHJ organic solar cells.\textsuperscript{[44]} By replacing the central thiophene unit with a fully planar and more electron-donating BDT unit, Chen et al. reported the DCAO3T(BDT)3T with enhanced electron delocalization along the molecular backbone, which will promote the co-facial π-π stacking in its solid state. Benefited from this π-π stacking, the relative charge transport ability is enhanced. As a result, BDT-containing DCAO3T(BDT)3T not only kept a notable FF value of 55.9% like DACA7T, but also achieved a higher $V_{oc}$ of 0.93 V, $J_{sc}$ of 9.77 mA/cm$^2$ and remarkable PCE of 5.44%. The original DACA7T showed $V_{oc}$ of 0.86 V, $J_{sc}$ of 10.74 mA/cm$^2$, FF of 55% and
In this chapter, we have constructed a series of A-D-A or A-π-D-π-A architectural small molecules, which use BDT as the central donor unit. These donor-acceptor extended π-conjugation systems will be expected to afford strong intra-molecular orbital overlap and charge transfer ability by utilizing the favorable “push-pull” architecture. Their photophysical, electrochemical and structural properties were fully studied and more importantly, their applications in OSCs have also been investigated.

3.2 Synthesis

3.2.1 Synthesis of BDT Unit

Generally, the method for preparing benzo[1,2-b:4,5-b′]dithiophene (BDT) is outlined in Scheme 3.4.
Firstly, thiophene-3-carboxylic acid, as the starting material, reacted with oxalyl chloride to prepare the thiophene-3-carboxylic chloride. Then, without any purification, the thiophene-3-carboxylic chloride was dealt with diethylamine to obtain $N, N$-diethylthiophene-3-carboxamide with a yield over 90% in two steps. After purification by vacuum distillation, this amide was treated with n-butyl lithium to obtain the intermediate benzo[1,2-$b$:4,5-$b'$]-4,8-dione with a yield of 75%.

On the other hand, alkyl substituted thiophene-lithium salt was synthesized by two steps: firstly, through reaction of thiophene with n-butyl lithium and then alkyl-bromide, alkyl substituted thiophene was obtained. Then, the alkyl substituted
thiophene reacted with n-butyl lithium again to prepare alkyl-thiophene-lithium reagent. By using this lithium reagent dealt with dione-intermediate followed by \textit{in-situ} reduction with SnCl$_2$/HCl aqueous solution, the final BDT unit was easily obtained with a yield over 50%.

By using BDT unit as the central donor moiety, benzothiadiazole (BT), dithienyl-benzothiadiazole (DTBT), fluoro-benzothiadiazole (fBT) or dithienyl-quinoxaline (DTQx) as acceptor unit, 2-ethylhexyl, 2-ethylhexyl-thienyl, 2-(4-(5-(2-ethylhexyl)-thiophen-2-yl)phenyl)-acetonitrile or triphenylamine as tail group, as well as for increasing the molecular solubility, a series of donor centered tail-acceptor-donor-acceptor-tail materials M$_5$–M$_{15}$ with symmetrical configuration have been synthesized. Also their photoelectric properties have been extensively investigated. Among them, M$_5$–M$_9$ were constructed by using BDT unit as central donor segment, benzothiadiazole (BT), dithienyl-benzothiadiazole (DTBT) or dithienyl-quinoxaline (DTQx) units as acceptor, and 2-ethylhexyl or 2-ethylhexyl-thienyl units as tail group, respectively. With similar strategy, M$_{10}$, M$_{11}$ and M$_{12}$ have been built by using BDT unit as central donor group, benzothiadiazole (BT) or dithienyl-benzothiadiazole (DTBT) unit as acceptor, and acetonitrile-substituted unit as tail group, respectively. Contributed by the more electron-deficient property of CN-group, M$_{10}$–M$_{12}$ owned better overlap with the
visible region in solar spectrum. Finally, by using BDT unit as central donor moiety, benzothiadiazole (BT) or fluoro-benzothiadiazole (fBT) as acceptor and triphenylamine derivatives as tail group, M13-M15 have been synthesized.

3.2.2 Synthesis of BDT-Based Small Molecules M5-M9

Scheme 3.5 shows the synthetic pathways of M5. Firstly, 3-hexyl-thiophene as the starting material reacted with n-butyl lithium and subsequently tributylchlorostannane to prepare the corresponding tributylstannane reagent. Then, it was coupled with 4, 7-dibromobenzothiadiazole under the Stille-coupling reaction condition to get L5-Br. On the other hand, BDT unit reacted with n-butyl lithium and then tributylchlorostannane to obtain the corresponding BDT-tributylstannane reagent. At last, M5 was achieved via the palladium catalyzed Stille-coupling reaction between L5-Br and the BDT-tributylstannane reagent.
**Scheme 3.5** The synthetic pathways of L5-Br and M5.

**M5** possesses a fully coplanar centrosymmetric backbone. Moreover, the four alkyl chains out of the molecular backbone not only ensured the molecular solubility, but also minimized the block to intermolecular π-π stacking. In conjugated polymers, there is evidence that side alkyl chains may play very important role on polymer solubility, molecular weight, inter- and intra-molecular interactions, charge transport, and active layer morphology. Then, for comparing with **M5**, we synthesized **M6** with different position of alkyl side chains. The synthetic route is shown in Scheme 3.6.

Firstly, thiophene was introduced with a 2-ethylhexyl side chain through reaction with n-butyl lithium followed by 2-ethylhexyl bromide. After treatment with n-butyl lithium and subsequently tributylchlorostannane, the tributylstannane reagent was obtained. Then, this tributylstannane reagent reacted with 4,
7-dibromobenzothiadiazole under the palladium-mediated Stille-coupling reaction condition to afford \textbf{L6-Br}. By using the same Stille-coupling reaction condition, \textbf{L6-Br} reacted with the corresponding BDT-tributylstannane reagent to get \textbf{M6}.

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

\textbf{Scheme 3.6} The synthetic pathways of \textbf{L6-Br} and \textbf{M6}.

As we know, thiophene unit is one of the most important functional groups in building abundant organic photovoltaic materials. Moreover, oligothiophene and its derivatives, as small molecular materials, present a higher hole mobility and notable FF value in OSCs. Based on these advantages of the thiophene unit, we designed to introduce one more thiophene unit into the $\pi$-conjugated backbone of \textbf{M6} for enhancing its absorption ability between acceptor and ending group. By using BDT as the central donor unit, benzothiadiazole (BT) as acceptor unit, and one more
thiophene unit in the middle of BT and 2-ethylhexyl-thiophene tail unit, M7 was produced. Scheme 3.7 shows the synthetic pathways of M7.

Scheme 3.7 The synthetic pathways of L7-Br and M7.

Firstly, 2-bromothiophene reacted with 2-thiophene-boronic acid under the palladium-mediated Suzuki cross-coupling reaction condition to prepare 2-(thiophen-2-yl)thiophene, which was further introduced with an alkyl chain by reaction with n-butyl lithium and subsequently alkyl bromide reagent. Then, the 2-(5-(2-ethylhexyl)thiophen-2-yl)thiophene reacted with n-butyl lithium and subsequently tributylchlorostannane to prepare the corresponding tributylstannane.
reagent. After coupling with 4, 7-dibromobenzothiadiazole under the Stille-coupling reaction condition, **L7-Br** was obtained. At last, **M7** was synthesized via the palladium catalyzed Stille-coupling reaction between **L7-Br** and the corresponding BDT-tributylstannane reagent.

Further modified molecule **M8** was achieved by adding one more thiophene unit in **M7** between its central donor unit and next acceptor units. Scheme 3.8 shows the chemical structures and synthetic routes for **L8-Br** and **M8**.

**Scheme 3.8** The synthetic pathways of **L8-Br** and **M8**.

By using 4, 7-dibromobenzothiadiazole as the starting material, under Suzuki
cross-coupling reaction condition with 2-thiophene-boronic acid.

4,7-di(thiophen-2-yl)benzothiadiazole was obtained which was then brominated by NBS in the mixture of acetic acid and chloroform solutions to get 4-(5-bromo thiophen-2-yl)-7-(thiophen-2-yl)benzothiadiazole. This bromide reagent was further treated with (5-(2-ethylhexyl)thiophen-2-yl)tributylstannane reagent to obtain L8. Subsequently, L8 reacted with NBS in the mixture of acetic acid and chloroform to obtain the key intermediate L8-Br. By using Stille-coupling reaction, L8-Br reacted with the corresponding BDT-tributylstannane reagent to prepare M8.

Compared with benzothiadiazole unit, quinoxaline unit is another kind of efficient acceptor material, which shows a promising candidate in building D-A alternating copolymers for high performance solar cells. By using it for building D-A molecule, M9 has been synthesized and investigated as organic photovoltaic materials in OSCs. The synthetic routes of M9 is shown in Scheme 3.9.

Firstly, 3-bromophenol was alkylated with n-octyl bromide under base condition to get 1-bromo-3-(octyloxy)benzene. After reaction with magnesium ribbon and LiBr/CuBr reagents, the corresponding Grignard reagent was obtained. The freshly prepared Grignard reagent was directly treated with oxalyl dichloride to obtain 1,2-bis(3-(octyloxy)phenyl)ethane-1,2-dione. On the other hand, the five-membered ring in benzothiadiazole of L8 was opened through the reduction reaction to obtain
benzene-1,2-diamine derivative. By further reacting it with 1,2-bis(3-(octyloxy)phenyl)ethane-1,2-dione under acetic acid condition, the quinoxaline derivative L9 was obtained. After bromination with NBS, L9-Br was achieved. Finally, M9 was synthesized via the palladium catalyzed Stille-coupling reaction between L9-Br and the corresponding BDT-tributylstannane reagent.

Scheme 3.9 The synthetic pathways of L9-Br and M9.
3.2.3 Synthesis of BDT-Based Small Molecules M10, M11 and M12

For enhancing material absorption capability on solar spectrum and effectively tailoring its corresponding HOMO and LUMO energy levels, there is a possible way through introducing functional electron-withdrawing cyano unit (-CN) into π-conjugated molecular backbone at appropriate positions. More importantly, the CN-containing molecule may increase the molecular π-π stacking and additional non-covalent intermolecular interactions for leading to higher charge-carrier mobility. Hence, we designed and synthesized a series of CN-containing molecules with BDT as the central donor. Their architectural backbones are expressed by CN-π-A-D-A-π-CN or CN-π-A-π-D-π-A-π-CN. In addition, the fully coplanar backbone of these structures is favorable for electron-transfer and lower molecular band gap. At last, the terminal cyano-groups are expected to extend molecular dipolar properties and hence enhance the relative solar cell performance.

M10 has a similar alkyl cyanoacetate ending groups like oligothiophene derivatives DCAO7T or DCAO3T(BDT)3T (Scheme 3.3 and 3.10). The primary difference between DCAO3T(BDT)3T and M10 is to use benzothiadiazole as acceptor unit in M10 instead of using full thiophene units in DCAO3T(BDT)3T. The synthetic pathway of M10 is given in Scheme 3.10 and the synthetic route of intermediate L11-aldehyde is shown in Scheme 3.11. By using 4,
7-dibromobenzothiadiazole as the starting material to undergo Stille-coupling reaction with tributyl(4-hexylthiophen-2-yl)stannane, **L5-Br** was made. Then, **L5-Br** was oxidized by POCl₃/DMF reagent to synthesize **L11-aldehyde**. After another Stille-coupling reaction between **L11-aldehyde** and the corresponding BDT-tributylstannane reagent, **L10-aldehyde** was obtained. Finally, by using a Knoevenagel condensation reaction between **L10-aldehyde** and octyl 2-cyanoacetate under base condition, **M10** was achieved.

**Scheme 3.10** The synthetic pathways of **L10-aldehyde** and **M10**.

Compared with **M10**, **M11** and **M12** contain different CN-substituted groups.
Their synthetic pathways are shown in Schemes 3.11 and 3.12, respectively. Unlike the synthetic pathways of M10 from L10-aldehyde, M11 was transformed from L11-Br. Firstly, 4-bromophenyl acetonitrile reacted with tributyl(5-(2-ethylhexyl)thiophen-2-yl)stannane under Stille-coupling reaction condition to obtain 2-(4-(5-(2-ethylhexyl)thiophen-2-yl)phenyl)acetonitrile. Then, by using a Knoevenagel-condensation reaction between this acetonitrile-derivative and L11-aldehyde, L11-Br was obtained. Finally, M11 was synthesized via the palladium catalyzed Stille-coupling reaction between L11-Br and the corresponding BDT-tributylstannane reagent.

Scheme 3.11 The synthetic pathways of L11-Br and M11.
Similarly, M12 was obtained from L12-Br. It was achieved by a few steps below: under the Stille-coupling reaction condition, 4, 7-dibromobenzothiadiazole reacted with excess tributyl(4-hexylthiophen-2-yl)stannane to get 4,7-bis(4-hexylthiophen-2-yl)benzothiadiazole. Then, after bromination reaction and oxidation reaction, L12-aldehyde was obtained. After that, by using Knoevenagel-condensation between 2-((4-(5-(2-ethylhexyl)thiophen-2-yl)phenyl)acetonitrile and L12-aldehyde, L12-Br was prepared. At last, by using Stille-coupling reaction condition, L12-Br reacted with the corresponding BDT-tributylstannane compound to obtain M12.

Scheme 3.12 The synthetic pathways of L12-Br and M12.
3.2.4 Synthesis of BDT-Based Small Molecules M13-M15

Instead of $\pi$-A-D-A-$\pi$ architectural small molecules, we also synthesized a series of D-A-D-A-D or D-A-$\pi$-D-$\pi$-A-D structural small molecules for application in organic solar cells. As mentioned before, triphenylamine (TPA) and its derivatives, as efficient functional groups, have been extensively applied in OSCs, because they have high hole transporting abilities and good electron donating properties. In M13-M15, a strong electron-donating BDT group is included into the central position of the centrosymmetrical molecule to ensure strong $\pi$-$\pi$ intermolecular interactions. Moreover, by choosing $N,N$-di-$p$-tolylbenzenamine unit as tail-D’ group to build D’-A-D-A-D’ or D’-A-$\pi$-D-$\pi$-A-D’ molecules, a more efficient intra-molecular charge transfer (ICT) and a higher hole mobility in M13-M15 can be achieved. The synthetic route for M13 is shown in Scheme 3.13. Firstly, 4-bromo-$N,N$-di-$p$-tolylbenzenamine was prepared by condensation reaction between 4-bromobenzenamine and 1-iodo-4-methylbenzene. Then, this bromide compound reacted with n-butyl lithium and subsequently tributylchlorostannane to prepare the corresponding tributylstannane reagent. After coupling reaction with 4, 7-dibromobenzothiadiazole under the Stille-coupling reaction condition, L13-Br was obtained. At last, M13 was achieved via the palladium catalyzed Stille-coupling reaction between L13-Br and the corresponding BDT-tributylstannane reagent.
Another material M14 has also been investigated by using fluorine substituted BT unit to replace the original BT unit in M13 (Scheme 3.14). As we have discussed before, fluorine atom normally plays a crucial role in organic solar cell materials because of its unique features like stable oxidation, elevated resistance to degradation, higher hydrophobicity, and larger effect on inter- and intra-molecular interaction via C–F $\text{H}$, $\text{F}$ $\text{S}$, and C–F $\pi_F$ interactions. The synthetic route is shown in Scheme 3.14.

Firstly, 4-fluorobenzene-1,2-diamine as the starting material reacted with thionyl chloride reagent through condensation reaction to afford 5-fluorobenzothiadiazole. Then, this compound was brominated by liquid bromine in hydrobromic acid solution to obtain 4,7-dibromo-5-fluorobenzothiadiazole. Under the Stille-coupling reaction condition, 4,7-dibromo-5-fluorobenzothiadiazole reacted with
$N,N$-di-$p$-tolylbenzenamine-tributylstannyl reagent to get $\text{L14-Br}$. Finally, $\text{M14}$ was synthesized via the palladium catalyzed Stille-coupling reaction between $\text{L14-Br}$ and the corresponding BDT-tributylstannane reagent.

Scheme 3.14 The synthetic pathways of $\text{L14-Br}$ and $\text{M14}$.

Compared with the D’-A-D-A-D’ architecture in both of $\text{M13}$ and $\text{M14}$, the D’-A-$\pi$-D-$\pi$-A-D’ structure in $\text{M15}$ has also been investigated (Scheme 3.15). By using $\text{L13-Br}$ as the starting material, it reacted with 2-thiopheneboronic acid reagent through Suzuki cross-coupling reaction and substituent NBS reagent to yield $\text{L15-Br}$. At last, under the same Stille-coupling reaction condition, $\text{L15-Br}$ reacted with the corresponding BDT-tributylstannane reagent via the palladium catalyzed
Stille-coupling reaction to achieve $\textbf{M15}$.

\[ \text{Scheme 3.15 The synthetic pathways of L15-Br and M15.} \]

### 3.3 Spectroscopic Characterization of M5-M15

All of the compounds were fully characterized by common spectroscopic techniques such as $^1\text{H}$, $^{13}\text{C}$ and $^{19}\text{F}$ NMR spectroscopy on a Bruker AV 400 MHz FT-NMR spectrometer and high resolution (HR) MALDI-TOF (matrix-assisted laser desorption/ionization time-of-flight) spectra were obtained by a Autoflex Bruker MALDI-TOF mass spectrometer. $^1\text{H}$ and $^{13}\text{C}$ NMR analyses clearly demonstrate a well-defined structure for $\textbf{M5-M15}$. $^1\text{H}$ NMR resonances stemming from the protons of the organic moieties were observed. The $^{13}\text{C}$ NMR spectral data give precise
information about the regiochemical structure of the compounds.

All the protons signals of aryl rings are on the downfield side, while the alkyl proton signals are shown at a high-field side. The proton signals of functional triphenylamine group are on the downfield region (above 7.20 ppm). The NMR data of intermediates and compounds are summarized in the Experimental part of Chapter 7.

3.3.1 $^1$H and $^{13}$C NMR Spectroscopy of M5-M15

The $^1$H NMR and $^{13}$C NMR spectra of the corresponding compounds are shown in Figures 3.1 to 3.6, respectively.

![Figure 3.1](image)

**Figure 3.1** $^1$H NMR spectrum of M5 in CDCl$_3$.
Figure 3.2 $^{13}$C NMR spectrum of M5 in CDCl$_3$.

Figure 3.3 $^1$H NMR spectrum of M6 in CDCl$_3$. 
Figure 3.4 $^{13}$C NMR spectrum of M6 in CDCl$_3$.

Figure 3.5 $^1$H NMR spectrum of M7 in CDCl$_3$. 

111
Figure 3.6 $^{13}$C NMR spectrum of M7 in CDCl$_3$.

Figure 3.7 $^1$H NMR spectrum of M8 in CDCl$_3$. 
Figure 3.8 $^{13}$C NMR spectrum of M8 in CDCl$_3$.

Figure 3.9 $^1$H NMR spectrum of M9 in CDCl$_3$. 
Figure 3.10 $^{13}$C NMR spectrum of M9 in CDCl$_3$.

Figure 3.11 $^1$H NMR spectrum of M10 in CDCl$_3$. 
Figure 3.12 $^{13}$C NMR spectrum of M10 in CDCl$_3$.

Figure 3.13 $^1$H NMR spectrum of M11 in CDCl$_3$. 
Figure 3.14 $^1$H NMR spectrum of M12 in CDCl$_3$.

Figure 3.15 $^1$H NMR spectrum of M13 in CDCl$_3$. 
Figure 3.16 $^{13}$C NMR spectrum of M13 in CDCl$_3$.

Figure 3.17 $^1$H NMR spectrum of M14 in CDCl$_3$. 
Figure 3.18 $^{19}$F NMR spectrum of M14 in CDCl$_3$.

Figure 3.19 $^{13}$C NMR spectrum of M14 in CDCl$_3$. 
Figure 3.20 $^1$H NMR spectrum of M15 in CDCl$_3$.

3.4 Photophysical Properties of M5-M15

To study the potential of M5-M15 in organic solar cells, optical properties of the newly synthesized compounds are presented. As shown in Figure 3.21 and Table 3.1, CH$_2$Cl$_2$ solutions of M5-M9 exhibit broad optical absorption with distinct high energy bands and low energy bands. The higher energy absorption bands (around 300–400 nm) are attributed to the localized $\pi-\pi^*$ transitions and the lower energy absorption bands can be assigned to the internal charge transfer (ICT). Such absorption profiles are typical of donor-acceptor architectural molecules. As shown by M6, replacing the 3-hexylthiophene group in M5 by 2-ethylhexylthiophene results in a slight red shift (<10 nm) of the absorption maximum ($\lambda_{\text{max}}$) and in the onset of absorption ($\lambda_{\text{onset}}$) in
CH$_2$Cl$_2$ solution. A red shift of approximately 30 nm in $\lambda_{\text{onset}}$ was observed when comparing M6 and M7, consistent with the increased conjugation length afforded by the two additional thiophene units. By inserting thiophene units in the middle of D-A segment in M7, only a slight blue shift of $\lambda_{\text{onset}}$ (6 nm) was observed in M8. This observation indicates that adding two thiophene units in the middle of D-A segment in M7 does not narrow down the relative optical band gap of M8. However, both of M8 and M9 exhibit higher molar absorption coefficient ($8.7 \times 10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$). Among them, M7 with $\pi$-A-D-A-$\pi$ structure has the furthest red-shifted spectrum in CH$_2$Cl$_2$, with a $\lambda_{\text{max}}$ of 556 nm and $\lambda_{\text{onset}}$ at 687 nm. Its corresponding energy gap ($E_g$) is 1.80 eV.
Figure 3.21 Normalized absorption spectra of M5-M9 in CH$_2$Cl$_2$ at 293 K.

Table 3.1 Photophysical data of M5-M9 in CH$_2$Cl$_2$ at 293K.

<table>
<thead>
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<th></th>
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<th></th>
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<tbody>
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<td>$\lambda_{\text{onset}}$ (nm)</td>
<td>$E_g$ [eV]$^a$</td>
<td></td>
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<td>633</td>
<td>1.96</td>
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</tr>
<tr>
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<td>649</td>
<td>1.91</td>
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<td>681</td>
<td>1.82</td>
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<td>679</td>
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$^a$ Optical band gap determined from the onset of absorption in solution phase.
The UV/Vis absorption spectra of M10-M12 in CH$_2$Cl$_2$ solution at room temperature are shown in Figure 3.22; see also Table 3.2. Three distinct absorption bands of M10-M12 in the range of 300~700 nm are found. Both of M11 and M12 exhibit higher molar absorption coefficient (11.5 and 14.3×10$^4$ dm$^3$mol$^{-1}$cm$^{-1}$) and longer $\lambda_{\text{max}}$ than M10. Also, the maximum absorption ($\lambda_{\text{max}}$) of M11 is red shifted by about 24 nm than the $\lambda_{\text{max}}$ of M12. Among them, M11 depicts the furthest red-shifted spectrum with a $\lambda_{\text{max}}$ of 576 nm and $\lambda_{\text{onset}}$ at 731 nm. Its corresponding energy gap ($E_g$) is 1.70 eV.

![Normalized absorption spectra of M10-M12 in CH$_2$Cl$_2$ at 293 K.](image)

Figure 3.22 Normalized absorption spectra of M10-M12 in CH$_2$Cl$_2$ at 293 K.
Table 3.2 Photophysical data of M10-M12 in CH$_2$Cl$_2$ at 293 K.

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon_{\text{max}}$ (10$^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{\text{onset}}$ (nm)</th>
<th>$E_g$ [eV]$^a$</th>
</tr>
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<tr>
<td>M11</td>
<td>576</td>
<td>11.5</td>
<td>731</td>
<td>1.70</td>
</tr>
<tr>
<td>M12</td>
<td>552</td>
<td>14.3</td>
<td>704</td>
<td>1.76</td>
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</tbody>
</table>

$^a$ Optical band gap determined from the onset of absorption in solution phase.

The UV/Vis absorption spectra of M13-M15 in CH$_2$Cl$_2$ solution at room temperature are shown in Figure 3.23. Main absorption bands in the range of 270~620 nm are present in compounds M13, M14 and M15, respectively. M13 and M14 exhibited similar absorption curve caused by their similar molecular structures. The difference of M14 from M13 lie in the replacement of one hydrogen atom by a fluorine atom, and this difference barely influences on their optical spectra in CH$_2$Cl$_2$ solutions. On the other hand, M15 with additional thiophene units in the middle of D-A segment of M13 showed the highest molar absorption coefficient of 14.3×10$^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$. However, its absorption maximum ($\lambda_{\text{max}}$) and $\lambda_{\text{onset}}$ are a little hypochromatically shifted, when compared M15 to M13, together with the emergence of one more band in the low energy region. Among them, M13 depicts the furthest
red-shifted spectrum at 631 nm in $\lambda_{\text{onset}}$ and the corresponding energy gap $E_g$ is 1.96 eV. The data are summarized in Table 3.3.

**Figure 3.23** Normalized absorption spectra of M13-M15 in CH$_2$Cl$_2$ at 293 K.

**Table 3.3** Photophysical data for compounds M13-M15 in CH$_2$Cl$_2$ at 293 K.

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon_{\text{max}}$ ($10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{\text{onset}}$ (nm)</th>
<th>$E_g$ [eV]$^a$</th>
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</thead>
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<tr>
<td>M13</td>
<td>532</td>
<td>10.4</td>
<td>631</td>
<td>1.96</td>
</tr>
<tr>
<td>M14</td>
<td>528</td>
<td>11.5</td>
<td>629</td>
<td>1.97</td>
</tr>
<tr>
<td>M15</td>
<td>525</td>
<td>14.3</td>
<td>625</td>
<td>1.98</td>
</tr>
</tbody>
</table>

$^a$Optical band gap determined from the onset of absorption in solution phase.
3.5 Electrochemical Properties of M5-M15

To evaluate the oxidation \( (E_{\text{ox}}) \) and reduction potentials \( (E_{\text{red}}) \) of these conjugated molecules, cyclic voltammetry (CV) was performed on their thin films on glassy carbon electrode measured in 0.10 M \([\text{Bu}_4\text{N}][\text{PF}_6]\) in acetonitrile with a Pt wire counter electrode and a Ag/AgCl reference electrode under N\(_2\) atmosphere at a scan rate of 50 mV/s. The resulting CV traces are depicted in Figures 3.24, 3.25 and 3.26, respectively, and the electrochemical data of onset oxidation and reduction potentials versus Ag/Ag\(^+\) are listed in Tables 3.4, 3.5 and 3.6, respectively. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were estimated from the onset oxidation \( (E_{\text{ox}}) \) and reduction potentials \( (E_{\text{red}}) \), respectively. There are a quasi-reversible oxidation wave and some irreversible reduction peaks for most of the compounds under CV conditions in Figures 3.24, 3.25 and 3.26, respectively. There is no clear evidence about which donor group is responsible for the quasi-reversible oxidation process. On the other hand, as for the first irreversible reduction process, it is probably attributed to the acceptor group. The similar LUMO energy levels of M5-M15 except for M14 are reasonably attributed to the similar BT acceptor unit in them. And in M14, the fluoro-containing BT unit relative to BT unit will influence its LUMO energy level.
3.5.1 Electrochemical Properties of M5-M9

All of M5-M9 have been investigated on the oxidation potentials and reduction potentials. The corresponding data are listed in Table 3.4. Among them, M8 and M9, which contain the most thiophene units in their backbone, show relative smaller energy gaps when compared to the others. The lower HOMO energy level of -5.22 eV in M5 is very efficient for obtaining higher $V_{oc}$ after blending with PCBM. From the current density versus voltage ($J$-$V$) curve of M5 shown in Figure 3.32, the $V_{oc}$ of 0.88 V based on M5/PC$_{61}$BM blend was obtained, which was further enhanced to 0.92 V using the M5/PC$_{71}$BM blend.
Figure 3.24 Cyclic voltammograms of M5, M6, M7, M8 and M9. top: cathodic scan in 0.10 M Bu$_4$NPF$_6$/CH$_3$CN, bottom: anodic scan in 0.10 M Bu$_4$NPF$_6$/CH$_3$CN; scan rate 100 mV/s; Y-axis (µA).

Table 3.4 Electrochemical properties of M5, M6, M7, M8 and M9.

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{ox}}$ (eV)$^a$</th>
<th>HOMO (eV)$^b$</th>
<th>$E_{\text{red}}$ (eV)$^a$</th>
<th>LUMO (eV)$^c$</th>
<th>$E_g$ (eV)</th>
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<td>-3.56</td>
<td>1.66</td>
</tr>
<tr>
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<tr>
<td>M7</td>
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<td>-1.16</td>
<td>-3.57</td>
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<tr>
<td>M8</td>
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<td>-1.17</td>
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<td>1.54</td>
</tr>
<tr>
<td>M9</td>
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<td>-5.11</td>
<td>-1.19</td>
<td>-3.54</td>
<td>1.57</td>
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</table>

$^a$ Onset oxidation and reduction potentials

$^b$ HOMO = $-e(E_{\text{ox}} + 4.73)$ (eV)

$^c$ LUMO = $-e(E_{\text{red}} + 4.73)$ (eV)
3.5.2 Electrochemical Properties of M10-M12

The effects of variation in the configuration of M10-M12 on both the oxidation potentials and reduction potentials were also investigated (Figure 3.25, Table 3.5). The HOMO energy levels of M10, M11 and M12 were -5.27, -5.34 and -5.37 eV, respectively, while the LUMO energy levels were -3.54, -3.57 and -3.58 eV, respectively. The corresponding energy gaps were 1.73, 1.77 and 1.59 eV, respectively. Among them, M10 with alkyl cyanoacetate units as tail group shows the smallest energy gap in the three compounds. These CN-containing compounds exhibit lower HOMO energy levels when compared to M5-M9. The lower HOMO energy level is crucial for obtaining higher $V_{oc}$ after being blended with PCBM. As a result, M10 with the HOMO energy level of -5.27 eV achieved a $V_{oc}$ of 0.93 V based on M10/PC$_{71}$BM, as shown from the current density versus voltage ($J$-$V$) curve in Figure 3.34.
Figure 3.25 Cyclic voltammograms of M10, M11 and M12. top: cathodic scan in 0.10 M Bu$_4$NPF$_6$/CH$_3$CN, bottom: anodic scan in 0.10 M Bu$_4$NPF$_6$/CH$_3$CN; scan rate 100 mV/s; Y-axis (µA).
Table 3.5 Electrochemical properties of M10, M11 and M12.

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{ox}}$ (eV)$^a$</th>
<th>HOMO (eV)$^b$</th>
<th>$E_{\text{red}}$ (eV)$^a$</th>
<th>LUMO (eV)$^c$</th>
<th>$E_g$ (eV)</th>
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<td>-3.54</td>
<td>1.73</td>
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</table>

$^a$ Onset oxidation and reduction potentials  
$^b$ HOMO = $-e(E_{\text{ox}} + 4.73)$ (eV)  
$^c$ LUMO = $-e(E_{\text{red}} + 4.73)$ (eV)

3.5.3 Electrochemical Properties of M13-M15

The electrochemical characterizations of M13-M15 which contain TPA units as tail group have also been investigated. The HOMO energy levels of M13, M14 and M15 were -5.23, -5.25 and -5.11 eV, respectively, while the LUMO energy levels were -3.58, -3.47 and -3.54 eV, respectively. The corresponding energy gaps were 1.65, 1.78 and 1.58 eV, respectively. The parallel molecular backbones of M13 and M14 result in their similar HOMO energy levels. However, the corresponding LUMO energy level of M14 is slightly lower by about 0.13 eV than M13, which is reasonably attributed to the presence of the fluoro-BT fragments. M15, which contains two more thiophene units than M13 and M14, shows a little higher HOMO energy level and the smallest energy gap of 1.58 eV. Among them, M13 with the HOMO energy level of -5.23 eV achieved a $V_{oc}$ of 0.92 V based on M13/PC$_{61}$BM, as shown in the current
density versus voltage (J-V) curve in Figure 3.36, which was further enhanced to 0.93 V based on M13/PC_{71}BM blend.
Figure 3.26 Cyclic voltammograms of M13, M14 and M15. top: cathodic scan in 0.10 M Bu₄NPF₆/CH₃CN, bottom: anodic scan in 0.10 M Bu₄NPF₆/CH₃CN; scan rate 100 mV/s; Y-axis (µA).

Table 3.6 Electrochemical properties of M13, M14 and M15.

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<th>HOMO (eV)$^b$</th>
<th>$E_{\text{red}}$ (eV)$^a$</th>
<th>LUMO (eV)$^c$</th>
<th>$E_g$ (eV)</th>
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<td>-1.26</td>
<td>-3.47</td>
<td>1.78</td>
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<tr>
<td>M15</td>
<td>0.39</td>
<td>-5.11</td>
<td>-1.19</td>
<td>-3.54</td>
<td>1.58</td>
</tr>
</tbody>
</table>

$^a$ Onset oxidation and reduction potentials

$^b$ HOMO = -e($E_{\text{ox}}$ + 4.73) (eV)

$^c$ LUMO = -e($E_{\text{red}}$ + 4.73) (eV)
3.6 Theoretical Studies of M5, M10, M13, M14 and M15

To understand the optical and electrochemical properties of our compounds, we have modeled the electronic structure by density functional theory (DFT) calculations using the hybrid B3LYP exchange-correlation functional and the split-valence 6-31G(d,p) basis set.[45,46] Contributed by the fully planar backbone structures (considered as A-D-A or A-π-D-π-A) of all these five compounds, the electronic distributions in the frontier molecular orbitals of each molecule are spread throughout the whole π-conjugated backbone in HOMO energy levels. Moreover, the fully coplanar configuration of these backbones will facilitate the π-electron delocalization along the conjugated backbone, leading to a smaller band gap. Contrarily, in the molecular LUMO energy levels, the electron distributions of all these compounds are mostly located on the benzothiadiazole moiety, which perfectly illuminated the structural advantages of the D-A structural molecules. More importantly, we believe that these electronic distributions in the frontier molecular orbitals will be favorable for molecular dipole-dipole interaction, which will effectively lower the Coulombic binding energy of the exciton in the excited state and leads to faster charge separation kinetics, thus facilitating the full separation of electrons and holes.
Figure 3.27 DFT/B3LYP/6-31G gap orbital energy and topologies of M5.

By using donor as central group linked with two acceptors side by side, the A-D-A structure will make a good influence on molecular dipolar change. After the exciton generated by absorbed sun light, it will be easily diffused along the molecular $\pi$-conjugated backbone toward both sides, and then dissociated.
Figure 3.28 DFT/B3LYP/6-31G gap orbital energy and topologies of M10.
Figure 3.29 DFT/B3LYP/6-31G gap orbital energy and topologies of M13.

By using triphenylamine unit as the tail group, M13, M14 and M15 exhibit similar topologies in HOMO-1, HOMO, LUMO and LUMO+1 energy levels. The
electron distributions are mostly located on triphenylamine moiety of all three compounds at their HOMO-1 energy level. Then, the electron distributions are located along the whole molecular backbone at the HOMO energy level. At the relative LUMO and LUMO+1 energy levels, the electron distributions are mostly resided in the benzothiadiazole moiety.

Figure 3.30 DFT/B3LYP/6-31G gap orbital energy and topologies of M14.
Figure 3.31 DFT/B3LYP/6-31G gap orbital energy and topologies of M15.
Table 3.7 HOMO-1, HOMO, LUMO and LUMO+1 energy levels and $E_g$ determined by theoretical calculation for M5, M10, M13-M15.

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<th>LUMO (eV)</th>
<th>LUMO+1 (eV)</th>
<th>$E_g$ (eV)</th>
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<td>-3.56</td>
<td>-3.32</td>
<td>1.69</td>
</tr>
<tr>
<td>M13</td>
<td>-4.88</td>
<td>-4.69</td>
<td>-2.85</td>
<td>-2.66</td>
<td>1.70</td>
</tr>
<tr>
<td>M14</td>
<td>-4.97</td>
<td>-4.74</td>
<td>-2.92</td>
<td>-2.75</td>
<td>1.82</td>
</tr>
<tr>
<td>M15</td>
<td>-4.86</td>
<td>-4.73</td>
<td>-2.88</td>
<td>-2.79</td>
<td>1.85</td>
</tr>
</tbody>
</table>

3.7 BHJ Solar Cells Performance of M5, M10 and M13-M15

BHJ solar cells based on M5, M10 and M13-M15 were fabricated in a typical configuration of ITO/PEDOT-PSS/active layer/Ca/Al and tested. PSCs were optimized empirically by scrutinizing variation in the blend ratios of the compounds to PC$_{61}$BM and PC$_{71}$BM, respectively. The resulting open circuit voltage ($V_{oc}$), short circuit current ($J_{sc}$), fill factor (FF), and power conversion efficiency (PCE) values were determined from the $J$-$V$ curves, and all of the relevant solar cell parameters are summarized in Tables 3.7-3.11.

The current density versus voltage $J$-$V$ curves of M5/PC$_{61}$BM and M5/PC$_{71}$BM with different weight blend ratios are shown in Figure 3.32, and the relative EQE curves are shown in Figure 3.33. The optimized results are summarized in Table 3.7.
Firstly, the device with PC$_{61}$BM as electron acceptor for a 1:2 blend ratio exhibited a $V_{oc}$ of 0.88 V, a $J_{sc}$ of 3.57 mA/cm$^2$, and FF of 37.9%, which yielded a PCE of 1.19%. With increasing the M5/PC$_{61}$BM blend ratio from 1:2 to 1:3, the optimized device gave the highest PCE of 1.30% (based on PC$_{61}$BM as acceptor), with a $V_{oc}$ of 0.85 V, a $J_{sc}$ of 4.29 mA/cm$^2$, and FF of 35.6%. With a further increase in the content of PC$_{61}$BM with a blend ratio of 1:4, a lower PCE of 0.87% with $V_{oc}$ of 0.81 V, $J_{sc}$ of 3.01 mA/cm$^2$, and FF of 35.4% were obtained. On the other hand, the device of M5 blended with PC$_{71}$BM was also fabricated. When a 1:1 blend ratio of M5/PC$_{71}$BM was used, a higher $V_{oc}$ of 0.92 V and $J_{sc}$ of 7.12 mA/cm$^2$ were obtained, with FF of 33.2% and PCE of 2.18%. As the M5/PC$_{71}$BM blend ratio was increased from 1:1 to 1:2, the optimized device gave the highest PCE of 2.24%, accompanied by a $V_{oc}$ of 0.90 V, a $J_{sc}$ of 6.87 mA/cm$^2$, and FF of 36.2%. With a further increase in the content of PC$_{71}$BM, the corresponding $J_{sc}$ and FF values were continuously decreased, together with the PCE value. By using a 1:3 blend ratio of M5/PC$_{71}$BM, a $V_{oc}$ of 0.87 V and $J_{sc}$ of 6.43 mA/cm$^2$ were obtained with a FF of 35.4% and PCE of 1.98%. At last, when using a 1:4 blend ratio of M5/PC$_{71}$BM, a $V_{oc}$ of 0.90 V, $J_{sc}$ of 5.65 mA/cm$^2$, FF of 33.5% and PCE of 1.70% were received.
Figure 3.32 Current density versus voltage ($J$-$V$) characteristics of optimized devices made from various blend ratios of M5: PC$_{61}$BM (top) and M5: PC$_{71}$BM (bottom).
Table 3.8 Device performance of M5 based BHJ devices.

<table>
<thead>
<tr>
<th>Blend Ratio</th>
<th>M5:PCBM (w:w)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:2</td>
<td>0.88</td>
<td>3.57</td>
<td>37.9</td>
<td>1.19</td>
<td></td>
</tr>
<tr>
<td>1:3</td>
<td>0.85</td>
<td>4.29</td>
<td>35.6</td>
<td>1.30</td>
<td></td>
</tr>
<tr>
<td>1:4</td>
<td>0.81</td>
<td>3.01</td>
<td>35.7</td>
<td>0.87</td>
<td></td>
</tr>
<tr>
<td>PC$_{61}$BM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:1</td>
<td>0.92</td>
<td>7.12</td>
<td>33.2</td>
<td>2.18</td>
<td></td>
</tr>
<tr>
<td>1:2</td>
<td>0.90</td>
<td>6.87</td>
<td>36.2</td>
<td>2.24</td>
<td></td>
</tr>
<tr>
<td>1:3</td>
<td>0.87</td>
<td>6.43</td>
<td>35.4</td>
<td>1.98</td>
<td></td>
</tr>
<tr>
<td>1:4</td>
<td>0.90</td>
<td>5.65</td>
<td>33.5</td>
<td>1.70</td>
<td></td>
</tr>
<tr>
<td>PC$_{71}$BM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 3.33 shows the external quantum efficiency (EQE) curve of the BHJ devices based on M5/PC$_{61}$BM and M5/PC$_{71}$BM with different blend ratios under monochromatic light. The EQE values mean that a percentage of incident photons in a given wavelength divided by the charges that are finally carried to an external circuit. In M5, the EQE curves exhibited monochromatic EQE maximum of 37% at 477 nm in the optimized blend ratio of M5/PC$_{61}$BM = 1:3 and broad response covering 300-650 nm, consistent with the optical absorption bands. In the optimized blend ratio of M5/PC$_{71}$BM = 1:2 conditions, a monochromatic EQE maximum of 49% at 469 nm was received. Moreover, the highest EQE maximum of 56% at 514 nm was achieved.
when using $\text{M5}/\text{PC}_{71}\text{BM} = 1:1$ blend ratio device. All the EQE curves based on for $\text{M5}/\text{PC}_{71}\text{BM}$ were broad in response covering 300-700 nm, consistent with the corresponding optical absorption bands.

**Figure 3.33** EQE curves of (a) $\text{M5}/\text{PC}_{61}\text{BM}$ and (b) $\text{M5}/\text{PC}_{71}\text{BM}$ with different blend ratios.
The current density versus voltage (J-V) curves of M10/PC$_{61}$BM and M10/PC$_{71}$BM with different weight blend ratios are shown in Figure 3.34, and the relative EQE curves are shown in Figure 3.35. The optimized results are summarized in Table 3.8. Firstly, the device with PC$_{61}$BM as electron acceptor for a 1:2 blend ratio exhibited a $V_{oc}$ of 0.63 V, a $J_{sc}$ of 0.88 mA/cm$^2$, and FF of 38.7%, which yielded a PCE of 0.21%. With increasing the M10/PC$_{61}$BM blend ratio from 1:2 to 1:3, the optimized device gave the highest PCE of 0.22%, with a $V_{oc}$ of 0.61 V, a $J_{sc}$ of 1.25 mA/cm$^2$, and FF of 29.4%. With a further increase in the content of PC$_{61}$BM with a blend ratio of 1:4, the PCE of 0.21% with $V_{oc}$ of 0.62 V, $J_{sc}$ of 1.05 mA/cm$^2$, and FF of 31.9% were obtained. On the other hand, the device of M10 blended with PC$_{71}$BM was also investigated. Compared with PC$_{61}$BM as acceptor, the $V_{oc}$ value based on M10/PC$_{71}$BM was greatly enhanced. When a 1:1 blend ratio of M10/PC$_{71}$BM was used, a higher $V_{oc}$ of 0.91 V was obtained with $J_{sc}$ of 1.11 mA/cm$^2$, higher FF of 46.3% and PCE of 0.47%. With increasing the M10/PC$_{71}$BM blend ratio from 1:1 to 1:2, the optimized device gave the highest PCE of 0.64% (based on M10 as donor), accompanied by a $V_{oc}$ of 0.93 V, a $J_{sc}$ of 1.33 mA/cm$^2$, and the highest FF of 52.0%. With a further increase in the content of PC$_{71}$BM to a 1:3 blend ratio of M10/PC$_{71}$BM, a $V_{oc}$ of 0.91 V and $J_{sc}$ of 1.01 mA/cm$^2$ were obtained with a FF of 47.1% and PCE of
0.43%. The relatively lower $J_{sc}$ values on both M10/PC$_{61}$BM and M10/PC$_{71}$BM are the main disadvantage which caused lower PCE values of M10-based devices.

![Current density versus voltage (J-V) characteristics of optimized devices](image)

**Figure 3.34** Current density versus voltage (J-V) characteristics of optimized devices made from various blend ratios of M10: PC$_{61}$BM (top) and M10: PC$_{71}$BM (bottom).
Table 3.9 Device performance of M10 based BHJ devices.

<table>
<thead>
<tr>
<th>Blend Ratio</th>
<th>M10:PCBM (w:w)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC61BM</td>
<td>1:2</td>
<td>0.63</td>
<td>0.88</td>
<td>38.7</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>1:3</td>
<td>0.61</td>
<td>1.25</td>
<td>29.4</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>1:4</td>
<td>0.62</td>
<td>1.05</td>
<td>31.9</td>
<td>0.21</td>
</tr>
<tr>
<td>PC71BM</td>
<td>1:1</td>
<td>0.91</td>
<td>1.11</td>
<td>46.3</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>0.93</td>
<td>1.33</td>
<td>52.0</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td>1:3</td>
<td>0.91</td>
<td>1.01</td>
<td>47.1</td>
<td>0.43</td>
</tr>
</tbody>
</table>

Figure 3.35 shows the external quantum efficiency (EQE) curve of the BHJ devices based on M10/PC61BM and M10/PC71BM with different blend ratios under monochromatic light. In M10, the EQE curves exhibited monochromatic EQE maximum of 8.4% at 422 nm in the optimized blend ratio of M10/PC61BM = 1:3, but the response covering 300-700 nm was not very consistent with the optical absorption bands. In the optimized blend ratio of M10/PC71BM = 1:2, a monochromatic EQE maximum of 7.4% at 546 nm was received. The EQE curves based on M5/PC71BM were broad in response covering 300-700 nm, consistent with the optical absorption bands. However, all of these EQE values based on M10/PCBM were relatively lower, which accounted for the lower PCE values for M10 based devices.
Figure 3.35 EQE curves of (a) M10/PC<sub>61</sub>BM and (b) M10/PC<sub>71</sub>BM with different blend ratios.
The current density versus voltage ($J-V$) curves of M13/PC$_{61}$BM and M13/PC$_{71}$BM with different weight blend ratios are shown in Figure 3.36, and the relative EQE curves are shown in Figure 3.37. The optimized results are summarized in Table 3.9. Firstly, the device with PC$_{61}$BM as electron acceptor for a 1:2 blend ratio exhibited a $V_{oc}$ of 0.92 V, a $J_{sc}$ of 4.61 mA/cm$^2$, and FF of 41.8%, which gave a PCE of 1.78%. With increasing the M13/PC$_{61}$BM blend ratio from 1:2 to 1:3, the optimized device gave the highest PCE of 1.98% (based on PC$_{61}$BM as acceptor), with a $V_{oc}$ of 0.92 V, a $J_{sc}$ of 4.68 mA/cm$^2$, and FF of 45.9%. Increasing the content of PC$_{61}$BM to a blend ratio of 1:4, the PCE of 1.86% with $V_{oc}$ of 0.90V, $J_{sc}$ of 4.85 mA/cm$^2$, and FF of 42.6% were obtained. On the other hand, the device of M13 blended with PC$_{71}$BM as electron acceptor was also fabricated. When a 1:1 blend ratio of M13/PC$_{71}$BM was used, the highest $V_{oc}$ of 0.95 V (based on M13 as donor) with $J_{sc}$ of 5.62 mA/cm$^2$, FF of 33.7% and PCE of 1.8% were obtained. With increasing the M13/PC$_{71}$BM blend ratio from 1:1 to 1:2, the optimized device gave the highest PCE of 3.51%, accompanied with a $V_{oc}$ of 0.93V, a $J_{sc}$ of 8.19 mA/cm$^2$, and a FF of 46.1%. With a further increase in the content of PC$_{71}$BM to a 1:3 blend ratio of M13/PC$_{71}$BM, a $V_{oc}$ of 0.89 V and $J_{sc}$ of 8.66 mA/cm$^2$ were obtained with a FF of 42.9% and PCE of 3.31%; By using a 1:4 blend ratio of M13/PC$_{71}$BM, a $V_{oc}$ of 0.91 V, $J_{sc}$ of 8.49 mA/cm$^2$, FF of 44.2% and PCE of 3.42% were achieved.
Figure 3.36 Current density versus voltage ($J$-$V$) characteristics of optimized devices made from various blend ratios of M13: PC$_{61}$BM (top) and M13: PC$_{71}$BM (bottom).

Table 3.10 Device performance of M13 based BHJ devices.

<table>
<thead>
<tr>
<th>M13:PCBM (w:w)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

149
Table: External Quantum Efficiency (EQE) Curves

<table>
<thead>
<tr>
<th>Blend Ratio</th>
<th>PC&lt;sub&gt;61&lt;/sub&gt;BM</th>
<th>PC&lt;sub&gt;71&lt;/sub&gt;BM</th>
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<tbody>
<tr>
<td>1:2</td>
<td>0.92</td>
<td>0.95</td>
</tr>
<tr>
<td>1:3</td>
<td>0.92</td>
<td>0.93</td>
</tr>
<tr>
<td>1:4</td>
<td>0.90</td>
<td>0.89</td>
</tr>
</tbody>
</table>


Figure 3.37 shows the external quantum efficiency (EQE) curve of the BHJ devices based on M<sub>13</sub>/PC<sub>61</sub>BM and M<sub>13</sub>/PC<sub>71</sub>BM with different blend ratios under monochromatic light. In M<sub>13</sub>, the EQE curves exhibited monochromatic EQE maximum of 33% at 540 nm in the optimized blend ratio of M<sub>13</sub>/PC<sub>61</sub>BM = 1:3 conditions and broad response covering 300-650 nm, consistent with the optical absorption bands. In the optimized blend ratio of M<sub>13</sub>/PC<sub>71</sub>BM = 1:2, a monochromatic EQE maximum of 60% at 492 nm was received. Moreover, the highest EQE maximum of 61% at 509 nm was achieved by using M<sub>13</sub>/PC<sub>71</sub>BM = 1:3 blend ratio. All the EQE curves based on M<sub>13</sub>/PC<sub>71</sub>BM were broad in response covering 300-700 nm, consistent with the optical absorption bands.
Figure 3.37 EQE curves of a M13/PC₆₁BM and M13/PC₇₁BM with different blend ratios.

The corresponding data of M14 and M15 are listed in Table 3.10 and Table 3.11, respectively. The current density versus voltage (J-V) curves of M14/PC₆₁BM, M14/PC₇₁BM, M15/PC₆₁BM and M15/PC₇₁BM with different weight blend ratios are shown in Figures 3.38-3.39, respectively.
Table 3.11 Device performance of M14 based BHJ devices.

<table>
<thead>
<tr>
<th></th>
<th>M14:PCBM (w:w)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC$_{61}$BM</td>
<td>1:1</td>
<td>0.95</td>
<td>5.50</td>
<td>36.2</td>
<td>1.89</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>0.92</td>
<td>8.50</td>
<td>42.6</td>
<td>3.33</td>
</tr>
<tr>
<td></td>
<td>1:3</td>
<td>0.91</td>
<td>5.88</td>
<td>46.6</td>
<td>2.49</td>
</tr>
<tr>
<td>PC$_{71}$BM</td>
<td>1:1</td>
<td>0.85</td>
<td>8.55</td>
<td>34.1</td>
<td>2.47</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>0.90</td>
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<td>43.1</td>
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</tr>
<tr>
<td></td>
<td>1:3</td>
<td>0.89</td>
<td>9.68</td>
<td>42.2</td>
<td>3.64</td>
</tr>
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</table>
Figure 3.38 Current density versus voltage ($J$-$V$) characteristics of optimized devices made from various blend ratios of M14: PC$_{61}$BM (top) and M14: PC$_{71}$BM (bottom).

Table 3.12 Device performance of M15 based BHJ devices.

<table>
<thead>
<tr>
<th>PC$_{61}$BM</th>
<th>M15:PCBM (w:w)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:2</td>
<td>0.88</td>
<td>5.38</td>
<td>40.8</td>
<td>1.93</td>
<td></td>
</tr>
<tr>
<td>1:3</td>
<td>0.90</td>
<td>5.32</td>
<td>46.8</td>
<td>2.24</td>
<td></td>
</tr>
<tr>
<td>1:3</td>
<td>0.73</td>
<td>3.94</td>
<td>34.6</td>
<td>0.99</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>PC$_{71}$BM</th>
<th>M15:PCBM (w:w)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>0.83</td>
<td>8.55</td>
<td>41.1</td>
<td>2.94</td>
<td></td>
</tr>
<tr>
<td>1:2</td>
<td>0.82</td>
<td>8.89</td>
<td>42.6</td>
<td>3.10</td>
<td></td>
</tr>
<tr>
<td>1:3</td>
<td>0.85</td>
<td>8.65</td>
<td>38.2</td>
<td>2.81</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.39 Current density versus voltage ($J$-$V$) characteristics of optimized devices made from various blend ratios of M15: PC$_{61}$BM (top) and M15: PC$_{71}$BM (bottom).
3.8 Conclusions

Fifteen different small molecules based on the BDT unit as the central donor group and BT unit or Qx as the acceptor were synthesized and characterized by using a variety of techniques. Also, the relative structure-property relationships have been comprehensively investigated. Among them, M5-M9 were constructed by 2-ethylhexyl or 2-ethylhexyl-thienyl units as the tail group. M10, M11 and M12 have been incorporated with cyanovinylene group, respectively. By using triphenylamine derivatives as the tail group, M13-M15 have been synthesized. The similar LUMO energy levels of M5-M15 except M14 are reasonably attributed to the similar BT or Qx acceptor unit in them. And in M14, the fluoro-containing BT unit relative to BT unit will influence its LUMO energy level. As shown in representative orbital energy diagrams contributed by DFT calculations, these molecules possess fully planar backbone structures (considered as A-D-A or A-π-D-π-A). More importantly, the electronic distributions in their HOMO energy levels of each molecule are spread throughout the whole π-conjugated backbone. Contrarily, the electron distributions of all these compounds are mostly located on the acceptor moiety in LUMO energy levels, which perfectly illuminated their structural advantages as D-A structural molecules. At last, based on BHJ solar cells fabricated by M5, M10 and M13-M15, M14 shows the best performance with a higher PCE of 3.91%.
References:


Chapter 4 Synthesis and Characterization of Cyclopenta[2,1-b:3,4-b’]dithiophene (CPT)-Based Small Molecules for Solution-Processed Organic Solar Cells

4.1 Introduction

4.1.1 CPT-Based Conjugated Polymers and Small Molecules

The cyclopentadithiophene (CPT) unit, which contains fused rings, is another kind of excellent donor group besides benzo[1,2-b:4,5-b’]dithiophene (BDT) unit in building D-A structural photovoltaic materials.\textsuperscript{[1-11]} As we know, the internal charge transfer along the backbone in CPT-containing D-A \( \pi \)-conjugated molecules is generally strong, which is contributed by the more electron-rich property of CPT unit relative to other kind of donors. Thus, the band gap of CPT-containing materials normally is lower. Moreover, the significantly higher \( J_{sc} \) value of some CPT-containing polymers (up to \(~17 \text{ mA/cm}^2\)) is a fascinating property in organic photovoltaic materials.\textsuperscript{[3,6]} The representative examples for CPT-containing materials are illustrated in Scheme 4.2, and the synthetic routes for CPT unit and its derivatives (dithienosilole (DTS) and dithieno[3,2-b;2’,3’-d]pyrrole (DTP)) are listed in Scheme 4.1.

The CPT unit was synthesized from 3-bromothiophene. Firstly,
3-bromothiophene reacted with n-butyllithium, which was then quenched with 3-formylthiophene to obtain the di(thiophen-3-yl)methanol. This di(thiophen-3-yl)methanol was selectively lithiated at the 2-position on thiophene unit. Then, an iodo unit was introduced to this position after in-situ reaction with excess iodine. By oxidizing the OH group with PCC, the bis(2-iodothiophen-3-yl)-methanone was obtained. The key intermediate of carbonyl compound was synthesized through intramolecular cyclization reaction by using Cu/DMF as the catalyst. The carbonyl group in the fused three rings was further reduced by the Wolff-Kishner reaction. At last, the typical CPT unit was achieved by using excess 2-ethylhexyl bromide to alkylate the reductive product which was obtained in the last step. On the other hand, the typical DTS unit can be synthesized from 3,5-dibromo-2-(3,5-dibromothiophen-2-yl)-thiophene. Firstly, through oriented lithiation reaction of the starting material with n-BuLi, and subsequent nucleophilic substitution by chlorotrimethylsilane, the triethylsilyl protected bithiophene compound was prepared. Then, by cyclization with dioctyldichlorosilane and following bromination with NBS, the DTS unit was obtained. At last, the DTP unit can be synthesized either by one-step cyclization reaction through Pd catalyzed amination reaction of 3,3′-dibromobithiophene with long aliphatic chain amine; or by three-step synthetic routes in which 3-bromothiophene was used as the starting
Scheme 4.1 Synthetic routes of CPT unit and its derivatives (DTS and DTP).

As shown in Scheme 4.2, for representative examples, a higher $J_{sc}$ of 15.5 mA/cm$^2$ with PCE of 2.7% was achieved by n-$C_{12}H_{25}$-PCPDTBT-based OSCs devices. Also, a higher $J_{sc}$ of 17.3 mA/cm$^2$ can be reached by PSBTBT-based devices,
in which PCE of 5.9% was obtained.\textsuperscript{[6]} For another example of PCPDTBT material, a higher $J_{sc}$ of 16.2 mA/cm$^2$ was observed in its OSC devices, and a PCE of 5.5% being harvested.\textsuperscript{[3]}

![Scheme 4.2](image)

**Scheme 4.2** The representative examples for materials of higher $J_{sc}$ based on CPT donor.

Except for building efficient photovoltaic polymer materials, CPT unit and its derivative like DTS also play a crucial role in building small molecular photovoltaic materials. In recent few years, Bazan’s research group has successfully developed a series of CPT or DTS-centered small molecules for OSCs.\textsuperscript{[12-30]} A few examples of D$_2$-A-D$_1$-A-D$_2$ architectures are shown in Scheme 4.3, while the D unit and A unit correspond to electron rich and electron deficient aromatic groups, respectively. This kind of structures were based on D$_1$ as the central core while D$_2$ as the end-capping units. Two PT acceptor units were linked through a central D$_1$ unit. A strong intramolecular charge transfer and broad low-energy optical transitions based on these
D$_2$-A-D$_1$-A-D$_2$ architectural molecules are displayed.

Scheme 4.3 Depiction of the D$_2$-A-D$_1$-A-D$_2$ architectural small molecules.

In accordance with a similar strategy, small molecules DTS(PTTh$_2$)$_2$ and DTS(FBTTh$_2$)$_2$ with higher PCE values in their BHJ organic solar cells have been reported by Bazan’s group (Scheme 4.3).$^{[31,32]}$ The 4-coordinate silicon atom with aliphatic side chains may ensure the solubility of these molecules in common organic solvents. The two PT units or f-BT units with high electron affinity across the $\pi$-conjugated backbone may deepen the highest occupied molecular orbital energy level and maintain the high oxidation potentials. Bithiophene ending units with hexyl chains are incorporated into the $\pi$-conjugated structure for extending the conjugation length, together with improving the film-forming property. The planar backbones of these molecules are favorable for promoting the co-facial $\pi$-$\pi$ stacking in the solid
state and thus benefiting relative charge transport in active layer. As a result, DTS(PTTh$_2$)$_2$-based material showed a FF of 59.3%, $V_{oc}$ of 0.78 V, $J_{sc}$ of 14.4 mA/cm$^2$ and remarkable PCE of 6.70%. Compared with DTS(PTTh$_2$)$_2$, DTS(FBTTh$_2$)$_2$-based material represent a $V_{oc}$ of 0.81 V, $J_{sc}$ of 12.8 mA/cm$^2$, FF of 68% and a PCE reaching up to 8.0%. It is one of the highest PCE values among the solution-processed small molecular BHJ solar cells.

**Scheme 4.4** The examples of successfully building D$_2$-A-D$_1$-A-D$_2$ architecture molecules with PCE over 6%.

In this chapter, we have synthesized a series of CPT-centered small molecules with A-D-A or A-π-D-π-A backbones. The extended π-conjugation system of CPT is expected to afford strong intramolecular orbital overlap and charge transfer ability by
utilizing the favorable D-A architecture. Their photophysical and electrochemical properties were fully investigated. Also, some of them have been applied into OSC devices.

### 4.2 Synthesis

By using CPT unit as the central donor, benzothiadiazole (BT), dithienyl-benzothiadiazole (DTBT), or dithienyl-quinoxaline (DTQx) unit as the acceptor, 2-ethylhexyl, 2-ethylhexyl-thienyl, 2-(4-(5-(2-ethylhexyl)-thiophen-2-yl)phenyl) -acetonitrile or triphenylamine unit as the ending-group, a series of organic small molecular materials \textbf{M16-M22} with symmetrical configuration have been synthesized. Among them, \textbf{M16-M19} were constructed by CPT unit as the central donor, benzothiadiazole (BT), dithienyl-benzothiadiazole (DTBT) or dithienyl-quinoxaline (DTQx) unit as the acceptor and 2-ethylhexyl or 2-ethylhexyl-thienyl unit as the ending group, respectively. Also \textbf{M20} was synthesized with similar strategy like \textbf{M16}, except for using acetonitrile-substitutable units as the tail group. Contributed by the more electron-deficient property of CN-group, \textbf{M20} displays better overlap with the visible region in solar spectrum. Finally, by using CPT unit as the central donor moiety, benzothiadiazole (BT) unit as the acceptor, triphenylamine unit as the ending group, \textbf{M21} and \textbf{M22} have been synthesized.
4.2.1 Synthesis of CPT-Based Small Molecules M16-M19

M16 possesses a fully coplanar asymmetric backbone. More importantly, four alkyl chains out of the molecular backbone may increase the molecular solubility without causing any additional twisting in the molecular backbone. Its synthetic routes are shown in Scheme 4.5. Firstly, thiophene, as the starting material, was functionalized by the 2-ethylhexyl side chain through reaction with n-butyl lithium followed by 2-ethylhexyl bromide. After treatment with n-butyl lithium and subsequently tributylchlorostannane, the corresponding tributylstannane reagent was obtained. Then, this reagent was coupled with 4, 7-dibromobenzothiadiazole under the palladium-mediated Stille-coupling reaction condition to afford L6-Br. Finally, M16 was prepared by L6-Br by reaction with the corresponding CPT-tributylstannane reagent under the similar Stille-coupling reaction condition.
Scheme 4.5 The synthetic pathways for L6-Br and M16.

Also, M17 with increased conjugation length afforded by introducing two additional thiophene units was synthesized. The extended π-conjugated backbone of M17 is designed for representing more internal charge transfer ability and lower energy gap. It is expected that using two thiophene units as the tail group will largely improve its material performance in its relative BHJ organic solar cells.\textsuperscript{30, 31} The synthetic pathways of M17 are shown in Scheme 4.6.
Scheme 4.6 The synthetic pathways of L7-Br and M17.

Firstly, 2-bromothiophene reacted with 2-thiopheneboronic acid under the palladium-mediated Suzuki cross-coupling reaction condition to prepare 2-(thiophen-2-yl)thiophene, which was further functionalized by an alkyl chain through reaction with n-butyl lithium and subsequently alkyl bromide reagent. Then, 2-(5-(2-ethylhexyl)thiophen-2-yl)thiophene reacted with n-butyl lithium and subsequently tributylchlorostannane to prepare the corresponding tributylstannane reagent. After coupling with 4, 7-dibromobenzothiadiazole under the Stille-coupling reaction condition, L7-Br was obtained. At last, M17 was synthesized via the palladium catalyzed Stille-coupling reaction between L7-Br and the corresponding CPT-tributylstannane reagent.

Introducing one more thiophene unit between central donor unit and next
acceptor units in M17, the modified molecule M18 was achieved. Scheme 4.8 shows the chemical structures and synthetic routes of L8-Br and M18.

Scheme 4.7 The synthetic pathways of L8-Br and M18.

By using 4, 7-dibromobenzo thiadiazole as the starting material, under Suzuki cross-coupling reaction condition with 2-thiophene-boronic acid, 4,7-di(thiophen-2-yl)benzo thiadiazole was obtained which was then brominated by NBS in the mixture of acetic acid and chloroform solutions to get 4-(5-bromo thiophen-2-yl)-7-(thiophen-2-yl)benzo thiadiazole. This bromide reagent was further treated with (5-(2-ethylhexyl)thiophen-2-yl)tributylstannane reagent to
obtain \textbf{L8}. Subsequently, \textbf{L8} reacted with NBS in the mixture of acetic acid and chloroform to obtain the key intermediate \textbf{L8-Br}. By using Stille-coupling reaction, \textbf{L8-Br} reacted with the corresponding CPT-tributylstannane reagent to prepare \textbf{M8}.

Quinoxaline is another kind of efficient electron-withdrawing unit, and it can be considered as a benzothiadiazole derivative. Like benzothiadiazole, quinoxaline unit is also a promising candidate for organic solar cells. By incorporating it into organic molecule, \textbf{M19} has been synthesized and investigated as organic photovoltaic materials in OSCs. The synthetic routes of \textbf{M19} are shown in Scheme 4.8. Firstly, 3-bromophenol was alkylated with n-octyl bromide under base condition to get 1-bromo-3-(octyloxy)benzene. After reaction with magnesium ribbon and LiBr/CuBr reagents, the corresponding Grignard reagent was obtained. The freshly prepared Grignard reagent directly reacted with oxalyl dichloride to obtain 1,2-bis(3-(octyloxy)phenyl)ethane-1,2-dione. On the other hand, the five-membered ring in benzothiadiazole of \textbf{L8} was opened through the reduction reaction to obtain benzene-1,2-diamine derivative. By further reacting it with 1,2-bis(3-(octyloxy)phenyl)ethane-1,2-dione under acetic acid condition, the quinoxaline derivative \textbf{L9} was obtained. After bromination with NBS, \textbf{L9-Br} was obtained. Finally, \textbf{M9} was synthesized via the palladium catalyzed Stille-coupling reaction between \textbf{L9-Br} and the corresponding CPT-tributylstannane reagent.
Scheme 4.8 The synthetic pathways for L9-Br and M19.

4.2.2 Synthesis of CPT-Based Small Molecule M20

The cyano unit (-CN) is another kind of electron-withdrawing group, which can be incorporated into π-conjugated building blocks at appropriate positions for increasing molecular electron affinity and dipole interactions. To explore the feasibility of using this class of compounds as n-type organic photovoltaic materials, M20 has been synthesized and characterized. The central fused CPT donor unit is
incorporated into the electron-withdrawing BT group, which is further linked to functional cyano unit along the π-conjugated backbone. This CN-π-A-D-A-π-CN architectural structure may enhance the intermolecular π-π stacking interaction, thus leading to higher charge-carrier mobilities. Also, the planar backbone of M20 may reduce the relative band gap, attributed to the presence of the cyanovinylene unit, together with the extension of absorption coverage.

The synthetic pathways of M20 are shown in Scheme 4.9. Firstly, 4-bromophenyl acetonitrile reacted with tributyl(5-(2-ethylhexyl)thiophen-2-yl)stannane under Stille-coupling reaction condition to obtain 2-(4-(5-(2-ethylhexyl)thiophen-2-yl)phenyl)acetonitrile. On the other hand, under the Stille-coupling reaction condition, 4,7-dibromobenzothiadiazole reacted with one equiv of tributyl(thiophen-2-yl)stannane to get 4-bromo-7-(thiophen-2-yl)benzothiadiazole. After subsequent oxidation reaction with POCl₃/DMF reagent, L20-aldehyde was obtained. At last, by using the Knoevenagel-condensation reaction between this acetonitrile derivative and the aldehyde, L20-Br was made. Finally, M20 was synthesized via the palladium catalyzed Stille-coupling reaction between L20-Br and the corresponding CPT-tributylstannane reagent.
4.2.3 Synthesis of CPT-Based Small Molecules M21 and M22

Instead of CPT-based π-A-D-A-π architectural small molecules, we also synthesized a series of CPT-derived D-A-D-A-D or D-A-π-D-π-A-D structural small molecules, in which triphenylamine (TPA) units were introduced as the ending group for increasing the π-conjugation length along the molecular backbone and for enhancing the intermolecular charge transfer. As mentioned before, materials with TPA segments as the electron donor have shown long-lived charge excited state and good hole-transporting ability. In symmetrical molecules M21 and M22, a strongly
electron-donating CPT group is located at the central position to ensure strong π-π intermolecular interactions. Moreover, through incorporated N,N-di-p-tolylbenzenamine unit as the tail-D’ group to build D’-A-D-A-D’ or D’-A-π-D-π-A-D’ molecules, a more efficient intra molecular charge transfer (ICT) and a higher hole-mobility may be accomplished.

The synthetic routes for M21 are shown in Scheme 4.10. Firstly, 4-bromo-N,N-di-p-tolylbenzenamine was prepared by condensation reaction between 4-bromobenzenamine and 1-iodo-4-methylbenzene. Then, this benzenamine compound reacted with n-butyl lithium and subsequently tributylchlorostannane to prepare the corresponding tributylstannane reagent. After the coupling reaction with 4,7-dibromobenzothiadiazole under the Stille-coupling reaction condition, L13-Br was obtained. At last, M21 was obtained via the palladium catalyzed Stille-coupling reaction between L13-Br and the corresponding CPT-tributylstannane reagent.
Scheme 4.10 The synthetic pathways of L13-Br and M21.

Compared with D'-A-D-A-D' architectural M21, M22 with D'-A-π-D-π-A-D' structure was also synthesized. The synthetic routes for M22 are shown in Scheme 4.11. By using L13-Br as the starting material, it reacted with 2-thiopheneboronic acid reagent through Suzuki cross-coupling reaction and substituently NBS reagent, L15-Br was obtained. Under the Stille-coupling reaction condition, M22 was achieved from the reaction of L15-Br with the corresponding CPT-tributylstannane reagent via the palladium catalyzed Stille-coupling reaction.
Scheme 4.11 The synthetic pathways of L15-Br and M22.

4.3 Spectroscopic Characterization of M16-M22

All of the compounds were fully characterized by common spectroscopic techniques such as $^1$H, $^{13}$C and $^{19}$F NMR spectroscopy on a Bruker AV 400 MHz FT-NMR spectrometer and high resolution (HR) MALDI-TOF (matrix-assisted laser desorption/ionization time-of-flight) spectra were obtained by a Autoflex Bruker MALDI-TOF mass spectrometer. $^1$H and $^{13}$C NMR analyses clearly demonstrate a well-defined structure for M16-M22. $^1$H NMR resonances stemming from the protons of the organic moieties were observed. The $^{13}$C NMR spectral data give precise information about the regiochemical structure of the compounds.

All the protons signals of aryl rings are on the downfield side, while the alkyl
proton signals are shown at a highfield side. The proton signals of functional triphenylamine group are on the downfield region (above 7.20 ppm). The NMR data of intermediates and other compounds are summarized in the Experimental part of Chapter 7.

4.3.1 $^1$H and $^{13}$C NMR Spectroscopy of M16-M22

The $^1$H NMR and $^{13}$C NMR spectra of the corresponding compounds are shown in Figures 4.1-4.14, respectively.

![Figure 4.1 $^1$H NMR spectrum of M16 in CDCl$_3$.](image-url)
Figure 4.2 $^{13}$C NMR spectrum of M16 in CDCl$_3$.

Figure 4.3 $^1$H NMR spectrum of M17 in CDCl$_3$. 
Figure 4.4 $^{13}$C NMR spectrum of M17 in CDCl$_3$.

Figure 4.5 $^1$H NMR spectrum of M18 in CDCl$_3$. 
Figure 4.6 $^{13}\text{C}$ NMR spectrum of M18 in CDCl$_3$.

Figure 4.7 $^1\text{H}$ NMR spectrum of M19 in CDCl$_3$. 
Figure 4.8 $^{13}$C NMR spectrum of M19 in CDCl$_3$.

Figure 4.9 $^1$H NMR spectrum of M20 in THF-d$_8$. 
Figure 4.10 $^{13}$C NMR spectrum of M20 in CDCl$_3$.

Figure 4.11 $^1$H NMR spectrum of M21 in CDCl$_3$. 
Figure 4.12 $^{13}\text{C}$ NMR spectrum of M21 in CDCl$_3$.

Figure 4.13 $^1\text{H}$ NMR spectrum of M22 in CDCl$_3$. 
4.4 Photophysical Properties of M16-M22

To study the potential of M16-M22 in organic solar cells, absorption spectra of the newly synthesized compounds have been investigated. Figure 4.15 shows the UV/Vis absorption spectra of M16-M19 in CH₂Cl₂ solution at room temperature. The two distinct absorption bands can be attributed to the localized π-π* transitions in the high energy region and internal charge transfer (ICT) in their low energy region.
respectively. Such absorption profiles are typical of donor-acceptor architectural molecules. An approximately 26 nm red shift of the $\lambda_{\text{onset}}$ was observed when compared to M16 and M17, consistent with the increased conjugation length of M17 afforded by the two additional thiophene units. M18 contains additional thiophene units in the middle of D-A segment of M17, but only a slight hypochromic shift of $\lambda_{\text{onset}}$ (2 nm) is observed. This observation indicates that adding thiophene units in the middle of D-A segments of M17 did not narrow down the relative optical band gap. On the other hand, both of M18 and M19 with more thiophene units in their backbone exhibit higher molar absorption coefficient (11.4 and 10.5×10$^4$ dm$^3$mol$^{-1}$cm$^{-1}$, respectively). Among them, M17 with $\pi$-A-D-A-$\pi$ structure has the furthest red-shifted spectrum in CH$_2$Cl$_2$, with a $\lambda_{\text{max}}$ of 609 nm and $\lambda_{\text{onset}}$ at 717 nm. Its corresponding energy gap ($E_g$) is 1.73 eV. The relevant data are summarized in Table 4.1.
Figure 4.15 Normalized absorption spectra of M16-M19 in CH$_2$Cl$_2$ at 293 K.

Table 4.1 Photophysical data for compounds M16-M19 in CH$_2$Cl$_2$ at 293 K.

<table>
<thead>
<tr>
<th></th>
<th>Absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$ (nm)</td>
</tr>
<tr>
<td>M16</td>
<td>583</td>
</tr>
<tr>
<td>M17</td>
<td>609</td>
</tr>
<tr>
<td>M18</td>
<td>582</td>
</tr>
<tr>
<td>M19</td>
<td>565</td>
</tr>
</tbody>
</table>

$^a$ Optical band gap determined from the onset of absorption in solution phase.
The UV/Vis absorption spectra of M20-M22 in CH₂Cl₂ solution at room temperature are shown in Figure 4.16; see also Table 4.2. The higher energy absorption bands (around 300~450 nm) can be attributed to the molecular π-π* transitions. The lower energy absorption bands (around 450~750 nm) can be assigned to the ICT. CN-containing M20 depicts the farthest red shift in its absorption maximum (λₘₐₓ), as well as in its onset of absorption (λₒₙₛᵉᵗ). All of M20–M22 exhibit higher molar absorption coefficient (11.2, 10.9 and 11.3 × 10⁴ dm³ mol⁻¹ cm⁻¹). Among them, M22 with additional thiophene units in the middle of D-A segments of M21 showed the highest molar absorption coefficient of 11.3×10⁴ dm³ mol⁻¹ cm⁻¹. However, its maximum absorption (λₘₐₓ) and λₒₙₛᵉᵗ are a little hypochromically-shifted, when comparing M22 to M21. In the three compounds, M20 displayed the furthest red-shifted spectrum at 767 nm in λₒₙₛᵉᵗ and the corresponding energy gap Eₓ is 1.62 eV. The relevant data are summarized in Table 4.2.
Figure 4.16 Normalized absorption spectra of M20-M22 in CH$_2$Cl$_2$ at 293 K.

Table 4.2 Photophysical data for compounds M20-M22 in CH$_2$Cl$_2$ at 293 K.

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon_{\text{max}}$ ($10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{\text{onset}}$ (nm)</th>
<th>$E_g$ [eV]$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M20</td>
<td>629</td>
<td>11.2</td>
<td>767</td>
<td>1.62</td>
</tr>
<tr>
<td>M21</td>
<td>566</td>
<td>10.9</td>
<td>670</td>
<td>1.85</td>
</tr>
<tr>
<td>M22</td>
<td>552</td>
<td>11.3</td>
<td>677</td>
<td>1.83</td>
</tr>
</tbody>
</table>

$^a$ Optical band gap determined from the onset of absorption in solution phase.
4.5 Electrochemical Properties of M16-M22

To evaluate the oxidation ($E_{\text{ox}}$) and reduction potentials ($E_{\text{red}}$) of these conjugated molecules, cyclic voltammetry (CV) was performed on their thin films on glassy carbon electrode measured in 0.10 M [Bu$_4$N][PF$_6$] in acetonitrile with a Pt wire counter electrode and a Ag/AgCl reference electrode under N$_2$ atmosphere at a scan rate of 50 mV/s. The resulting CV traces are depicted in Figures 4.17 and 4.18, respectively, and electrochemical data of onset oxidation and reduction potentials versus Ag/Ag$^+$ are listed in Tables 4.3 and 4.4, respectively. There are a quasi-reversible oxidation wave and some irreversible reduction peaks for most of the compounds under CV conditions in Figures 4.17, and 4.18, respectively. The quasi-reversible oxidation process is probably attributed to the central donor group and the first irreversible reduction process to the acceptor group. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were estimated from the onset oxidation ($E_{\text{ox}}$) and reduction potentials ($E_{\text{red}}$), respectively.
4.5.1 Electrochemical Properties of M16-M19

All of M16-M19 have been investigated on the oxidation potentials and reduction potentials. Interestingly, both of the π-A-D-A-π configurational M17 and π-A-π-D-π-A-π M19 gave the smaller band gaps of around 1.51~1.52 eV.
Figure 4.17 Cyclic voltammograms of M16, M17, M18 and M19. top: cathodic scan in 0.10 M Bu4NPF6/CH3CN, bottom: anodic scan in 0.10 M Bu4NPF6/CH3CN; scan rate 100 mV/s; Y-axis (µA).

Table 4.3 Electrochemical properties of M16, M17, M18 and M19.

<table>
<thead>
<tr>
<th></th>
<th>(E_{ox}) (eV)(^{a})</th>
<th>HOMO (eV)(^{b})</th>
<th>(E_{red}) (eV)(^{a})</th>
<th>LUMO (eV)(^{c})</th>
<th>(E_g) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M16</td>
<td>0.42</td>
<td>-5.15</td>
<td>-1.23</td>
<td>-3.50</td>
<td>1.65</td>
</tr>
<tr>
<td>M17</td>
<td>0.36</td>
<td>-5.09</td>
<td>-1.14</td>
<td>-3.58</td>
<td>1.51</td>
</tr>
<tr>
<td>M18</td>
<td>0.46</td>
<td>-5.19</td>
<td>-1.26</td>
<td>-3.47</td>
<td>1.72</td>
</tr>
<tr>
<td>M19</td>
<td>0.31</td>
<td>-5.04</td>
<td>-1.21</td>
<td>-3.52</td>
<td>1.52</td>
</tr>
</tbody>
</table>

\(^{a}\) Onset oxidation and reduction potentials

\(^{b}\) HOMO = -e\((E_{ox} + 4.73)\) (eV)

\(^{c}\) LUMO = -e\((E_{red} + 4.73)\) (eV)
4.5.2 Electrochemical Properties of M20-M22

The effects of variation in the configuration of M20-M22 on both oxidation potentials and reduction potentials were also investigated. The HOMO energy levels of M20, M21 and M22 were -5.16, -5.26 and -5.13 eV, respectively, while the corresponding LUMO energy levels were -3.54, -3.48 and -3.54 eV, respectively. Their energy gaps were 1.62, 1.78 and 1.59 eV, respectively. Among them, cyano-containing M20 and A-π-D-π-A configurational M22 were show to have the smaller energy gap. M21 and M22 containing similar triphenylamine units as the ending groups, and the HOMO energy level of M22 was higher than M21. However, the relative LUMO energy level of M22 was lower than M21. As a result, the energy gap of M22 was smaller than M21 by about 0.19 eV. On the other hand, M21 with HOMO energy level of -5.26 eV is very efficient for obtaining higher $V_{oc}$ after being blending with PCBM. As shown in the current density versus voltage ($J$-$V$) curve in Figure 4.21, the $V_{oc}$ of 0.88 V based on M21/PC$_{61}$BM blend was obtained, in which similar $V_{oc}$ of 0.83 V was achieved after blending with PC$_{71}$BM.
Figure 4.18 Cyclic voltammograms of M20, M21 and M22. top: cathodic scan in 0.10 M Bu₄NPF₆/CH₃CN, bottom: anodic scan in 0.10 M Bu₄NPF₆/CH₃CN; scan rate 100 mV/s; Y-axis (μA).
Table 4.4 Electrochemical properties of M20, M21 and M22.

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{ox}}$ (eV)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>HOMO (eV)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>$E_{\text{red}}$ (eV)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>LUMO (eV)&lt;sup&gt;c&lt;/sup&gt;</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M20</td>
<td>0.43</td>
<td>-5.16</td>
<td>-1.19</td>
<td>-3.54</td>
<td>1.62</td>
</tr>
<tr>
<td>M21</td>
<td>0.53</td>
<td>-5.26</td>
<td>-1.25</td>
<td>-3.48</td>
<td>1.78</td>
</tr>
<tr>
<td>M22</td>
<td>0.40</td>
<td>-5.13</td>
<td>-1.19</td>
<td>-3.54</td>
<td>1.59</td>
</tr>
</tbody>
</table>

<sup>a</sup> Onset oxidation and reduction potentials
<sup>b</sup> HOMO = -$e(E_{\text{ox}} + 4.73)$ (eV)
<sup>c</sup> LUMO = -$e(E_{\text{red}} + 4.73)$ (eV)

4.6 Theoretical Studies of M21 and M22

To understand the optical and electrochemical properties of these compounds, we have modeled the electronic structure by density functional theory (DFT). The electronic distributions in the frontier molecular orbitals of the selected compounds are displayed in Figures 4.19 and 4.20. For both of M21 and M22, the electron distributions in their HOMO-1 energy level are generally located at the ending-TPA units. It is impressive that the electron distributions of M21 in its HOMO energy level are located throughout the whole molecular backbones. The similar feature is observed in the case of M22. As a typical D-A materials, the electron distributions are most located on their acceptor moieties in the LUMO energy level. These features implied that the relative strength of intermolecular charge transition will be stronger.
both in M21 and M22. It is readily observed in Figures 4.19 and 4.20. Also, the electron distributions are mostly located on the BT moieties, not only in their LUMO energy level, but also in their LUMO+1 energy level.

![Figure 4.19 DFT/B3LYP/6-31G gap orbital energy and topologies of M21.](image)
More importantly, by using donor as the central group incorporated with two acceptors along the molecular backbone, this A-D-A structure will make a good influence on the molecular dipolar change. After the exciton was generated by absorbing photon, it will be easily diffused along the molecular \( \pi \)-conjugated backbone toward both sides, and then dissociated.

Figure 4.20 DFT/B3LYP/6-31G gap orbital energy and topologies of M22.
Table 4.5 HOMO-1, HOMO, LUMO and LUMO+1 energy levels and $E_g$ determined by theoretical calculation for M21 and M22.

<table>
<thead>
<tr>
<th></th>
<th>HOMO-1 (eV)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>LUMO+1 (eV)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M21</td>
<td>-4.88</td>
<td>-4.62</td>
<td>-2.92</td>
<td>-2.69</td>
<td>1.70</td>
</tr>
<tr>
<td>M22</td>
<td>-4.86</td>
<td>-4.61</td>
<td>-2.90</td>
<td>-2.77</td>
<td>1.71</td>
</tr>
</tbody>
</table>

4.7 BHJ Solar Cell Performance of M21 and M22

BHJ solar cells based on M21 and M22 were fabricated in a typical configuration of ITO/PEDOT-PSS/active layer/Ca/Al and tested. PSCs were optimized empirically by scrutinizing variation in the blend ratios of the compounds to PC$_{61}$BM and PC$_{71}$BM, respectively. The resulting open circuit voltage ($V_{oc}$), short circuit current ($J_{sc}$), fill factor (FF), and power conversion efficiency (PCE) values were determined from the $J$-$V$ curves, and all of the relevant solar cell parameters are summarized in Tables 4.5 and 4.6, respectively.

The current density versus voltage ($J$-$V$) curves of M21/PC$_{61}$BM and M21/PC$_{71}$BM with different weight blend ratios are shown in Figure 4.21, and the relative EQE curves are shown in Figure 4.22. The optimized results are summarized
in Table 4.5. Firstly, the device with PC\textsubscript{61}BM as electron acceptor for a 1:1 blend ratio exhibited a $V_{oc}$ of 0.88 V, a $J_{sc}$ of 2.79 mA/cm$^2$, and FF of 25.9%, which yielded a PCE of 0.64%. For a 1:2 blend ratio of M\textsubscript{21}/PC\textsubscript{61}BM, it exhibited a $V_{oc}$ of 0.78 V, a $J_{sc}$ of 3.92 mA/cm$^2$, and a FF of 31.0%, which gave a PCE of 0.95%. With increasing the M\textsubscript{21}/PC\textsubscript{61}BM blend ratio from 1:2 to 1:3, the optimized device gave the highest PCE of 1.22% (based on PC\textsubscript{61}BM as acceptor), with a $V_{oc}$ of 0.72 V, a $J_{sc}$ of 4.86 mA/cm$^2$, and a FF of 35.0%. With a further increase in the content of PC\textsubscript{61}BM with a blend ratio of 1:4, a lower PCE of 1.02% with the lower values for $V_{oc}$ of 0.70 V, $J_{sc}$ of 4.56 mA/cm$^2$, and a FF of 32.1% were obtained. On the other hand, the device of M\textsubscript{21} blended with PC\textsubscript{71}BM as electron acceptor was also fabricated. When a 1:1 blend ratio of M\textsubscript{21}/PC\textsubscript{71}BM was used, a $V_{oc}$ of 0.78 V and $J_{sc}$ of 5.67 mA/cm$^2$ were obtained, with a FF of 31.2% and PCE of 1.38%. As the M\textsubscript{21}/PC\textsubscript{71}BM blend ratio was increased from 1:1 to 1:2, the optimized device gave the highest PCE of 2.36%, accompanied by a $V_{oc}$ of 0.83 V, a $J_{sc}$ of 7.35 mA/cm$^2$, and a FF of 38.7%. With a further increase in the content of PC\textsubscript{71}BM, the corresponding $J_{sc}$ and FF values as well as the PCE were decreased. By using a 1:3 blend ratio of M\textsubscript{21}/PC\textsubscript{71}BM, a $V_{oc}$ of 0.81 V and a $J_{sc}$ of 5.45 mA/cm$^2$ were obtained with a FF of 46.3% and a PCE of 2.04%.
Figure 4.21 Current density versus voltage (J-V) characteristics of optimized devices made from various blend ratios of M21: PC_{61}BM (top) and M21: PC_{71}BM (bottom).
Table 4.6 Device performance of M21-based BHJ devices.

<table>
<thead>
<tr>
<th>Blend Ratio</th>
<th>M21:PCBM (w:w)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>0.88</td>
<td>2.79</td>
<td>25.9</td>
<td>0.64</td>
<td></td>
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<tr>
<td>1:2</td>
<td>0.78</td>
<td>3.92</td>
<td>31.0</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>1:3</td>
<td>0.72</td>
<td>4.86</td>
<td>35.0</td>
<td>1.22</td>
<td></td>
</tr>
<tr>
<td>1:4</td>
<td>0.70</td>
<td>4.56</td>
<td>32.1</td>
<td>1.02</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Blend Ratio</th>
<th>M21:PCbm (w:w)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>0.78</td>
<td>5.67</td>
<td>31.2</td>
<td>1.38</td>
<td></td>
</tr>
<tr>
<td>1:2</td>
<td>0.83</td>
<td>7.35</td>
<td>38.7</td>
<td>2.36</td>
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<tr>
<td>1:3</td>
<td>0.81</td>
<td>5.45</td>
<td>46.3</td>
<td>2.04</td>
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</tbody>
</table>

Figure 4.22 shows the external quantum efficiency (EQE) curve of the BHJ devices based on M21/PC61BM and M21/PC71BM with different blend ratios under monochromatic light. In M21, the EQE curves exhibited monochromatic EQE maximum of 21% at 598 nm in the optimized blend ratio of M21/PC61BM = 1:3 and broad in response covering 300-700 nm, consistent with the optical absorption bands. In the optimized blend ratio of M21/PC71BM = 1:2, the highest monochromatic EQE maximum of 48% at 578 nm was received. All the EQE curves based on M21/PC71BM were broad in response covering 300-700 nm, consistent with the corresponding optical absorption bands.
Figure 4.22 EQE curves of a M21/PC\textsubscript{61}BM and M21/PC\textsubscript{71}BM with different blend ratios.
Table 4.7 Device performance of M22 based BHJ devices.

<table>
<thead>
<tr>
<th>M22:PCBM (w:w)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC$_{61}$BM</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:1</td>
<td>0.81</td>
<td>3.13</td>
<td>33.6</td>
<td>0.85</td>
</tr>
<tr>
<td>1:2</td>
<td>0.80</td>
<td>4.23</td>
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<tr>
<td>1:3</td>
<td>0.75</td>
<td>4.52</td>
<td>36.7</td>
<td>1.24</td>
</tr>
<tr>
<td>PC$_{71}$BM</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:1</td>
<td>0.57</td>
<td>5.09</td>
<td>28.2</td>
<td>0.82</td>
</tr>
<tr>
<td>1:2</td>
<td>0.81</td>
<td>6.66</td>
<td>41.0</td>
<td>2.21</td>
</tr>
<tr>
<td>1:3</td>
<td>0.78</td>
<td>5.87</td>
<td>45.3</td>
<td>2.07</td>
</tr>
</tbody>
</table>

![Graph showing current density vs. voltage for M22:PC$_{61}$BM](image-url)
Figure 4.23 Current density versus voltage ($J$-$V$) characteristics of optimized devices made from various blend ratios of M22: PC$_{61}$BM (top) and M22: PC$_{71}$BM (bottom).

4.8 Conclusion

Seven different small molecules based on the CPT unit as the central donor group and BT or Qx unit as the acceptor were synthesized and characterized. Also, the structure-property relationships have been comprehensively investigated. Among them, M16-M19 were constructed by using 2-ethylhexyl or 2-ethylhexyl-thienyl units as the ending group. M20 was incorporated with cyanovinylene group for modifying its energy levels. Also, by using triphenylamine derivatives as the ending group, M21
and M22 have been synthesized. As shown in the representative orbital energy diagrams contributed by DFT calculations, these molecules possess fully planar backbone structures (considered as A-D-A or A-π-D-π-A). More importantly, the electronic distributions in their HOMO energy levels of each molecule are spread throughout the whole π-conjugated backbone. Contrarily, the electron distributions of all these compounds are mostly located on the acceptor moiety in their LUMO energy levels. These features perfectly illuminated the D-A molecular advantages. At last, based on BHJ solar cells fabricated by M21/PC71BM, the best performance with a higher PCE of 2.36% has been achieved.

References:


Chapter 5 Synthesis and Characterization of Star-Shaped Small Molecules with Triphenylamine Core for Solution-Processed Organic Solar Cells

5.1 Introduction

5.1.1 Triphenylamine (TPA)-Based Small Molecules

Triphenylamine (TPA) units, with its high hole transporting ability and good electron donating property, has been widely investigated as efficient photovoltaic materials.\[1-13\] In addition, many star-shaped molecular structures, so-called starburst molecules in which TPA is used as the central core, have been tested for their applications in organic solar cells. The advantages like high solution-processable ability, easy purification and chemically well-defined structures in these star-shaped small molecules make them become a novel class of organic photovoltaic materials.\[14-16\] Normally, the structures of these star-shaped molecules are composed by D-\(\pi\)-A architecture or D-A-D architecture. For D-\(\pi\)-A architecture, a central TPA donor unit will link with the acceptor units by \(\pi\)-conjugated bridge for building a D-\(\pi\)-A block. In another case, a central TPA unit may directly link to an acceptor for building a primary D-A block. Then, by introducing another donor ending groups, a D-A-D architectural molecule can be constructed. Furthermore, their photophysical
and electrochemical properties may be tuned by the branched parts of star-shaped molecules, which function as a light harvesting antennae.\textsuperscript{17-29} On the other hand, constructed by benzothiadiazole (BT) unit as the acceptor, both of the donor-acceptor architectural organic small molecules and polymers represent attractive properties, because they impart high solution-processable ability for effective bulk heterojunction morphologies together with broad absorptions in the solar spectrum. Some good examples of TPA-based small molecules are shown in Schemes 5.1 and 5.2.

\textbf{Scheme 5.1} Examples of small molecules based on TPA core.
By using TPA unit as the central donor, oligothiophene or more electron donating EDOT unit containing oligothiophene as the branched part, TPA-1 and TPA-2 were synthesized by Roncali and co-workers. TPA-2 showed a red-shifted absorption and emission maxima relative to TPA-1. A high hole mobility (ca. 1.1×10⁻² cm²/Vs) was observed in TPA-1 by OFET measurements. The molecules of TPA-1 and TPA-2 showed PCEs of 0.3% and 0.1% in OSCs, respectively.⁷⁰ Star-shaped molecule TPA-3 was composed by TPA unit as central core as well as
ending groups which were incorporated with benzothiadiazole unit in the middle of them. Its device showed a PCE of 1.3%, $V_{oc}$ of 0.81 V, $J_{sc}$ of 4.8 mA/cm$^2$ and FF of 39%.\textsuperscript{[1]} By using TPA unit as the central donor group, dithiophene as a π-bridge linked with cyano groups, a star-shaped D-π-A architectural **TPA-4** has been synthesized, which covered a broad wavelength range from 380 to 750 nm. Its BHJ device showed a PCE of 3.0%, $V_{oc}$ of 0.88 V, $J_{sc}$ of 7.8 mA/cm$^2$ and FF of 44%.\textsuperscript{[31]}

Some examples of TPA-centred small molecules with good PCE values in relative BHJ organic solar cell devices are shown in Scheme 5.2. **S(TPA-3BT)** exhibited a PCE of 2.3% based on PC$_{61}$BM with $V_{oc}$ of 0.86 V, $J_{sc}$ of 5.9 mA/cm$^2$ and FF of 46%. After blended with PC$_{71}$BM, the higher PCE of 4.3% was achieved with $V_{oc}$ of 0.87 V, $J_{sc}$ of 9.5 mA/cm$^2$ and FF of 52%.\textsuperscript{[2]} This PCE is one of the highest values based on branched small molecules for solution-processed BHJ organic solar cells. On the other hand, two and three-branched TPA-oligothiophene hybrids **L(TPA-3BT-CA)** and **S(TPA-3BT-CA)** were reported by Zhan et al.\textsuperscript{[13]} By using TPA unit as the central donor, oligothiophene as the π-bridge, and alkyl cyanoacetate as the acceptor end group, both molecules showed excellent thermal stability and strong optical absorption at 300-700 nm, together with deeper HOMO energy levels of around -5.17- 5.28 eV and higher hole mobilities of around $1.5 \times 10^{-3}$ cm$^2$/Vs~7.8 $\times 10^{-3}$ cm$^2$/Vs, respectively. The PCE values based on **S(TPA-3BT-CA)/PC$_{71}$BM** and
In this chapter, a series of TPA-centered small molecules with D-π-A or D-A-D configuration have been synthesized. TPA unit, as the central core and electron-donating group in these molecules, play an important role in these compounds. The extended π-conjugated system incorporated with TPA is expected to afford strong intramolecular orbital overlap and enhance charge transfer ability by utilizing the favorable “D-A” architecture. Their photophysical, electrochemical and structural properties were fully investigated.

5.2 Synthesis

By using TPA unit as the central donor moiety, benzothiadiazole (BT) or thienopyrazine unit as the acceptor, alkynyl-thiophene unit as the bridge, star-shaped D-π-A architectural molecules M22-M24 were synthesized. Also, by using one TPA unit as the central donor, another TPA unit as the ending group, and BT or f-BT unit as the π-bridge, star-shaped D-A-D architectural molecules M25-M26 were prepared.

5.2.1 Synthesis of M23 and M24

The chemical structures and synthetic strategies of M23 and M24 are shown in
Schemes 5.3 and 5.4, respectively. Firstly, 3-hexyl-thiophene as the starting material reacted with n-butyl lithium and subsequently tributylchlorostannane to prepare the corresponding tributylstannane reagent. Then, this reagent reacted with 4, 7-dibromobenzothiadiazole under the Stille-coupling reaction condition to get dithienyl-benzothiadiazole. After bromination with NBS, M23-Br was obtained. Conversion of M23-Br to its corresponding diethynyl congener (M23-Alkyne) can be readily achieved by the typical organic synthetic protocols for alkynylation of aromatic halides. On the other hand, triphenylamine underwent iodation reaction by potassium iodide and potassium iodate to prepare the key precursor tris(4-iodophenyl)amine for the next Sonogashira reaction. At last, M23 was achieved by reacting tris(4-iodophenyl)amine with M23-Alkyne under cuprous iodide and Pd(PPh3)4 catalytic condition.
Scheme 5.3 The synthetic pathways of M23-Alkyne and M23.

Similar strategy for preparing M24 was applied. Firstly, 2,5-dibromo-3,4-dinitrothiophene reacted with tributyl(thiophen-2-yl)stannane under Stille-coupling reaction condition to afford 3,4-dinitro-2,5-di(thiophen-2-yl)thiophene. Then, it underwent reduction reaction by tin chloride to get an amine congener and further condensed with hexacosane-dione to obtain the key precursor 2,3-didodecyl-5,7-di(thiophen-2-yl)thienopyrazine.
Scheme 5.4 The synthetic pathways of M24-Alkyne and M24.

Then, M24-Br was easily obtained after brominating this precursor with NBS. Converting M24-Br to its corresponding diethynyl congener (M24-Alkyne) can be readily achieved by the organic synthetic protocols for alkynylation of aromatic halides. With similar Sonogashira reaction, M24 was achieved by reacting M24-Alkyne with tris(4-iodophenyl)amine.
5.2.2 Synthesis of M25 and M26

Instead of D-π-A architectural small molecules, a series of D-A-D structural small molecules were also synthesized as organic photovoltaic materials for application in organic solar cells. As mentioned before, triphenylamine (TPA) and its derivatives have been extensively applied in OSCs as efficient functional groups for building π-conjugated block because of its long lived charge excited state and good hole-transporting ability. In both M25 and M26, TPA unit was not only used as electron donating group for building D-A branch, but also applied for constructing star-shaped molecule via its propeller structure. The synthetic routes for M25 are shown in Scheme 5.5. 4-Bromo-N,N-di-p-tolylbenzenamine was achieved by condensation reaction between 4-bromobenzenamine and 1-iodo-4-methylbenzene. This bromide compound reacted with n-butyl lithium and subsequently tributylchlorostannane to prepare the corresponding tributylstannane reagent. Then, coupling this reagent with 4, 7-dibromobenzothiadiazole under the Stille-coupling reaction condition gave L13-Br. On the other hand, triphenylamine was brominated with liquid bromine to get tris(4-bromophenyl)amine. Then, it reacted with n-butyl lithium and subsequently tributylchlorostannane to prepare the corresponding TPA-tributylstannane reagent. At last, M25 was achieved via the palladium catalyzed Stille-coupling reaction between L13-Br and the corresponding TPA-tributylstannane
Another material \textbf{M26} which uses fluorine substituted BT unit to replace the BT unit in \textbf{M25} has also been investigated (Scheme 5.5). As we discussed before, fluorine atoms may play a crucial role in organic solar cell materials because of its unique features like stable oxidation, elevated resistance to degradation, higher hydrophobicity, and larger effect on inter- and intra-molecular interaction via C–F H, F S, and C–F $\pi_F$ interactions. The synthetic routes are shown in Scheme 5.6. By using
4-fluorobenzene-1,2-diamine as the starting material, it reacted with thionyl chloride reagent through condensation reaction to produce 5-fluorobenzothiadiazole. Then, this compound was brominated by liquid bromine in hydrobromic acid to obtain 4,7-dibromo-5-fluorobenzothiadiazole. Under the Stille-coupling reaction condition, \(N,N\)-di-\(p\)-tolylbenzenamine-tributylstannyl reagent reacted with 4,7-dibromo-5-fluorobenzothiadiazole to get \(L14\text{-Br}\). Finally, \(M14\) was synthesized via the palladium catalyzed Stille-coupling reaction between \(L14\text{-Br}\) and the corresponding TPA-tributylstannane reagent.

**Scheme 5.6** The synthetic pathways of \(L14\text{-Br}\) and \(M26\).
5.3 Spectroscopic Characterization of M23-M26

All of M23-M26 were fully characterized by common spectroscopic techniques such as $^1$H, $^{13}$C, $^{19}$F and NMR spectroscopy on a Bruker AV 400 MHz FT-NMR spectrometer and high resolution (HR) MALDI-TOF (matrix-assisted laser desorption/ionization time-of-flight) spectra were obtained by a Autoflex Bruker MALDI-TOF mass spectrometer. $^1$H and $^{13}$C NMR analyses clearly demonstrate a well-defined structure for M23-M26. $^1$H NMR resonances stemming from the protons of the organic moieties were observed. The $^{13}$C NMR spectral data give precise information about the regiochemical structure of the compounds. The NMR data of intermediates and other compounds are summarized in the Experimental part of Chapter 7.

5.3.1 $^1$H and $^{13}$C NMR Spectroscopy of M23-M26

The $^1$H NMR and $^{13}$C NMR spectra of M23-M26 are shown in Figures 5.1-5.8, respectively. All the proton signals of aryl rings are on the downfield side, while the alkyl proton signals are shown at a high field side. The proton signals of functional triphenylamine group are on the downfield region (above 7.20 ppm).
Figure 5.1 $^1$H NMR spectrum of M23 in CDCl$_3$.

Figure 5.2 $^{13}$C NMR spectrum of M23 in CDCl$_3$. 
Figure 5.3 $^1$H NMR spectrum of M24 in CDCl$_3$.

Figure 5.4 $^{13}$C NMR spectrum of M24 in CDCl$_3$. 
Figure 5.5 $^1$H NMR spectrum of M25 in CDCl$_3$.

Figure 5.6 $^{13}$C NMR spectrum of M25 in CDCl$_3$. 
Figure 5.7 $^1$H NMR spectrum of M26 in CDCl$_3$.

Figure 5.8 $^{13}$C NMR spectrum of M26 in CDCl$_3$. 
5.4 Photophysical Properties of M23-M26

As shown in Figures 5.9 and 5.10 and in Tables 5.1 and 5.2, the UV/Vis absorption spectra of M23-M26 at room temperature in CH₂Cl₂ solutions were investigated. The two distinct absorption bands can be attributed to the localized π-π* transitions in high energy transition region and internal charge transitions (ICT) in their low energy transition region, respectively. A red shift of approximate 48 nm in λ_{onset} is observed when comparing M24 to M23, consistent with the increased electron-withdrawing ability of thienopyrazine unit relative to BT unit. The difference of BT and f-BT in M25 and M26 does not result in a large change on the relative optical spectra in CH₂Cl₂ solutions. Hence, the two distinct absorption bands which are typical profile of D-A type π-conjugated molecules can be observed. However, the corresponding molar absorption coefficients of M23-M26 of around 5.3~6.8 × 10⁴ dm³mol⁻¹cm⁻¹ are respectable. At last, in M23-M24, the largest λ_{onset} of 671 nm of M24 was observed and the corresponding energy gap E_g was 1.81 eV. In M25-M26, the largest λ_{onset} of 577 nm of M26 was measured and the corresponding energy gap E_g was 2.15 eV.
**Figure 5.9** Normalized absorption spectra of M23-M26 in CH$_2$Cl$_2$ at 293 K.

**Table 5.1** Photophysical data for compounds M23-M26 in CH$_2$Cl$_2$ at 293 K.

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon_{\text{max}}$ ($10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{\text{onset}}$ (nm)</th>
<th>$E_g$ [eV]$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M23</td>
<td>497</td>
<td>5.5</td>
<td>623</td>
<td>1.99</td>
</tr>
<tr>
<td>M24</td>
<td>537</td>
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<td>671</td>
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</tr>
<tr>
<td>M25</td>
<td>478</td>
<td>5.3</td>
<td>577</td>
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<tr>
<td>M26</td>
<td>468</td>
<td>5.6</td>
<td>573</td>
<td>2.16</td>
</tr>
</tbody>
</table>

$^a$ Optical band gap determined from the onset of absorption in solution phase.
5.5 Electrochemical Properties of M23-M26

The electronic levels of an organic semiconductor are crucial for governing the overall photovoltaic performance. To evaluate the oxidation ($E_{\text{ox}}$) and reduction potentials ($E_{\text{red}}$) of these conjugated molecules, cyclic voltammetry (CV) was performed on their thin films on glassy carbon electrode measured in 0.10 M [Bu$_4$N][PF$_6$] in acetonitrile with a Pt wire counter electrode and a Ag/AgCl reference electrode under N$_2$ atmosphere at a scan rate of 50 mV/s. The cyclic voltammograms and the electrochemical data versus Ag/Ag$^+$ are depicted in Table 5.2. There are a couple of irreversible oxidation peaks and a single irreversible reduction peak for M23-M24 under CV conditions in Figure 5.10, also a quasi-reversible oxidation wave and some irreversible reduction peaks for M25-M26 in Figure 5.11, respectively. The quasi-reversible oxidation process is probably attributed to the central donor group and the first irreversible reduction process to the acceptor group. The structural difference between M23, M25 and M26 only causes a slight shift on the $E_{\text{ox}}$ and $E_{\text{red}}$. However, the $E_{\text{ox}}$ of M24 was significantly raised to 0.30 eV, as a result, the corresponding HOMO energy level of -5.03 eV was obtained. It is a disadvantage of M24 as a potential solar cell material, because normally the higher HOMO energy level will match with the smaller $V_{\text{oc}}$ value in OSCs. The HOMO energy levels of M23, M24, M25 and M26 are -5.28, -5.03, -5.27 and -5.29 eV, respectively, while the
corresponding LUMO energy levels are -3.47, -3.47, -3.46 and -3.39 eV, respectively. The difference between the LUMO energy levels of M\textsuperscript{23-M26} and PC\textsubscript{71}BM (-4.0 eV) were in the range of 0.51~0.54 eV, which is very efficient for electron transfer from the donor to acceptor. Also, the lower HOMO energy levels of M\textsuperscript{23}, M\textsuperscript{25} and M\textsuperscript{26} are very important for obtaining higher $V_{oc}$ in OPVs. However, the relative larger band gap of M\textsuperscript{25} and M\textsuperscript{26} may result in no sufficient absorption of incident photon in OSC devices.
Figure 5.10 Cyclic voltammograms of M23 and M24; top: cathodic scan in 0.10 M Bu₄NPF₆/CH₃CN, bottom: anodic scan in 0.10 M Bu₄NPF₆/CH₃CN; scan rate 100 mV/s; Y-axis (µA).
Figure 5.11 Cyclic voltammograms of M25 and M26; top: cathodic scan in 0.10 M Bu₄NPF₆/CH₃CN, bottom: anodic scan in 0.10 M Bu₄NPF₆/CH₃CN; scan rate 100 mV/s; Y-axis (µA).

Table 5.2 Electrochemical properties of M23-M26.

<table>
<thead>
<tr>
<th></th>
<th>$E_{ox}$ (eV) a</th>
<th>HOMO (eV) b</th>
<th>$E_{red}$ (eV) a</th>
<th>LUMO (eV) c</th>
<th>$E_g$ (eV)</th>
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<tbody>
<tr>
<td>M23</td>
<td>0.55</td>
<td>-5.28</td>
<td>-1.26</td>
<td>-3.47</td>
<td>1.81</td>
</tr>
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<td>M24</td>
<td>0.30</td>
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<td>-1.26</td>
<td>-3.47</td>
<td>1.56</td>
</tr>
<tr>
<td>M25</td>
<td>0.54</td>
<td>-5.27</td>
<td>-1.27</td>
<td>-3.46</td>
<td>1.81</td>
</tr>
<tr>
<td>M26</td>
<td>0.56</td>
<td>-5.29</td>
<td>-1.24</td>
<td>-3.49</td>
<td>1.80</td>
</tr>
</tbody>
</table>

a Onset oxidation and reduction potentials

b HOMO = $-e(E_{ox} + 4.73)$ (eV)

c LUMO = $-e(E_{red} + 4.73)$ (eV)
5.6 Theoretical Studies of M25 and M26

Density functional theory (DFT) calculations using the hybrid B3LYP exchange-correlation functional and the split-valence 6-31G(d,p) basis set were applied to set forth the optical and electrochemical properties of these compounds.\[^{32,33}\] The electronic distributions in the frontier molecular orbitals of the selected compounds are displayed in Figures 5.12 and 5.13. For both of M25 and M26, the electron distributions in their HOMO-1 energy level are generally located on the TPA ending units. It is impressive that the electron distributions of both M25 and M26 in their HOMO energy levels are located not only on the branched D-A block, but also cross the central TPA unit. Contrarily, the electron distributions are generally located on the BT units, both in their LUMO and LUMO+1 energy levels. Also, substitution of fluorine on BT segment does not give rise to significant change on the photophysical properties or on the electronic distributions in the molecular orbitals.
Figure 5.12 DFT/B3LYP/6-31G gap orbital energy and topologies of M25.
Figure 5.13 DFT/B3LYP/6-31G gap orbital energy and topologies of M26.

Table 5.3 HOMO-1, HOMO, LUMO and LUMO+1 energy levels and $E_g$ determined by theoretical calculation for M25 and M26.

<table>
<thead>
<tr>
<th></th>
<th>HOMO-1 (eV)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>LUMO+1 (eV)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M25</td>
<td>-4.82</td>
<td>-4.65</td>
<td>-2.65</td>
<td>-2.64</td>
<td>2.00</td>
</tr>
<tr>
<td>M26</td>
<td>-4.91</td>
<td>-4.67</td>
<td>-2.73</td>
<td>-2.72</td>
<td>1.94</td>
</tr>
</tbody>
</table>
5.7 Conclusion

To search for the potential of TPA-based star-shaped small molecules for OSCs, by the Sonogashira-type dehydrohalogenation reaction for M23 and M24 or by the Stille-coupling reaction for M25 and M26, four compounds were synthesized. All of the compounds were carefully purified by column chromatography over silica gel and repeated precipitation by methanol, leading to the compounds in good yields and high purity. All of them are air-stable and well characterized by different spectroscopic methods and photophysical measurements. Also, the structure-property relationships have been comprehensively investigated. Among them, star-shaped D-π-A architectural molecules M23-M24 were constructed by using benzothiadiazole (BT) or thienopyrazine unit as the acceptor and alkynyl-thiophene unit as the π-bridge; another kinds of star-shaped D-A-D architectural molecules M25-M26 were prepared by using BT or f-BT unit as acceptor and TPA units as the donor. As shown in the representative orbital energy diagrams contributed by DFT calculations, M25-M26 possess 3D-propeller structure. More importantly, the electronic distributions in their LUMO energy levels are mostly located on the acceptor moiety, related to the HOMO energy levels, where the electronic distributions are spread throughout the whole π-conjugated backbone. Further work will be focused on investigating the material performance on organic solar cells.
References:


Chem. 2008, 18, 4085.


2006, 18, 2584.


Chapter 6 Synthesis and Characterization of New Metallopolyyne Polymers for Solution-Processed Organic Solar Cells

6.1 Introduction

Except for D-A copolymers as classical organic photovoltaic materials applied in OSCs, there are another kind of versatile photovoltaic materials which are based on metal-containing π-conjugated polymers. These metal-containing polymers are normally synthesized through Sonogashira-type dehydrohalogenation reactions of diethynyl precursor and platinum complex (normally trans-Pt(PBu₃)₂Cl₂) with 1:1 mole ratio. Hence, this class of metal-containing polymers is so called metallopolyyne polymers and platinum is the most employed metal so far.

More importantly, a lot of advantages can be expected when using metallopolyyne polymers as donor material in BHJ organic solar cells. The overlaps of d-orbitals of Pt unit with the p-orbitals of the adjacent alkyne units give rise to enhancement of π-electron delocalization and intramolecular charge transfer along the molecular backbone, which will significantly lower the energy gap. On the other hand, the triplet excitons in materials may be readily formed by enhancing the spin-orbit coupling. Also, contributed by the longer lifetime of triplet excitons in metal-containing material, the extended diffusion lengths of excitation in active layer
may be achieved.

The first single-layer metallopolyyne polymer was reported by A. Kohler et al. in which a PCE of 0.6% was obtained. A Pt-containing copolymer synthesized from platinum complexes with thiophene-acetylide precursor was shown to have a PCE of 0.27% after blended with PCBM in its OSCs. Recently, metallopolyyne polymers 1-5 have been reported by our research group, and the structures are shown in Figure 6.1. Among them, Pt-containing poly(aryleneethynylene)s 1-4 were synthesized through Sonogashira-type dehydrohalogenation polymerization of Pt complex with bithiazole-acetylide unit which was modified by different number of thiophene units. The higher PCE of 2.66% was obtained from 3 with a FF of 46%, a $V_{oc}$ of 0.90 V and a $J_{sc}$ of 6.39 mA/cm$^2$. By using the similar polymerization method, Pt-containing polymer 5 based on 4,7-di-2'-thienyl-2,1,3-benzothiadiazole unit was synthesized. The higher power conversion efficiency of 4.10% and moderate hole mobility of $1 \times 10^{-4}$ cm$^2$/Vs were achieved, with a corresponding a FF of 37%, a $V_{oc}$ of 0.82 V and $J_{sc}$ of 13.1 mA/cm$^2$. Also, by coupling the terminal dialkynyl-thieno[3,2-b]thiophene connected 2,1,3-benzothiadiazole units with the trans-dichlorobis(trialkylphosphine) platinum unit through the Sonogashira-type dehydrohalogenation polymerization reaction, 6-8 have been synthesized by Alex K.-Y. Jen et al. Among them, 8 showed the best PCE of 4.13%, with a $V_{oc}$ of 0.787 V, a FF of 49.3%, and a $J_{sc}$ of 9.61
mА/cm², and the higher hole mobility of $1.0 \times 10^{-2}$ cm²/Vs was observed.\cite{19}

It is worth noting that platinum-acetylide oligomers, as small organic photovoltaic materials, also show a great potential in solution-processed BHJ organic...
solar cells. Some examples are shown in Figure 6.1. The direct incorporation of platinum into the conjugated block leads to a high yield of triplet excitons, together with the enhancing intrachain charge transport in these materials.\textsuperscript{[20-22]} Jean M. J. Frechet et al. reported the Pt-oligomers 9-11 through the reaction of different oligothiophene-based alkynyl ligands with chloroplatinum complexes in the presence of a catalytic amount of CuI. The advantages like extended absorption in the low energy range, promoted solid-state packing accommodated by the different π-conjugated length of oligothiophene units and prevention of intermolecular aggregation afforded by tetrahedral trialkylphosphine units are contributed by the well designed crystalline platinum-acetylide oligomers.\textsuperscript{[23]} The best PCE value of 3.0\% of 10 was obtained with a $V_{oc}$ of 0.82 V, a FF of 43\%, and a $J_{sc}$ of 8.45 mA/cm$^2$. On the other hand, platinum-bis(aryleneethynylene) complexes 12-14 were synthesized by the reaction of TPA-BT based alkynyl ligands with chloroplatinum complexes in the presence of a catalytic amount of CuI. Among them, high PCE of 2.37\% and 2.34\% were observed for 12 and 13, respectively.\textsuperscript{[24]}

In this chapter, a series of Pt-containing polymers have been synthesized and investigated. Substitution of fluorine on BT unit allowed for fine control over relative energy levels and modified intermolecular interaction. Also, the improved solubility can be obtained by using the substituted alkyl chains on thiophene units. At last, their
photophysical and electrochemical properties were fully investigated. The corresponding structures of Pt-containing polymers are shown in Scheme 6.2.

Scheme 6.2 Pt-containing polymers for OSCs.

6.2 Synthesis

The common structures of new Pt-containing polymers **P5-P8** are listed in Figure 6.2. The dibromo precursors (**P5-Br**, **P6-Br**, **P7-Br** and **P8-Br**) were synthesized via Stille-coupling reaction or Suzuki-coupling reaction of BT unit or f-BT unit with the corresponding thiophene-boronic acid reagent or thiophene-tributylstannane reagent, followed by subsequent bromination reaction of the coupling product with NBS reagent, respectively. After the Sonogashira-type reaction condition, these dibromo precursors (**P5-Br**, **P6-Br**, **P7-Br** and **P8-Br**) were turned to the corresponding TMS-compounds. By cleaving the TMS groups under
basic condition, diethynyl precursors (P5-alkyne, P6-alkyne, P7-alkyne and P8-alkyne) were obtained. At last, the Pt-containing polymers P5-P8 were obtained by the Sonogashira-type dehydrohalogenation reaction of each of the diethynyl precursors with trans-dichlorobis(trialkylphosphine)platinum in the presence of a catalytic amount of CuI.

6.2.1 Synthesis of Pt-Containing Polymers P5-P8

The synthetic routes for P5 are shown in Scheme 6.1. By using 4,7-dibromobenzothiadiazole as a starting material, under Suzuki cross-coupling reaction condition with 2-thiopheneboronic acid, 4,7-di(thiophen-2-yl)benzothiadiazole was obtained. After subsequent bromination reaction with NBS in the mixture of acetic acid and chloroform solutions, P5-Br was prepared. Conversion of P5-Br to P5-alkyne was readily achieved by the typical organic synthetic protocols for alkynylation of aromatic halides. The Pt-containing polymer P5 was achieved by the Sonogashira-type dehydrohalogenation reaction between P5-alkyne and trans-dichlorobis(trialkylphosphine)platinum in the presence of a catalytic amount of CuI.
Scheme 6.3 The synthetic pathways for P5-Br and P5.

The synthetic pathways of P6 are shown in Scheme 6.2. By using 4, 7-dibromobenzothiadiazole as a starting material, under Suzuki cross-coupling reaction condition with 4-hexylthiophen-2-yl-2-boronic acid, 4,7-bis(4-hexylthiophen-2-yl)-benzothiadiazole was obtained. After bromination by NBS in the mixture of acetic acid and chloroform solutions, P6-Br was synthesized. P6-alkyne can be easily prepared from P6-Br by the typical organic synthetic protocols for alkynylation of aromatic halides. The Pt-containing polymer P6 was achieved by the Sonogashira-type dehydrohalogenation reaction between P6-alkyne and trans-dichlorobis(trialkylphosphine)platinum in the presence of a catalytic amount of CuI.
Scheme 6.4 The synthetic pathways of P6-Br and P6.

Scheme 6.3 shows the synthetic routes for P7. Firstly, by cyclization reaction of 4-fluorocyclohexa-3,5-diene-1,2-diamine with SOCl₂, 5-fluorobenzothiadiazole was produced through bromination reaction with liquid bromide in hydrobromic acid, 4,7-dibromo-5-fluorobenzothiadiazole was obtained. It further reacted with tributyl(4-hexylthiophen-2-yl)stannane under Stille-coupling reaction condition and subsequently treated with NBS to get P7-Br. P7-alkyne can be easily prepared from P7-Br by the typical organic synthetic protocols for alkylation of aromatic halides. The Pt-containing polymer P7 was achieved by the Sonogashira-type dehydrohalogenation reaction between P7-alkyne and
trans-dichlorobis(trialkylphosphine)platinum in the presence of a catalytic amount of CuI.

Scheme 6.5 The synthetic pathways of P7-Br and P7.

The synthetic pathways of P8 are displayed in Scheme 6.4. Firstly 4,5-difluoro-2-nitrobenzenamine was reduced by metal tin to prepare 4,5-difluorobenzene-1,2-diamine. Through subsequent cyclization reaction of their diamine with SOCl₂, 5,6-difluorobenzothiadiazole was achieved. After bromination reaction with liquid bromide in hydrobromic acid, 4,7-dibromo-4,5-difluorobenzothiadiazole was obtained. It further reacted with tributyl(4-hexylthiophen-2-yl)stannane under Stille-coupling reaction condition and
subsequent treatment with NBS to get **P8-Br**. **P8-alkyne** can be easily prepared from **P8-Br** by the typical organic synthetic protocols for alkynylation of aromatic halides.

The Pt-containing polymer **P7** was achieved by the Sonogashira-type dehydrohalogenation reaction between **P8-alkyne** and *trans*-dichlorobis(trialkylphosphine)platinum in the presence of a catalytic amount of CuI.

**Scheme 6.6** The synthetic pathways for **P8-Br** and **P8**.
6.3 Spectroscopic Characterization

All of the compounds (except polymers) were fully characterized by common spectroscopic techniques such as $^1$H, $^{13}$C and $^{19}$F NMR spectroscopy on a Bruker AV 400 MHz FT-NMR spectrometer and high resolution (HR) MALDI-TOF (matrix-assisted laser desorption/ionization time-of-flight) spectra were obtained by a Autoflex Bruker MALDI-TOF mass spectrometer. $^1$H and $^{13}$C NMR analyses clearly demonstrate a well-defined structure for all of the precursors P5-Br-P8-Br, P5-alkyne-P8-alkyne. $^1$H NMR resonances stemming from the protons of the organic moieties were observed. The $^{13}$C NMR spectral data give precise information about the regionchemical structure of the compounds. All the proton signals of aryl rings are on the downfield side, while the alkyl proton signals are shown at a high-field side. The proton signals of functional triphenylamine group are on the downfield region (above 7.20 ppm). The terminal acetylenic proton (C≡C-H) is located at around 3.0 ppm in their $^1$H NMR spectrum, and the corresponding terminal carbon signals are located at around 83-85 ppm. The NMR data of intermediates and other compounds are summarized in the Experimental part of Chapter 7.

6.3.1 $^1$H and $^{13}$C NMR of P5-alkyne-P8-alkyne

The $^1$H NMR and $^{13}$C NMR spectra of the corresponding ligands are shown in
Figures 6.3-6.10, respectively.

Figure 6.1 $^1$H NMR spectrum of P5-alkyne in CDCl$_3$.

Figure 6.2 $^{13}$C NMR spectrum of P5-alkyne in CDCl$_3$. 
Figure 6.3 $^1$H NMR spectrum of P6-alkyne in CDCl$_3$.

Figure 6.4 $^{13}$C NMR spectrum of P6-alkyne in CDCl$_3$. 
Figure 6.5 $^1$H NMR spectrum of P7-alkyne in CDCl$_3$.

Figure 6.6 $^{13}$C NMR spectrum of P7-alkyne in CDCl$_3$. 
Figure 6.7 $^1$H NMR spectrum of P8-alkyne in CDCl$_3$.

Figure 6.8 $^{13}$C NMR spectrum of P8-alkyne in CDCl$_3$. 
6.4 Photophysical Properties of P5-P8

To study the potential of P5-P8 in organic solar cells, absorption spectra of the newly synthesized compounds have been investigated. Figure 6.11 shows the UV/Vis absorption spectra of P5-P8 in CHCl3 solution at room temperature. The two distinct absorption bands can be attributed to the localized $\pi$-$\pi^*$ transitions in the high energy region and internal charge transitions (ICT) in their low energy region, respectively. In P5-P8, the largest $\lambda_{onset}$ of 699 nm of P6 was observed and the corresponding energy gap $E_g$ was 1.77 eV.

![Normalized absorption spectra of P5-P8 in CHCl2 at 293 K.](image)

Figure 6.9 Normalized absorption spectra of P5-P8 in CHCl2 at 293 K.
Table 6.1 Photophysical data for compounds P5-P8 in CHCl₃ at 293 K.

<table>
<thead>
<tr>
<th></th>
<th>( \lambda_{\text{max}} ) (nm)</th>
<th>( \lambda_{\text{onset}} ) (nm)</th>
<th>( E_g ) [eV] (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P5</td>
<td>559</td>
<td>671</td>
<td>1.85</td>
</tr>
<tr>
<td>P6</td>
<td>577</td>
<td>699</td>
<td>1.77</td>
</tr>
<tr>
<td>P7</td>
<td>574</td>
<td>689</td>
<td>1.80</td>
</tr>
<tr>
<td>P8</td>
<td>559</td>
<td>662</td>
<td>1.87</td>
</tr>
</tbody>
</table>

\(^a\) Optical band gap determined from the onset of absorption in solution phase.

Normalized thin film absorption spectra of P5, P6, P7 and P8 are shown in Figure 6.12. Comparison of each part of Figure 6.12 shows that transition from solution to solid state gives rise to a red shift in absorption of \( \lambda_{\text{onset}} \) by about 39, 37, 29 and 27 nm for P5, P6, P7 and P8, respectively. The corresponding optical band gaps were determined from \( \lambda_{\text{onset}} \) to be 1.75, 1.68, 1.73 and 1.80 eV, respectively. The summarized data are listed in Table 6.2. Among them, the largest \( \lambda_{\text{onset}} \) of 736 nm of P6 was observed and the corresponding energy gap \( E_g \) was 1.68 eV.
Figure 6.10 Normalized absorption spectra of P5-P8 in thin film and in solution, respectively.

Table 6.2 Photophysical data for compounds P5-P8 in thin films on quartz.

<table>
<thead>
<tr>
<th></th>
<th>Absorption (thin film)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$ (nm)</td>
</tr>
<tr>
<td>P5</td>
<td>574</td>
</tr>
<tr>
<td>P6</td>
<td>607</td>
</tr>
<tr>
<td>P7</td>
<td>602</td>
</tr>
<tr>
<td>P8</td>
<td>567</td>
</tr>
</tbody>
</table>

$^a$ Optical band gap determined from the onset of absorption in thin film.
6.5 Electrochemical Properties of P5-P8

To evaluate the oxidation ($E_{\text{ox}}$) and reduction potentials ($E_{\text{red}}$) of these conjugated polymers, cyclic voltammetry (CV) was performed on their thin films on glassy carbon electrode measured in 0.10 M [Bu$_4$N][PF$_6$] in acetonitrile with a Pt wire counter electrode and a Ag/AgCl reference electrode under N$_2$ atmosphere at a scan rate of 50 mV/s. The resulting CV traces are depicted in Figure 6.13 and the electrochemical data of onset oxidation and reduction potentials versus Ag/Ag$^+$ are listed in Table 6.3. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were estimated from the onset oxidation ($E_{\text{ox}}$) and reduction potentials ($E_{\text{red}}$), respectively.

The structural difference among P5, P6, P7 and P8 only causes a slight shift on the $E_{\text{ox}}$ and $E_{\text{red}}$. Among them, only P7 shows both a quasi-reversible oxidation wave and quasi-reversible reduction wave under CV conditions in Figure 6.11. The slightly high HOMO energy level of P6 results in the smallest band gap among them. The difference between the LUMO energy levels of M23-M26 and PC$_{71}$BM (-4.0 eV) were in the range of 0.48~0.49 eV, which is very efficient for electron transfer from the donor to acceptor. Also, the lower HOMO energy levels of P5, P6, P7 and P8 are very important for obtaining higher $V_{\text{oc}}$ in OPVs.
Figure 6.11 Cyclic voltammograms of P5, P6, P7 and P8. top: cathodic scan in 0.10 M Bu₄NPF₆/CH₃CN, bottom: anodic scan in 0.10 M Bu₄NPF₆/CH₃CN; scan rate 100 mV/s; Y-axis (μA).
Table 6.3 Electrochemical properties of P5, P6, P7 and P8.

<table>
<thead>
<tr>
<th></th>
<th>$E_{ox}$ (eV)$^a$</th>
<th>HOMO (eV)$^b$</th>
<th>$E_{red}$ (eV)$^a$</th>
<th>LUMO (eV)$^c$</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P5</td>
<td>0.47</td>
<td>-5.20</td>
<td>-1.22</td>
<td>-3.51</td>
<td>1.69</td>
</tr>
<tr>
<td>P6</td>
<td>0.44</td>
<td>-5.17</td>
<td>-1.21</td>
<td>-3.52</td>
<td>1.65</td>
</tr>
<tr>
<td>P7</td>
<td>0.46</td>
<td>-5.19</td>
<td>-1.22</td>
<td>-3.51</td>
<td>1.67</td>
</tr>
<tr>
<td>P8</td>
<td>0.51</td>
<td>-5.24</td>
<td>-1.21</td>
<td>-3.52</td>
<td>1.72</td>
</tr>
</tbody>
</table>

$^a$ Onset oxidation and reduction potentials

$^b$ HOMO = -e($E_{ox}$ + 4.73) (eV)

$^c$ LUMO = -e($E_{red}$ + 4.73) (eV)

6.6 GPC Analysis of P5-P8

The GPC analysis is very efficient for evaluating polymer properties such as molecular weight and polydispersity, etc. By using polystyrene as a standard, THF as the solvent medium, the properties of the samples of P5-P8 were measured. The flow-time curves of each sample are shown in Figure 6.14, and the data are listed in Table 6.4.
Figure 6.12 GPC curves of P5-P8 and standard.
Contributed by the same polymerization condition for all materials, P5-P7 showed similar molecular weights and smaller polydispersities. It is important that the different molecular weights of conjugated polymers may significantly influence material carrier mobility properties. However, different flow-time curve with two main peaks was shown in P8. As a result, a broad PDI of 2.10 with a higher $M_n$ of 24.0 kDa was obtained. On the other hand, a higher degree of polymerization (DP) of around 19~20 were obtained in P5 and P8, respectively.

<table>
<thead>
<tr>
<th></th>
<th>$M_n$ (kDa)$^a$</th>
<th>$M_w$ (kDa)$^b$</th>
<th>PDI ($M_w/M_n$)$^c$</th>
<th>DP$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P5</td>
<td>18.2</td>
<td>28.0</td>
<td>1.53</td>
<td>19</td>
</tr>
<tr>
<td>P6</td>
<td>18.3</td>
<td>24.8</td>
<td>1.35</td>
<td>16</td>
</tr>
<tr>
<td>P7</td>
<td>19.0</td>
<td>26.8</td>
<td>1.41</td>
<td>16</td>
</tr>
<tr>
<td>P8</td>
<td>24.0</td>
<td>50.4</td>
<td>2.10</td>
<td>20</td>
</tr>
</tbody>
</table>

$^a M_n$ = Number-average molecular weight
$^b M_w$ = Weight-average molecular weight
$^c$ PDI = Polydispersity index
$^d$ DP = Degree of polymerization (Calculated from $M_n$ values)
6.7 Conclusion

Four Pt-containing polymers were synthesized and characterized by a variety of techniques. The synthetic routes for Pt-containing polymers P5-P8 involve a Sonogashira-type dehydrohalogenation reaction of each of the diethynyl precursors with the trans-dichlorobis(trialkylphosphine)platinum in the presence of a catalytic amount of CuI. Among them, the largest \( \lambda_{\text{onset}} \) of 699 nm in solution and \( \lambda_{\text{onset}} \) of 736 nm in thin film of P6 were observed and the corresponding energy gap \( E_g \) was 1.77 eV and 1.68 eV, respectively. After evaluating these polymeric oxidation and reduction potentials, P6 also shows the smallest band gap of 1.65 eV with the corresponding HOMO and LUMO energy of -5.17 eV and -3.52 eV, respectively. At last, through GPC-analysis of these polymers, P5-P7 show similar molecular weight data. The highest \( M_n \) of 24.0 kDa and \( M_w \) of 50.4 kDa with the PDI of 2.10 were observed in P8. Work is currently in progress to investigate the photovoltaic properties of these polymers.

References:


Chapter 7 Concluding Remarks and Future Work

By virtue of the rational design of molecular architecture, a series of dipyrrin-containing compounds and donor-centered small molecules were successfully synthesized and fully characterized by spectroscopic and photophysical measurements (Figures 7.1 and 7.2). All of the dipyrrin-containing compounds have been used in the fabrication of solar cells. The power conversion efficiency (PCE) of 0.58%, in which a $V_{oc}$ of 0.81V, $J_{sc}$ of 3.03 mA/cm$^2$ and FF of 0.24 was obtained with a solar cell based on M4 under illumination of an AM 1.5 solar cell simulator in a 1:3 (M4:PC$_{71}$BM) blend ratio.

![Diagram for dipyrrin based small molecules.](image)

**Figure 7.1** Diagram for dipyrrin based small molecules.

Furthermore, constructed by BDT, CPT or TPA as central unit, a new class of donor-centered small molecules have been synthesized and researched for solar cell
applications. With careful chemical modification, a high PCE of 3.91% was achieved by BDT-centered fluorine-containing molecule M14, with a $V_{oc}$ of 0.90V, $J_{sc}$ of 10.08 mA/cm$^2$ and FF of 0.43 in the 1:2 (M14:PC$_{71}$BM) blend ratio.

Figure 7.2 Diagram for donor-centered small molecules.
Finally, through introducing a different number of fluorine atoms in a polymeric backbone, we have synthesized a class of Pt-containing polymers for organic solar cell applications. Their energy gap and absorption can be fine-tuned through chemical engineering. Different energy band gaps of 1.65-1.72 eV and narrow polydispersities of 1.35-2.10 with good degree of polymerization of 26-20 have been obtained from these D-A based linear polymers. Future work will focus on systematically investigate the photovoltaic properties of these polymers. (Figure 7.3)

![Diagram of Pt-containing polymers for OSCs.](image)

R₁ = R₂ = H  
or R₁ = R₂ = F  
or R₁ = H, R₂ = F

**Figure 7.3** Diagram of Pt-containing polymers for OSCs.

Future work of this project will be concentrated on the device optimization of these small molecules and polymers. Also, the structure-property relationships of these small molecules and polymers will be comprehensively investigated. Furthermore, the design and synthesis of more efficient organic molecules will be of interest through modification of the molecule **M14** which shows the best performance.
in these donor-centered small molecules. (Figures 7.2 and 7.4)

**Figure 7.4** A future design for organic solar cell materials derived from M14.
Chapter 8 Experimental Details

8.1 Experimental Details for Chapter 2

Synthesis of L3-Br:

To a 100 mL round-bottom flask was added Pd(PPh$_3$)$_4$ (60 mg, 0.05 mmol), 2 M Na$_2$CO$_3$ (11.6 mL, 24 mmol), triphenylamine-boronic acid (2.0 g, 6.8 mmol) and 2,7-dibromo-2,1,3-benzothiadiazole (0.98 g, 3.4 mmol) in THF (30 mL). The mixture was heated to reflux for 24 h under nitrogen atmosphere. After removal of solvents, the crude product was purified by column chromatography on silica gel eluting with hexane/CH$_2$Cl$_2$ (2:1, v/v) solvent mixture. Yellow solid (0.7 g, 45%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.90 (d, 1H, $J = 7.6$ Hz), 7.80 (d, 2H, $J = 8.8$ Hz), 7.55 (d, 1H, $J = 7.6$ Hz), 7.30 (m, 4H), 7.19 (m, 6H), 7.08 (t, 2H, $J = 7.3$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 153.1, 148.4, 147.5, 147.3, 133.5, 132.4, 129.9, 129.8, 129.4, 129.3, 127.3, 125.1, 124.9, 123.3, 122.9, 122.6, 112.2 ppm. MALDI [M+1]$^+$: found: 460.01, calcd: 460.02.

Synthesis of L3-aldehyde:

Pd(PPh$_3$)$_4$ (310 mg, 0.27 mmol), 2 M Na$_2$CO$_3$ (5.8 mL, 12 mmol) and L3-Br (0.99
g, 2.16 mmol) were added to a 100 mL round-bottom flask in THF (50 mL). Then, 5-formylthiophen-2-yl-2-boronic acid was added to this solution (0.51 g, 3.2 mmol). The mixture was heated to reflux for 24 h under nitrogen atmosphere and solvent was then removed on a rotary evaporator in vacuo. The crude product was purified by column chromatography on silica gel eluting with hexane/CH₂Cl₂ (2:1, v/v) solvent mixture. Red solid (611 mg, 57.9%).

¹H NMR (400 MHz, CDCl₃): δ = 9.98 (s, 1H), 8.22 (d, 1H, J = 4.0 Hz), 8.06 (d, 1H, J = 9.6 Hz), 7.89 (d, 2H, J = 8.8 Hz), 7.86 (d, 1H, J = 4.0 Hz), 7.75 (d, 1H, J = 7.6 Hz), 7.30 (m, 4H), 7.20 (m, 6H), 7.09 (t, 2H, J = 7.4 Hz); ¹³C NMR (100 MHz, CDCl₃): δ = 183.4, 153.8, 152.7, 148.9, 148.6, 147.3, 143.2, 136.9, 134.6, 130.0, 129.9, 129.4, 127.8, 127.6, 126.7, 125.1, 124.1, 123.6, 122.4 ppm. MALDI [M+1]⁺: found: 490.10, calcd: 490.10.

**Synthesis of L3-dipyrromethane:**

To a mixture of L3-aldehyde (1 g, 2.0 mmol) and pyrrole (2.7 mL, 15 mmol) in 50 mL round bottom flask was added one drop of trifluoroacetic acid. The mixture was stirred at room temperature for one day under N₂. Then, water was added and the mixture was extracted with ethyl acetate. The combined organic phase was dried over Na₂SO₄, evaporated and the residue was purified by neutral Al₂O₃ column
chromatography using ethyl acetate:hexane (1:5, v/v) as eluant. Brown solid (0.92 g, 76%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.10$ (br, 2H), 8.01 (d, 1H, $J = 3.6$ Hz), 7.84 (d, 2H, $J = 8.8$ Hz), 7.81 (d, 1H, $J = 7.6$ Hz), 7.65 (d, 1H, $J = 7.6$ Hz), 7.31–7.27 (m, 4H), 7.21–7.17 (m, 6H), 7.06 (m, 2H), 6.99 (dd, 1H, $J = 0.8$ Hz, $J = 3.8$ Hz), 6.73 (m, 2H), 6.19 (m, 2H), 6.12 (br, 2H), 5.80 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 153.9, 152.8, 148.2, 147.6, 147.4, 138.7, 132.2, 131.9, 130.8, 130.1, 129.6, 127.4, 127.3, 126.7, 125.8, 125.6, 125.1, 123.6, 122.9, 108.6, 107.4$ ppm. MALDI [M+1]$^+$: found: 606.16, calcd: 606.17.

**Synthesis of L3:**

To L3-dipyrromethane (0.5 g, 0.82 mmol) in 50 mL of CH$_2$Cl$_2$ was added a solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (0.18 g, 0.82 mmol) in 10 mL of CH$_2$Cl$_2$ under N$_2$ at room temperature. The mixture was stirred for another 1 h and washed with water. After drying over Na$_2$SO$_4$, the residue was purified by alkaline Al$_2$O$_3$ column chromatography using CH$_2$Cl$_2$:hexane (1:2, v/v) as eluant. Red solid (0.18 g, 36%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.20$ (d, 1H, $J = 4.0$ Hz), 8.00 (d, 1H, $J = 7.4$ Hz), 7.90 (d, 2H, $J = 8.8$ Hz), 7.77 (d, 1H, $J = 7.6$ Hz), 7.67 (br, 2H), 7.50 (d, 1H, $J = 3.8$ Hz),...
Hz), 7.32–7.28 (m, 4H), 7.23–7.18 (m, 6H), 7.12 (dd, 2H, $J = 1.0$ Hz, $J = 4.2$ Hz), 7.08 (m, 2H), 6.48 (dd, 2H, $J = 1.4$ Hz, $J = 4.2$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 152.7, 151.5, 147.1, 146.3, 142.7, 139.5, 138.0, 133.1, 131.8, 131.6, 129.3, 128.8, 128.3, 127.7, 126.1, 125.9, 125.0, 123.9, 123.8, 123.7, 122.4, 121.6, 116.7 ppm.


*General procedures for the synthesis of dipyrrin-based metal complexes M1–M4:*

In a 30 mL round bottom flask, a mixture of L3 (200 mg, 0.33 mmol) and the corresponding metal acetate (0.16 mmol) in tetrahydrofuran (10 mL) was added 1 mL NEt$_3$. The mixture was stirred at 50 °C for one day under N$_2$ condition. The reaction mixture was washed with aqueous NaHCO$_3$ and H$_2$O and then dried over Na$_2$SO$_4$. The residue was purified by neutral Al$_2$O$_3$ column chromatography using CH$_2$Cl$_2$:hexane (2:1, v/v) as eluant.

**M1:** Red solid (100 mg, 71%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.29$ (br, 4H), 8.20 (d, 2H, $J = 3.8$ Hz), 8.00 (d, 2H, $J = 7.6$ Hz), 7.92 (d, 4H, $J = 8.6$ Hz), 7.75 (d, 2H, $J = 7.6$ Hz), 7.50 (d, 2H, $J = 3.9$ Hz), 7.33–7.28 (m, 12H), 7.23–7.19 (m, 12H), 7.10 (t, 4H, $J = 7.2$ Hz), 6.90 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 152.7, 151.6, 150.5, 147.1, 146.3, 142.3, 138.0,
135.3, 134.8, 131.9, 129.3, 128.9, 128.3, 128.2, 127.2, 126.1, 125.9, 125.2, 124.5, 123.9, 123.7, 123.5, 121.7 ppm. MALDI [M+1]^+: found: 1263.24, calcd: 1263.23.

**M2:** Red solid (40 mg, 67%).

$^1$H NMR (400 MHz, CDCl$_3$): $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.22$ (d, 2H, $J = 3.8$ Hz), 8.04 (d, 2H, $J = 7.4$ Hz), 7.91 (d, 4H, $J = 8.6$ Hz), 7.71 (m, 2H), 7.57 (m, 4H), 7.53 (d, 2H, $J = 3.8$ Hz), 7.33–7.29 (m, 8H), 7.25–7.19 (m, 16H), 7.08 (t, 4H, $J = 7.2$ Hz), 6.49 (dd, 4H, $J = 1.2$ Hz, $J = 4.2$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$): 153.9, 152.8, 150.3, 148.3, 147.4, 141.9, 140.6, 133.1, 132.9, 130.5, 129.9, 129.4, 127.1, 126.6, 126.1, 125.1, 125.0, 123.5, 122.8, 117.4 ppm. MALDI [M+1]^+: found: 1269.23, calcd: 1269.22.

**M3:** Red solid (30 mg, 52%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.23$ (d, 2H, $J = 3.8$ Hz), 8.03 (d, 2H, $J = 7.6$ Hz), 7.93 (d, 4H, $J = 8.8$ Hz), 7.77 (d, 2H, $J = 7.6$ Hz), 7.60 (d, 2H, $J = 3.8$ Hz), 7.43 (br, 4H), 7.33–7.29 (m, 8H), 7.25–7.19 (m, 16H), 7.10–7.06 (t, 4H, $J = 7.2$ Hz), 6.45 (dd, 4H, $J = 1.6$ Hz, $J = 4.4$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$): 153.9, 152.8, 151.9, 148.3, 147.4, 142.3, 140.1, 139.0, 137.0, 133.1, 132.5, 131.2, 130.5, 129.9, 129.4, 127.1, 126.2, 125.0, 123.5, 122.7, 117.3 ppm. MALDI [M+1]^+: found: 1311.20, calcd:
Synthesis of M4:

To 6 (0.23 g, 0.41 mmol) in 50 mL of CH$_2$Cl$_2$ was added a solution of DDQ (90 mg, 0.41 mmol) in 10 mL CH$_2$Cl$_2$ under N$_2$ at room temperature. The reaction was allowed to proceed for 4 h at room temperature. Triethylamine (1.7 mL, 12.4 mmol) was added to the solution and the mixture was stirred for a further 30 min. BF$_3$/Et$_2$O (2.1 mL, 16.6 mmol) was added and stirring was maintained for 1 h. The reaction mixture was washed with water and the aqueous solution was extracted with CH$_2$Cl$_2$. The combined organic layer was dried over Na$_2$SO$_4$, filtered and evaporated. The crude product was purified by silica gel column chromatography CH$_2$Cl$_2$:hexane (1:2, v/v) to afford a purple compound (80 mg, 30%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.24 (d, 1H, $J$ = 4.0 Hz), 8.06 (d, 1H, $J$ = 7.6 Hz), 7.95 (s, 2H), 7.91 (d, 2H, $J$ = 8.8 Hz), 7.77 (d, 1H, $J$ = 7.6 Hz), 7.70 (d, 1H, $J$ = 4.0 Hz), 7.43 (d, 2H, $J$ = 4.0 Hz), 7.33–7.29 (m, 4H), 7.23–7.19 (m, 6H), 7.09 (t, 2H, $J$ = 7.2 Hz), 6.63–6.61 (d,d, 2H, $J$ = 1.6 Hz, $J$ = 4.2 Hz); $^{13}$C NMR (400 MHz, CDCl$_3$): 153.4, 152.2, 148.3, 147.0, 146.2, 143.2, 139.2, 135.2, 134.4, 133.7, 133.6, 131.2, 129.9, 129.7, 129.4, 127.7, 126.8, 126.7, 124.9, 123.6, 122.0, 118.5 ppm. $^{19}$F NMR (370 MHz, CDCl$_3$): -145.11, -145.19, -145.27, -145.34 ppm; MALDI [M+1]$^+$: found:
652.16, calcd: 652.15.

8.2 Experimental Details for Chapter 3

Synthesis of M5:

To a 100 mL round-bottom flask was added Pd(PPh$_3$)$_4$ (25 mg, 0.02 mmol), L5-Br (0.41 g, 1.1 mmol) and BDT-tributylstannane (0.57 g, 0.5 mmol) in toluene (30 mL). The mixture was heated to reflux for 48 h under nitrogen atmosphere. After removal of solvents, the crude product was purified by column chromatography on silica gel eluting with hexane/CH$_2$Cl$_2$ (4:1 to 2:1, v/v) solvent mixture. Brown solid (0.2 g, 34%).

$^1$H NMR (400 MHz, CDCl$_3$): δ = 8.72 (s, 2H), 7.79 (s, 2H), 7.69 (d, 2H, $J$ = 7.6 Hz), 7.65 (d, 2H, $J$ = 7.6 Hz), 7.38 (d, 2H, $J$ = 3.4 Hz), 6.93 (d, 2H, $J$ = 3.4 Hz), 6.89 (s, 2H), 2.90 (d, 4H, $J$ = 6.8 Hz), 2.55 (t, 4H, $J$ = 7.8 Hz), 1.76–1.70 (m, 4H), 1.58–1.54 (m, 8H), 1.44-1.24 (m, 28H), 0.97 (t, 6H, $J$ = 7.2 Hz), 0.89 (t, 6H, $J$ = 7.0 Hz), 0.83 (t, 6H, $J$ = 6.8 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$): 151.1, 144.1, 142.7, 137.9, 137.5, 136.7, 136.3, 136.2, 127.2, 127.1, 125.3, 124.8, 124.2, 123.6, 123.5, 123.0, 122.2, 120.0, 40.5, 33.3, 31.6, 30.7, 29.4, 29.0, 28.2, 28.0, 24.7, 22.2, 21.6, 13.3, 13.1, 10.1

Synthesis of M6:

To a 100 mL round-bottom flask was added Pd(PPh₃)₄ (10 mg, 8 µmol), L₆-Br (0.2 g, 0.49 mmol) and BDT-tributylstannane (0.27 g, 0.24 mmol) in toluene (30 mL). The mixture was heated to reflux for 48 h under nitrogen atmosphere. After removal of solvents, the crude product was purified by column chromatography on silica gel eluting with hexane/CH₂Cl₂ (4:1 to 2:1, v/v) solvent mixture. Brown solid (0.1 g, 33%).

¹H NMR (400 MHz, CDCl₃): δ = 8.41 (s, 2H), 7.45 (d, 2H, J = 3.6 Hz), 7.31 (m, 4H), 7.25 (d, 2H, J = 3.4 Hz), 6.88 (d, 2H, J = 3.4 Hz), 6.41 (d, 2H, J = 3.6 Hz), 2.91 (d, 4H, J = 6.4 Hz), 2.48 (d, 4H, J = 6.5 Hz), 1.79–1.71 (m, 2H), 1.56–1.38 (m, 16H), 1.17 (br, 12H), 1.01 (t, 6H, J = 7.2 Hz), 0.92 (t, 6H, J = 7.0 Hz), 0.81 (m, 12H); ¹³C NMR (100 MHz, CDCl₃): 151.2, 151.1, 145.1, 144.2, 138.1, 136.8, 136.4, 136.3, 135.7, 127.0, 125.9, 125.5, 125.1, 124.9, 123.2, 123.1, 123.0, 122.2, 40.5, 40.2, 33.3, 31.6, 31.3, 28.0, 27.8, 24.7, 24.4, 22.2, 22.0, 13.3, 13.1, 10.1, 9.7 ppm. MALDI [M+1]⁺: found: 1235.43, calcd: 1235.43.

Synthesis of M7:
To a 100 mL round-bottom flask was added Pd(PPh$_3$)$_4$ (10 mg, 8 µmol), L7-Br (0.25 g, 0.51 mmol) and BDT-tributylstannane (0.29 g, 0.25 mmol) in toluene (30 mL). The mixture was heated to reflux for 48 h under nitrogen atmosphere. After removed solvents, the crude product was purified by column chromatography on silica gel eluting with hexane/CH$_2$Cl$_2$ (4:1 to 2:1, v/v) solvent mixture. Brown solid (80 mg, 23%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.11$ (s, 2H), 7.11 (d, 2H, $J = 3.6$ Hz), 7.07 (d, 2H, $J = 3.6$ Hz), 6.98 (m, 4H), 6.83 (d, 2H, $J = 3.2$ Hz), 6.58 (d, 2H, $J = 3.2$ Hz), 6.39 (d, 2H, $J = 3.6$ Hz), 6.31 (d, 2H, $J = 3.6$ Hz), 2.92 (br, 4H), 2.44 (d, 4H, $J = 6.4$ Hz), 1.79 (m, 2H), 1.58–1.33 (m, 16H), 1.16 (br, 6H), 1.06 (t, 6H, $J = 7.2$ Hz), 0.98 (t, 12H, $J = 7.0$ Hz), 0.80 (m, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$): 150.8, 150.7, 143.7, 142.7, 137.6, 137.5, 136.4, 136.3, 135.9, 135.7, 133.8, 127.0, 126.1, 124.9, 124.5, 124.0, 123.0, 122.9, 122.8, 121.9, 121.7, 40.5, 40.2, 33.3, 32.9, 31.7, 31.2, 28.1, 27.8, 24.8, 24.3, 22.2, 22.0, 13.4, 13.1, 10.2, 9.7 ppm. MALDI [M+1$^+$]: found: 1399.41, calcd: 1399.41.

**Synthesis of L8-Br:** To L8 (0.3 g, 0.60 mmol) in 50 mL of CHCl$_3$/AcOH mixture solution was added NBS (0.12 g, 0.72 mmol) at 0 °C. The mixture was stirred overnight and washed with water. After drying over Na$_2$SO$_4$, the residue was purified
by silica gel chromatography by using CH$_2$Cl$_2$:hexane (1:3, v/v) as eluant. Red-brown solid (0.25 g, 72%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.03$ (d, 1H, $J = 3.8$ Hz), 7.80 (m, 3H), 7.19 (d, 1H, $J = 3.8$ Hz), 7.16 (d, 1H, $J = 4.0$ Hz), 7.11 (d, 1H, $J = 3.6$ Hz), 6.70 (d, 1H, $J = 3.6$ Hz), 2.76 (t, 2H, $J = 7.8$ Hz), 1.61–1.59 (m, 1H), 1.32–1.29 (m, 8H), 0.90 (m, 6H);

$^{13}$C NMR (100 MHz, CDCl$_3$): 154.2, 143.0, 140.9, 138.0, 136.7, 134.2, 131.2, 129.6, 129.1, 128.4, 128.0, 126.8, 125.9, 111.8, 41.8, 35.2, 34.2, 29.7, 28.2, 23.1, 11.9 ppm.

MALDI [M+1]$^+$: found: 573.02, calcd: 573.01.

**Synthesis of M8:**

To a 100 mL round-bottom flask was added Pd(PPh$_3$)$_4$ (15 mg, 13 µmol), **L8-Br** (0.18 g, 0.31 mmol) and BDT-tributylstannane (0.17 g, 0.15 mmol) in toluene (30 mL). The mixture was heated to reflux for 48 h under nitrogen atmosphere. After removal of solvents, the crude product was purified by column chromatography on silica gel eluting with hexane/CHCl$_3$ (4:1 to 2:1, v/v) solvent mixture. Brown solid (80 mg, 34%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.71$ (d, 2H, $J = 3.6$ Hz), 7.65 (d, 2H, $J = 3.6$ Hz), 7.44 (d, 2H, $J = 7.4$ Hz), 7.39 (d, 2H, $J = 7.4$ Hz), 7.23 (d, 2H, $J = 8.2$ Hz), 6.97 (d, 2H, $J = 3.2$ Hz), 6.86 (t, 6H, $J = 3.6$ Hz), 6.54 (d, 2H, $J = 3.4$ Hz), 2.98 (d, 4H, $J = 6.7$ Hz).
Hz), 2.64 (d, 4H, \( J = 6.6 \) Hz), 1.84 (m, 2H), 1.60–1.46 (m, 16H), 1.26 (br, 6H), 1.09 (t, 6H, \( J = 7.2 \) Hz), 1.02 (t, 6H, \( J = 7.0 \) Hz), 0.88 (m, 18H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 152.0, 151.9, 135.2, 144.1, 138.8, 138.6, 138.0, 137.3, 137.2, 136.9, 136.8, 134.8, 129.0, 128.2, 127.8, 127.3, 125.8, 125.3, 125.1, 124.9, 124.4, 123.2, 122.5, 118.6, 41.6, 41.3, 34.5, 34.1, 32.7, 32.4, 31.6, 29.1, 28.9, 25.9, 25.5, 23.3, 23.0, 22.7, 14.4, 14.2, 14.1, 11.2, 10.8 ppm. MALDI [M+1]\(^+\): found: 1563.37, calcd: 1563.38.

**Synthesis of L9-Br:**

To L9 (0.3 g, 0.33 mmol) in 50 mL of CHCl\(_3\)/AcOH mixture solution was added a NBS (58 mg, 0.33 mmol) at 0 °C. The mixture was stirred overnight and washed with water. After drying over Na\(_2\)SO\(_4\), the residue was purified by silica gel chromatography by using CH\(_2\)Cl\(_2\):hexane (1:2, v/v) as eluant. Red solid (0.25 g, 78%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.91 \) (d, 2H, \( J = 3.6 \) Hz), 7.60 (d, 1H, \( J = 4.0 \) Hz), 7.48 (br, 11H), 7.42 (br, 1H), 7.39 (d, 1H, \( J = 4.0 \) Hz), 7.12 (m, 3H), 7.03-6.97 (m, 4H), 6.88 (m, 2H), 6.59 (d, 1H, \( J = 3.6 \) Hz), 3.98 (t, 2H, \( J = 6.4 \) Hz), 3.85 (t, 2H, \( J = 6.4 \) Hz), 2.68 (t, 2H, \( J = 6.8 \) Hz), 1.72 (m, 2H), 1.62 (m, 2H), 1.41 (m, 1H), 1.31–1.18 (m, 28H), 0.86–0.79 (m, 12H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 159.5, 159.3, 151.3, 144.1, 141.5, 139.8, 139.6, 139.5, 136.6, 136.3, 136.2, 135.6, 130.9, 129.7, 129.0,
Synthesis of M9:

To a 100 mL round-bottom flask was added Pd(PPh₃)₄ (10 mg, 8 µmol), L9-Br (0.3 g, 0.31 mmol) and BDT-tributylstannane (0.15 g, 0.14 mmol) in toluene (30 mL). The mixture was heated to reflux for 48 h under nitrogen atmosphere. After removal of solvents, the crude product was purified by column chromatography on silica gel eluting with hexane/CHCl₃ (4:1 to 2:1, v/v) solvent mixture. Brown solid (70 mg, 21%).

¹H NMR (400 MHz, CDCl₃): δ = 7.74 (d, 4H, J = 3.6 Hz), 7.57 (d, 2H, J = 3.4 Hz), 7.50 (br, 4H), 7.44 (br, 4H), 7.28 (d, 6H, J = 8.2 Hz), 7.20 (d, 2H, J = 3.2 Hz), 7.14 (d, 2H, J = 3.6 Hz), 7.08 (s, 2H), 7.02 (d, 2H, J = 3.2 Hz), 6.95 (br, 10H), 6.60 (d, 2H, J = 3.0 Hz), 3.94 (t, 4H, J = 6.4 Hz), 3.75 (t, 4H, J = 6.4 Hz), 3.00 (d, 4H, J = 6.4 Hz), 2.69 (d, 4H, J = 6.2 Hz), 1.81 (m, 2H), 1.73 (m, 4H), 1.59–1.22 (m, 56H), 1.04–0.90 (m, 24H); ¹³C NMR (100 MHz, CDCl₃): 158.1, 157.5, 149.7, 149.6, 144.1, 142.6, 140.0, 138.9, 138.7, 138.6, 137.3, 137.2, 136.7, 136.3, 136.0, 135.5, 135.4, 135.3,

MALDI [M+1]+: found: 2372.12, calcd: 2372.11.

**Synthesis of L10-aldehyde:**

To a 100 mL round-bottom flask was added Pd(PPh₃)₄ (20 mg, 16 µmol), **L11-aldehyde** (0.3 g, 0.73 mmol) and BDT-tributylstannane (0.4 g, 0.35 mmol) in toluene (30 mL). The mixture was heated to reflux for 48 h under nitrogen atmosphere. After removal of solvents, the crude product was purified by column chromatography on silica gel eluting with CHCl₃ as the solvent. Brown solid (120 mg, 21%).

^1H NMR (400 MHz, CDCl₃): δ = 9.38 (s, 2H), 7.87 (s, 2H), 7.10 (s, 2H), 7.04 (d, 2H, J = 7.2 Hz), 6.89 (s, 2H), 6.81 (s, 4H), 2.96 (m, 4H), 2.31 (m, 4H), 1.84 (m, 2H), 1.64–1.51 (m, 16H), 1.33–1.01 (m, 24H), 0.84 (m, 10H); ^13C NMR (100 MHz, CDCl₃): 180.9, 152.4, 151.3, 151.2, 146.1, 144.9, 137.7, 137.1, 136.8, 136.5, 136.4, 128.7, 128.2, 125.9, 125.7, 125.3, 124.9, 124.5, 123.2, 122.9, 41.5, 34.3, 32.8, 31.6, 31.5, 30.9, 29.2, 29.1, 28.2, 25.7, 23.3, 22.7, 22.6, 14.5, 14.1, 14.0, 11.2 ppm. MALDI [M+1]+: found: 1235.36, calcd: 1235.36.
Synthesis of M10:

To a 100 mL round-bottom flask was added **L10-aldehyde** (85 mg, 0.069 mmol) and octyl 2-cyanoacetate (0.3 ml, 1.38 mmol) in dry CHCl₃ (30 mL) with a few drop of NEt₃. The mixture was stirred for three days under nitrogen atmosphere. After removal of solvents, the crude product was purified by column chromatography on silica gel eluting with CHCl₃ as the solvent. Dark solid (90 mg, 81%).

$^1$H NMR (400 MHz, CDCl₃): $\delta = 8.14$ (s, 2H), 7.87 (s, 2H), 7.46 (s, 2H), 7.35 (d, 2H, $J = 7.2$ Hz), 7.10 (s, 4H), 6.88 (s, 2H), 4.08 (br, 4H), 2.96 (m, 4H), 2.39 (m, 4H), 1.82 (m, 2H), 1.64–1.44 (m, 16H), 1.25 (br, 24H), 1.08 (t, 6H, $J = 7.2$ Hz), 0.99 (t, 6H, $J = 7.0$ Hz), 0.85 (m, 12H); $^{13}$C NMR (100 MHz, CDCl₃): 161.9, 153.7, 150.3, 145.2, 144.0, 136.7, 136.2, 135.6, 135.5, 129.1, 127.4, 125.0, 124.3, 124.0, 122.0, 121.7, 114.9, 94.6, 65.2, 30.8, 28.3, 28.2, 21.7, 21.6, 13.4, 13.0 ppm. MALDI [M+1]$^+$: found: 1593.63, calcd: 1593.62.

Synthesis of L11-Br:

To a 100 mL round-bottom flask was added **L11-aldehyde** (0.26 g, 0.63 mmol) and 2-(4-(5-(2-ethylhexyl)thiophen-2-yl)phenyl)acetonitrile (0.2 g, 0.63 mmol) in ethanol (40 mL) with 70 mg of NaOH. The mixture was refluxed for 24 h under nitrogen atmosphere. After removal of solvents, the crude product was purified by
column chromatography on silica gel eluting with CHCl₃ as the solvent. Red solid (0.21 g, 48%).

¹H NMR (400 MHz, CDCl₃): δ = 8.13 (s, 1H), 7.89 (d, 1H, J = 3.8 Hz), 7.83 (d, 1H, J = 4.0 Hz), 7.75 (s, 1H), 7.64 (br, 4H), 7.21 (d, 1H, J = 3.4 Hz), 6.75 (d, 1H, J = 3.6 Hz), 2.85 (t, 2H, J = 7.8 Hz), 2.76 (d, 2H, J = 6.8 Hz), 1.72 (br, 2H), 1.32 (br, 14H), 0.90 (m, 12H); ¹³C NMR (100 MHz, CDCl₃): 153.6, 151.3, 149.9, 145.1, 140.9, 140.4, 134.9, 132.8, 132.4, 132.0, 130.6, 126.3, 125.8, 125.7, 125.4, 123.2, 118.2, 113.4, 106.5, 41.4, 34.3, 32.4, 31.7, 31.1, 29.3, 29.1, 28.9, 25.6, 23.1, 22.7, 14.3, 14.2, 10.9 ppm. MALDI [M+1]^+: found: 702.16, calcd: 702.16.

**Synthesis of M11:**

To a 100 mL round-bottom flask was added Pd(PPh₃)₄ (15 mg, 13 µmol), L₁₁-Br (0.23 g, 0.33 mmol) and BDT-tributylstannane (0.17 g, 0.15 mmol) in toluene (30 mL). The mixture was heated to reflux for 48 h under nitrogen atmosphere. After removal of solvents, the crude product was purified by column chromatography on silica gel eluting with CHCl₃ as the solvent. Brown solid (85 mg, 31%).

¹H NMR (400 MHz, CDCl₃): δ = 7.67 (br, 2H), 7.02-6.76 (br, 15H), 6.64 (br, 6H), 6.39 (s, 2H), 2.97 (br, 4H), 2.39 (br, 4H), 1.57 (br, 22H), 1.19-1.11 (m, 16H), 0.87-0.78 (m, 18H); ¹³C NMR (100 MHz, CDCl₃): 151.2, 148.3, 143.8, 141.2, 140.7,
137.6, 137.3, 136.8, 136.2, 132.6, 132.0, 129.5, 128.3, 126.0, 124.9, 123.1,
122.6, 122.3, 117.2, 103.8, 41.5, 41.3, 34.1, 33.8, 32.8, 32.2, 31.7, 29.9, 29.5, 29.1,
28.7, 28.3, 25.6, 25.2, 24.9, 24.8, 24.6, 24.5, 24.3, 24.1, 23.9, 23.3, 22.9, 22.7, 14.1,
13.7, 13.6, 10.7, 10.1 ppm. MALDI [M+1]⁺: found: 1821.67, calcd: 1821.68.

_Synthesis of L12-Br:

To a 100 mL round-bottom flask was added **L12-aldehyde** (0.37 g, 0.64 mmol)
and 2-(4-(5-(2-ethylhexyl)thiophen-2-yl)phenyl)acetonitrile (0.2 g, 0.64 mmol) in
ethanol (40 mL) with 70 mg of NaOH. The mixture was refluxed for 24 h under
nitrogen atmosphere. After removal of solvents, the crude product was purified by
column chromatography on silica gel eluting with CHCl₃ as the solvent. Red solid
(0.31 g, 56%).

¹H NMR (400 MHz, CDCl₃): δ = 7.99 (s, 1H), 7.75 (d, 1H, J = 3.8 Hz), 7.64 (s, 1H),
7.60 (d, 1H, J = 7.6 Hz), 7.56 (s, 1H), 7.18 (s, 1H), 7.08 (d, 1H, J = 3.4 Hz), 6.64 (d,
1H, J = 3.4 Hz), 2.68 (m, 4H), 2.51 (m, 2H), 1.59 (m, 5H), 1.27 (br, 20H), 0.84 (m,
12H); ¹³C NMR (100 MHz, CDCl₃): 151.0, 150.9, 144.0, 141.9, 140.8, 139.6, 137.3,
133.8, 131.6, 131.4, 129.6, 128.8, 126.9, 125.3, 125.2, 127.4, 124.6, 124.4, 123.3,
123.1, 122.1, 117.3, 111.1, 104.7, 40.3, 33.2, 31.3, 30.6, 30.5, 29.9, 28.7, 28.6, 28.2,
28.0, 27.9, 27.8, 24.5, 22.0, 21.6, 13.2, 13.1, 9.8 ppm. MALDI [M+1]⁺: found: 868.24,
Synthesis of M12

To a 100 mL round-bottom flask was added Pd(PPh$_3$)$_4$ (15 mg, 13 µmol), L11-Br (0.23 g, 0.27 mmol) and BDT-tributylstannane (0.15 g, 0.13 mmol) in toluene (30 mL). The mixture was heated to reflux for 48 h under nitrogen atmosphere. After removal of solvents, the crude product was purified by column chromatography on silica gel eluting with CHCl$_3$ as the solvent. Black solid (120 mg, 41%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.52$ (br, 2H), 7.34 (br, 4H), 7.14 (br, 7H), 7.02 (br, 5H), 6.83 (br, 5H), 6.37 (br, 2H), 3.04 (br, 4H), 2.40-2.25 (br, 10H), 1.92 (br, 2H), 1.57-1.36 (m, 54H), 1.17-0.97 (m, 42H), 0.82-0.75 (m, 15H); $^{13}$C NMR (100 MHz, CDCl$_3$): 151.5, 148.8, 144.1, 142.6, 140.4, 138.8, 137.4, 137.1, 135.5, 134.1, 133.6, 131.8, 130.9, 129.1, 128.3, 125.9, 124.9, 124.8, 122.9, 122.5, 121.4, 117.9, 102.9, 41.5, 41.0, 34.5, 33.8, 31.6, 30.5, 30.1, 25.6, 25.2, 14.5, 14.3, 14.1, 10.9, 10.5 ppm. MALDI [M+1]$^+$: found: 2168.85, calcd: 2168.86.

Synthesis of L13-Br:

To a 100 mL round-bottom flask was added Pd(PPh$_3$)$_4$ (60 mg, 0.05 mmol) triphenylamine-tributylstannane (1.7 g, 3.0 mmol) and 4, 7-dibromobenzothiadiazole
(0.88 g, 3.0 mmol) in toluene (50 mL). The mixture was heated to reflux for 24 h under nitrogen atmosphere. After removal of solvents, the crude product was purified by column chromatography on silica gel eluting with hexane/CH₂Cl₂ (5:1, v/v) solvent mixture. Yellow solid (1.2 g, 82%).

¹H NMR (400 MHz, CDCl₃): δ = 7.28 (d, 1H, J = 3.8 Hz), 7.70 (d, 2H, J = 8.6 Hz), 7.45(d, 1H, J = 3.4 Hz), 7.06-6.99(m, 10H), 2.26 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): 153.1, 148.4, 147.5, 147.3, 133.5, 132.4, 129.9, 129.8, 129.4, 129.3, 127.3, 125.1, 124.9, 123.3, 122.9, 122.6, 112.2, 24.1 ppm. MALDI [M+1]^+: found: 486.06, calcd: 486.06.

**Synthesis of M13:**

To a 100 mL round-bottom flask was added Pd(PPh₃)₄ (10 mg, 8 µmol), **L13-Br** (0.15 g, 0.31 mmol) and BDT-tributylstannane (0.17 g, 0.15 mmol) in toluene (30 mL). The mixture was heated to reflux for 48 h under nitrogen atmosphere. After removal of solvents, the crude product was purified by column chromatography on silica gel eluting with hexane/CHCl₃ (4:1 to 2:1, v/v) solvent mixture. Brown solid (75 mg, 36%).

¹H NMR (400 MHz, CDCl₃): δ = 8.83 (s, 2H), 7.88 (d, 2H, J = 3.8 Hz), 7.77 (d, 4H, J = 8.6 Hz), 7.61 (d, 2H, J = 3.4 Hz), 7.06-6.92 (m, 20H), 2.88, (d, 4H, J = 6.8 Hz),
2.27 (s, 12H), 1.70 (br, 2H), 1.57-1.36 (m, 18H), 0.94 (t, 6H, $J = 7.2$ Hz), 0.86 (t, 6H, $J = 6.8$ Hz); $^{13}$C NMR (100 MHz, CDCl₃): 152.7, 151.7, 147.3, 144.5, 143.8, 138.8, 137.3, 136.7, 136.3, 131.9, 131.8, 128.8, 128.5, 128.3, 126.9, 126.2, 125.5, 124.4, 124.1, 123.9, 123.3, 122.7, 120.3, 40.5, 33.3, 31.6, 27.9, 24.7, 22.1, 19.8, 13.2, 10.1 ppm. MALDI [M+1]$^+$: found: 1389.47, calcd: 1389.48.

**Synthesis of L14-Br:**

To a 100 mL round-bottom flask was added Pd(PPh₃)$_4$ (100 mg, 0.08 mmol) $N,N$-di-$p$-tolylbenzenamine-tributylstannyl (2.2 g, 3.9 mmol) and 4,7-dibromo-5-fluorobenzothiadiazole (1.2 g, 3.9 mmol) in toluene (50 mL). The mixture was heated to reflux for 24 h under nitrogen atmosphere. After removal of solvents, the crude product was purified by column chromatography on silica gel eluting with hexane/CH₂Cl₂ (5:1, v/v) solvent mixture. Yellow solid (1.1 g, 56%).

$^1$H NMR (400 MHz, CDCl₃): $\delta = 7.78$ (d, 2H, $J = 8.9$ Hz), 7.50 (d, 2H, $J = 10.1$ Hz), 7.11-7.06 (m, 10H), 2.33 (s, 6H); $^{13}$C NMR (100 MHz, CDCl₃): 162.2, 159.6, 154.5, 154.4, 150.3, 149.4, 144.6, 134.3, 134.2, 133.5, 130.1, 127.3, 127.2, 125.5, 120.9, 95.7, 95.5, 19.8 ppm. MALDI [M+1]$^+$: found: 504.02, calcd: 504.02.

**Synthesis of M14:**
To a 100 mL round-bottom flask was added Pd(PPh\textsubscript{3})\textsubscript{4} (10 mg, 8 µmol), L14-Br (0.25 g, 0.49 mmol) and BDT-tributylstannane (0.26 g, 0.23 mmol) in toluene (30 mL). The mixture was heated to reflux for 48 h under nitrogen atmosphere. After removal of solvents, the crude product was purified by column chromatography on silica gel eluting with hexane/CHCl\textsubscript{3} (4:1 to 2:1, v/v) solvent mixture. Brown solid (75 mg, 36%).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta = 8.67 \) (s, 2H), 7.60 (d, 2H, \( J = 8.4 \) Hz), 7.39 (br, 4H), 6.96-6.89 (m, 22H), 2.88, (d, 4H, \( J = 6.8 \) Hz), 2.24 (s, 12H), 1.69 (br, 2H), 1.49-1.32 (m, 18H), 1.17 (s, 4H), 0.99-0.87 (m, 12H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): 160.3,157.7, 152.8, 152.7, 149.9, 147.9, 144.6, 143.5, 138.3, 138.2, 136.2, 135.6, 132.7, 132.6, 132.3, 132.1, 131.9, 128.9, 128.6, 127.1, 126.7, 125.4, 125.3, 124.5, 124.3, 122.6, 119.9, 116.9, 116.7, 109.5, 109.3, 40.5, 33.3, 31.6, 28.7, 28.0, 24.7, 22.1, 19.8, 13.2, 10.0 ppm. MALDI [M+1]\textsuperscript{+}: found: 1425.45, calcd: 1425.46.

\textit{Synthesis of L15-Br:}

To L15 (0.1 g, 0.2 mmol) in 50 mL of CHCl\textsubscript{3}/AcOH mixture solution was added NBS (36 mg, 0.2 mmol) at 0 °C. The mixture was stirred overnight and washed with water. After drying over Na\textsubscript{2}SO\textsubscript{4}, the residue was purified by silica gel chromatography by using CH\textsubscript{2}Cl\textsubscript{2}:hexane (1:2, v/v) as eluant. Red solid (90 mg,
79%.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.84$ (m, 3H), 7.80 (d, 1H, $J = 3.4$ Hz), 7.68 (d, 1H, $J = 7.4$ Hz), 7.15 (br, 3H), 7.12-7.09 (m, 8H), 2.33 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): 207.0, 153.8, 152.5, 148.6, 144.8, 140.9, 133.2, 132.9, 130.6, 130.0, 129.8, 129.4, 126.8, 125.5, 125.2, 124.6, 123.5, 121.4, 119.5, 114.1, 20.8 ppm. MALDI [M+1]$^+$: found: 568.03, calcd: 568.04.

**Synthesis of M15:**

To a 100 mL round-bottom flask was added Pd(PPh$_3$)$_4$ (15 mg, 13 µmol), L15-Br (0.25 g, 0.44 mmol) and BDT-tributylstannane (0.24 g, 0.21 mmol) in toluene (30 mL). The mixture was heated to reflux for 48 h under nitrogen atmosphere. After removal of solvents, the crude product was purified by column chromatography on silica gel eluting with hexane/CHCl$_3$ (4:1 to 2:1, v/v) solvent mixture. Brown solid (65 mg, 29%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.05$ (d, 2H, $J = 4.0$ Hz), 7.91 (d, 2H, $J = 7.4$ Hz), 7.85 (d, 4H, $J = 8.6$ Hz), 7.77 (s, 2H), 7.69 (d, 2H, $J = 7.6$ Hz), 7.15-7.09 (m, 20H), 6.97 (d, 2H, $J = 3.5$ Hz), 2.94 (d, 4H, $J = 6.8$ Hz), 2.33 (s, 12H), 1.70 (br, 2H), 1.57-1.36 (m, 16H), 1.01-0.86 (m, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$): 153.9, 152.7, 148.5, 146.0, 144.9, 138.4, 137.8, 137.4, 133.1, 129.9, 129.7, 129.5, 127.9, 126.9,
126.0, 125.5, 125.2, 124.9, 121.5, 119.3, 41.5, 34.4, 32.6, 31.6, 29.0, 25.9, 23.1, 22.7, 20.9, 14.3, 14.2, 11.1 ppm. MALDI [M+1]$^+$: found: 1553.45, calcd: 1553.46.

8.3 Experimental Details for Chapter 4

**Synthesis of M16:**

To a 100 mL round-bottom flask was added Pd(PPh$_3$)$_4$ (11 mg, 10 µmol), L6-Br (0.25 g, 0.61 mmol) and CPT-tributylstannane (0.29 g, 0.30 mmol) in toluene (30 mL). The mixture was heated to reflux for 48 h under nitrogen atmosphere. After removal of solvents, the crude product was purified by column chromatography on silica gel eluting with hexane/CHCl$_3$ (4:1 to 2:1, v/v) solvent mixture. Brown solid (80 mg, 25%).

$^1$H NMR (400 MHz, CDCl$_3$): δ = 8.04 (t, 2H, $J$ = 8.0 Hz), 7.84 (m, 2H), 7.66 (m, 2H), 7.63 (m, 2H), 6.74 (d, 2H, $J$ = 3.6 Hz), 2.73 (d, 4H, $J$ = 6.8 Hz), 1.98 (s, 4H), 1.57 (br, 2H), 1.30-1.24 (m, 16H), 0.98-0.92 (m, 16H), 0.84 (m, 14H), 0.59 (m,12H); $^{13}$C NMR (100 MHz, CDCl$_3$): 158.2, 158.1, 151.6, 151.3, 145.2, 139.2, 139.1, 137.8, 136.1, 126.2, 125.3, 125.2, 124.3, 124.0, 123.1, 121.8, 53.1, 42.2, 40.4, 34.3, 33.3, 31.4, 27.9, 27.6, 26.5, 24.5, 22.0, 21.8, 13.2, 13.1, 9.8, 9.7 ppm. MALDI [M+1]$^+$: found: 1059.47, calcd: 1059.46.
**Synthesis of M17:**

To a 100 mL round-bottom flask was added Pd(PPh\(_3\))\(_4\) (15 mg, 13 \(\mu\)mol), L7-Br (0.2 g, 0.41 mmol) and CPT-tributylstannane (0.19 g, 0.20 mmol) in toluene (30 mL). The mixture was heated to reflux for 48 h under nitrogen atmosphere. After removal of solvents, the crude product was purified by column chromatography on silica gel eluting with hexane/CHCl\(_3\) (4:1 to 2:1, v/v) solvent mixture. Brown solid (75 mg, 31%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.14\) (t, 2H, \(J = 8.0\) Hz), 7.94 (m, 2H), 7.72 (m, 4H), 7.13 (d, 2H, \(J = 4.0\) Hz), 7.08 (d, 2H, \(J = 4.0\) Hz), 6.68 (d, 2H, \(J = 3.2\) Hz), 2.76 (d, 4H, \(J = 6.8\) Hz), 2.08 (s, 4H), 1.57 (br, 2H), 1.39-1.30 (m, 16H), 1.01 (m, 16H), 0.91 (m, 14H), 0.67 (m, 12H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 159.4, 152.5, 152.3, 144.5, 140.3, 139.1, 139.0, 137.5, 134.9, 127.9, 126.5, 126.0, 125.1, 124.7, 123.7, 123.6, 54.2, 43.2, 41.5, 35.4, 34.3, 34.2, 28.9, 28.6, 27.6, 25.6, 23.1, 22.9, 14.2, 14.1, 10.9, 10.8 ppm. MALDI [M+1]^+: found: 1223.42, calcd: 1223.43.

**Synthesis of M18:**

To a 100 mL round-bottom flask was added Pd(PPh\(_3\))\(_4\) (15 mg, 13 \(\mu\)mol), L8-Br (0.25 g, 0.43 mmol) and CPT-tributylstannane (0.20 g, 0.21 mmol) in toluene
(30 mL). The mixture was heated to reflux for 48 h under nitrogen atmosphere. After removal of solvents, the crude product was purified by column chromatography on silica gel eluting with hexane/CHCl₃ (4:1 to 1:1, v/v) solvent mixture. Brown solid (65 mg, 22%).

¹H NMR (400 MHz, CDCl₃): δ = 7.99 (m, 4H), 7.78 (m, 4H), 7.18 (m, 4H), 7.17 (d, 2H, J = 3.4 Hz), 7.10 (d, 2H, J = 4.0 Hz), 6.71 (d, 2H, J = 3.2 Hz), 2.77 (d, 4H, J = 6.8 Hz), 1.95 (m, 4H), 1.62 (br, 2H), 1.32-1.25 (m, 16H), 1.06 (m, 16H), 0.94 (m, 14H), 0.78 (t, 6H, J = 7.2 Hz), 0.69 (t, 6H, J = 6.8 Hz); ¹³C NMR (100 MHz, CDCl₃): 158.4, 152.1, 144.3, 139.7, 139.1, 137.6, 137.2, 137.0, 136.5, 134.9, 128.0, 125.9, 124.8, 124.5, 123.5, 123.4, 118.8, 54.1, 43.0, 41.4, 35.2, 34.2, 32.4, 28.9, 28.6, 27.5, 25.5, 23.0, 14.2, 14.1, 10.8, 10.7 ppm. MALDI [M+1]⁺: found: 1387.40, calcd: 1387.41.

**Synthesis of M19:**

To a 100 mL round-bottom flask was added Pd(PPh₃)₄ (15 mg, 13 µmol), L9-Br (0.3 g, 0.31 mmol) and CPT-tributylstannane (0.14 g, 0.15 mmol) in toluene (30 mL). The mixture was heated to reflux for 48 h under nitrogen atmosphere. After removal of solvents, the crude product was purified by column chromatography on silica gel eluting with hexane/CHCl₃ (4:1 to 2:1, v/v) solvent mixture. Brown solid
(90 mg, 27%).

\[^1\text{H} \text{NMR (}400 \text{ MHz, CDCl}_3\text{): } \delta = 7.82 \text{ (br, 4H), } 7.50 \text{ (m, 8H), } 7.18 \text{ (m, 4H), } 7.30 \text{ (t, 2H, } J = 8.0 \text{ Hz), } 7.22-7.16 \text{ (br, 8H), } 7.03 \text{ (br, 6H), } 6.92 \text{ (m, 4H), } 6.66 \text{ (d, 2H, } J = 3.4 \text{ Hz), } 3.90 \text{ (t, 4H, } J = 6.4 \text{ Hz), } 3.85 \text{ (t, 4H, } J = 3.8 \text{ Hz), } 2.76 \text{ (d, 4H, } J = 6.8 \text{ Hz), } 1.97 \text{ (br, 4H), } 1.70 \text{ (br, 10H), } 1.40-1.29 \text{ (m, 60H), } 1.06 \text{ (m, 16H), } 0.92 \text{ (m, 28H), } 0.70 \text{ (m, 12H); } \[^{13}\text{C} \text{NMR (}100 \text{ MHz, CDCl}_3\text{): } 159.1, 158.9, 158.8, 158.7, 158.4, 151.3, 151.2, 143.8, 141.7, 141.2, 139.8, 139.6, 138.1, 136.8, 136.7, 136.5, 136.3, 135.6, 130.4, 130.3, 129.2, 128.9, 127.3, 126.8, 126.0, 125.9, 123.1, 122.9, 122.7, 122.6, 118.5, 116.4, 116.3, 115.9, 115.6, 68.1, 68.0, 54.1, 43.1, 41.4, 35.3, 34.4, 34.2, 32.4, 31.9, 31.8, 29.5, 29.4, 29.3, 29.2, 29.1, 28.9, 28.6, 27.5, 26.1, 26.0, 25.5, 23.1, 22.9, 22.7, 22.6, 14.2, 14.1, 14.0, 10.9, 10.8, 10.7 \text{ ppm. MALDI [M+1]^+: } \text{found: } 2196.12, \text{ calcd: } 2196.13.\]

**Synthesis of L20-Br:**

To a 100 mL round-bottom flask was added \textbf{L20-aldehyde} (0.46 g, 1.4 mmol) and 2-(4-(5-thiophen-2-yl)phenyl)acetonitrile (0.42 g, 1.4 mmol) in ethanol (40 mL) with a NaOH of 0.16 g. The mixture was refluxed for 6 h under nitrogen atmosphere. After removal of solvents, the crude product was purified by column chromatography on silica gel eluting with CHCl\textsubscript{3} solvent. Red solid (0.30 g, 34%).
$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.21$ (d, 1H, $J = 4.0$ Hz), 7.90 (d, 1H, $J = 7.6$ Hz), 7.84 (d, 1H, $J = 7.6$ Hz), 7.72 (d, 1H, $J = 3.2$ Hz), 7.70 (s, 1H), 7.65-7.62 (m, 4H), 7.21 (d, 2H, $J = 3.6$ Hz), 6.76 (d, 2H, $J = 3.6$ Hz), 2.78 (d, 2H, $J = 6.8$ Hz), 2.23 (s, 1H), 1.31 (br, 8H), 0.91 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): 153.8, 151.5, 145.5, 142.6, 140.5, 139.0, 135.5, 133.6, 132.6, 131.9, 128.7, 126.5, 126.0, 125.9, 125.7, 123.4, 118.0, 113.8, 108.3, 41.5, 34.3, 32.4, 28.9, 25.5, 23.1, 14.2, 10.9 ppm.

MALDI [M+1]$^+$: found: 618.06, calcd: 618.06.

**Synthesis of M20:**

To a 100 mL round-bottom flask was added Pd(PPh$_3$)$_4$ (15 mg, 13 $\mu$mol), L20-Br (0.25 g, 0.41 mmol) and CPT-tributylstannane (0.23 g, 0.20 mmol) in toluene (30 mL). The mixture was heated to reflux for 48 h under nitrogen atmosphere. After removed solvents, the crude product was purified by column chromatography on silica gel eluting with CHCl$_3$. Brown solid (75 mg, 31%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.28$ (br, 2H), 8.17 (s, 2H), 7.96 (br, 2H), 7.89 (bs, 4H), 7.69-7.54 (m, 10H), 7.19 (s, 2H), 6.68 (s, 2H), 2.70 (t, 4H, $J = 6.4$ Hz), 2.07 (br, 4H), 1.25-1.18 (m, 24H), 1.01-0.81 (m, 24H), 0.60 (m, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$): 159.6, 152.2, 151.9, 145.2, 143.7, 140.6, 140.4, 140.2, 138.3, 135.1, 133.4, 132.4, 131.9, 127.6, 126.3, 126.2, 125.8, 125.6, 123.3, 118.2, 107.1, 54.2, 43.0, 41.4,
Synthesis of M21:

To a 100 mL round-bottom flask was added Pd(PPh₃)₄ (15 mg, 13 µmol), L13-Br (0.25 g, 0.41 mmol) and CPT-tributylstannane (0.23 g, 0.20 mmol) in toluene (30 mL). The mixture was heated to reflux for 48 h under nitrogen atmosphere. After removed solvents, the crude product was purified by column chromatography on silica gel eluting with hexane/CHCl₃ (4:1 to 2:1, v/v) solvent mixture. Brown solid (75 mg, 31%).

¹H NMR (400 MHz, CDCl₃): δ = 8.06 (t, 2H, J = 5.6 Hz), 7.82-7.79 (m, 2H), 7.78-7.77 (m, 4H), 7.62 (d, 2H, J = 5.6 Hz), 7.09 (d, 2H, J = 8.6 Hz), 7.02 (s, 8H), 2.26 (s, 6H), 1.20 (br, 16H), 0.80 (m, 12H); ¹³C NMR (100 MHz, CDCl₃): 159.1, 153.9, 152.6, 147.9, 147.4, 140.0, 138.8, 131.4, 130.8, 129.8, 129.3, 127.3, 126.7, 124.9, 124.3, 123.3, 122.9, 122.8, 54.2, 43.2, 35.3, 34.3, 28.6, 27.5, 22.8, 14.1, 10.8 ppm. MALDI [M+1]⁺: found: 1477.51, calcd: 1477.51.

Synthesis of M22:

To a 100 mL round-bottom flask was added Pd(PPh₃)₄ (15 mg, 13 µmol),
**L15-Br** (0.25 g, 0.44 mmol) and CPT-tributylstannane (0.24 g, 0.21 mmol) in toluene (30 mL). The mixture was heated to reflux for 48 h under nitrogen atmosphere. After removed solvents, the crude product was purified by column chromatography on silica gel eluting with hexane/CHCl₃ (4:1 to 2:1, v/v) solvent mixture. Brown solid (70 mg, 24%).

$^1$H NMR (400 MHz, CDCl₃): $\delta = 8.04$ (m, 2H), 7.91 (d, 2H), 7.85 (d, 4H), 7.69 (d, 2H, $J = 5.6$ Hz), 7.18 (s, 2H), 7.10 (br, 18H), 2.34 (s, 12H), 1.93 (br, 4H), 1.07-0.98 (br, 18H), 0.76 (t, 6H, $J = 7.6$ Hz), 0.68 (t, 6H, $J = 7.6$ Hz); $^{13}$C NMR (100 MHz, CDCl₃): 158.7, 158.6, 158.5, 153.9, 152.7, 148.5, 144.9, 139.6, 137.5, 136.5, 133.1, 132.1, 130.1, 130.0, 129.9, 129.8, 129.7, 128.1, 126.9, 125.2, 123.5, 121.6, 119.1, 119.0, 54.2, 54.1, 43.3, 35.3, 34.3, 28.7, 27.6, 23.0, 22.9, 20.9, 20.8, 14.3, 14.2, 10.8, 10.7 ppm. MALDI [M+1]⁺: found: 1377.47, calcd: 1377.48.

### 8.4 Experimental Details for Chapter 5

**Synthesis of M23:**

To a 100 mL round-bottom flask was added CuI (4 mg, 0.016 mmol), **L23-alkyne** (62 mg, 0.12 mmol) and tris(4-iodophenyl)amine (20 mg, 0.03 mmol) in
NEt₃/THF mixture solution (30 mL). The mixture was heated to reflux for 48 h under nitrogen atmosphere. After removal of solvents, the crude product was purified by column chromatography on silica gel eluting with hexane/CHCl₃ (4:1 to 2:1, v/v) solvent mixture. Red solid (40 mg, 78%).

¹H NMR (400 MHz, CDCl₃): δ = 7.99 (d, 6H, J = 1.6 Hz), 7.93 (s, 3H), 7.83 (s, 6H), 7.46 (d, 6H, J = 8.6 Hz), 7.13 (d, 6H, J = 8.6 Hz), 7.05 (s, 3H), 2.84 (m, 6H), 2.69 (m, 6H), 1.36 (br, 12H), 1.76-1.25 (br, 30H), 0.90 (m, 24H);

¹³C NMR (100 MHz, CDCl₃): 151.5, 151.4, 147.5, 145.6, 143.3, 137.9, 137.8, 131.5, 128.1, 127.4, 125.3, 124.4, 124.3, 124.1, 123.0, 120.7, 118.8, 116.9, 96.0, 81.7, 30.7, 30.6, 29.6, 29.4, 29.3, 28.0, 21.6, 13.1, 13.0 ppm. MALDI [M+1]^+: found: 1716.59, calcd: 1716.60.

**Synthesis of M24:**

To a 100 mL round-bottom flask was added CuI (8 mg, 0.032 mmol), L₂₄-alkyne (100 mg, 0.16 mmol) and tris(4-iodophenyl)amine (29 mg, 0.046 mmol) in NEt₃/THF mixture solution (40 mL). The mixture was heated to reflux for 48 h under nitrogen atmosphere. After removal of solvents, the crude product was purified by column chromatography on silica gel eluting with hexane/CHCl₃ (4:1 to 2:1, v/v) solvent mixture. Purple solid (40 mg, 78%).

¹H NMR (400 MHz, CDCl₃): δ = 7.59 (dd, 3H, J = 1.0 Hz, J = 3.6 Hz), 7.44 (d, 6H, J
\[ \delta = 8.6 \text{ Hz}, \] 7.42 (d, 3H, \( J = 4.0 \text{ Hz} \)), 7.36 (dd, 3H, \( J = 1.0 \text{ Hz}, J = 3.6 \text{ Hz} \)), 7.21 (d, 3H, 
\( J = 4.0 \text{ Hz} \)), 7.10 (m, 9H), 2.89 (m, 12H), 1.95 (m, 12H), 1.58-1.23 (br, 102H), 0.88 (m, 24H); \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)): 155.4, 155.2, 145.5, 136.9, 136.4, 135.2, 133.8, 131.5, 130.7, 125.9, 125.2, 123.1, 122.9, 122.8, 122.4, 122.2, 121.8, 116.8, 93.7, 82.5, 33.9, 30.9, 28.7, 28.6, 28.5, 28.4, 28.3, 25.7, 25.6, 21.7, 13.2, 13.1 ppm.  
MALDI [M+1]^+: found: 2221.15, calcd: 2221.16.

**Synthesis of M25:**

To a 100 mL round-bottom flask was added Pd(PPh\(_3\))\(_4\) (30 mg, 26 \( \mu \text{mol} \)), L13-Br (0.3 g, 0.62 mmol) and TPA-tributylstannane (0.21 g, 0.19 mmol) in toluene (30 mL). The mixture was heated to reflux for 48 h under nitrogen atmosphere. After removal of solvents, the crude product was purified by column chromatography on silica gel eluting with hexane/CHCl\(_3\) (2:1 to 1:1, v/v) solvent mixture. Red solid (95 mg, 34%).

\( ^{1}H \) NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.94 \) (d, 6H, \( J = 8.6 \text{ Hz} \)), 7.83 (d, 6H, \( J = 8.6 \text{ Hz} \)), 7.70 (m, 6H), 7.40 (d, 6H, \( J = 8.6 \text{ Hz} \)), 7.15 (d, 6H, \( J = 8.6 \text{ Hz} \)), 7.08 (br, 24H), 2.31 (s, 18H); \( ^{13}C \) NMR (100 MHz, CDCl\(_3\)): 154.2, 154.1, 148.4, 147.3, 145.0, 133.0, 132.5, 132.3, 131.7, 130.2, 130.0, 129.9, 129.8, 127.7, 127.2, 125.2, 124.4, 121.7, 20.9 ppm. MALDI [M+1]^+: found: 1461.50, calcd: 1461.51.
**Synthesis of M26:**

To a 100 mL round-bottom flask was added Pd(PPh\(_3\))\(_4\) (20 mg, 17 µmol), L14-Br (0.2 g, 0.39 mmol) and TPA-tributylstannane (0.12 g, 0.11 mmol) in toluene (30 mL). The mixture was heated to reflux for 48 h under nitrogen atmosphere. After removal of solvents, the crude product was purified by column chromatography on silica gel eluting with hexane/CHCl\(_3\) (2:1 to 1:1, v/v) solvent mixture. Red solid (95 mg, 57%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.85\) (d, 6H, \(J = 8.8\) Hz), 7.82 (d, 6H, \(J = 8.6\) Hz), 7.63 (d, 3H, \(J = 11.8\) Hz), 7.46 (d, 6H, \(J = 8.6\) Hz), 7.14 (d, 6H, \(J = 8.6\) Hz), 7.08 (br, 24H), 2.34 (s, 18H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 160.9, 158.5, 155.3, 155.2, 151.2, 149.0, 147.2, 144.7, 133.4, 133.3, 131.7, 130.1, 129.8, 128.4, 126.1, 125.4, 124.1, 121.2, 118.6, 118.3, 116.2, 116.1, 20.9 ppm. MALDI [M+1]\(^+\): found: 1515.48, calcd: 1515.49.

8.5 Experimental Details for Chapter 6

*General procedures for the synthesis of (P5-8)-alkyne from (P5-8)-Br:*
To an ice-cooled mixture of P5-Br (220 mg, 0.48 mmol) in freshly distilled triethylamine (20 mL) and CH₂Cl₂ (20 mL) solution under nitrogen was added Pd(OAc)₂ (10 mg), PPh₃ (30 mg) and CuI (10 mg). After the solution was stirred for 30 min, trimethylsilylacetylene (0.78 mL, 5.45 mmol) was then added and the suspension was stirred for another 30 min in the ice-bath before being warmed to room temperature. After reacting for 30 min at room temperature, the mixture was heated to 50 °C for 24 h. The solution was then allowed to cool to room temperature and the solvents were removed on a rotary evaporator in vacuo. The crude product was purified by column chromatography on silica gel eluting with hexane/CH₂Cl₂ (4:1, v/v) to provide P5-TMS (160 mg, 84%) as a red solid.

A mixture of P5-TMS (160 mg, 0.4 mmol) and K₂CO₃ (114 mg, 0.85 mmol) in a solution mixture of methanol (5 mL) and CH₂Cl₂ (20 mL), under the nitrogen atmosphere, was stirred at room temperature overnight. The mixture was added to CH₂Cl₂ (30 mL) washed with water (20 mL) three times and dried over anhydrous Na₂SO₄. The solvents were removed on a rotary evaporator in vacuo. The crude product was purified by column chromatography on silica gel eluting with hexane/CH₂Cl₂ (6:1, v/v) to provide P5-alkyne (120 mg, 86%) as a red solid.

**Synthesis of P5-alkyne:**
$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.95$ (d, 2H, $J = 3.8$ Hz), 7.82 (s, 2H), 7.35 (d, 2H, $J = 3.8$ Hz), 3.48 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): 152.3, 140.6, 133.9, 127.1, 125.7, 125.6, 123.5, 83.1 ppm. MALDI [M+1]$^+$: found: 378.97, calcd: 378.98.

*Synthesis of P6-alkyne:*

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.83$ (s, 2H), 7.70 (s, 2H), 3.57 (s, 2H), 2.74 (t, 4H, $J = 7.6$ Hz), 1.69 (m, 4H), 1.41-1.31 (m, 12H), 0.90 (t, 6H, $J = 6.8$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$): 152.3, 149.9, 139.0, 128.4, 125.4, 118.6, 85.0, 31.6, 30.2, 29.7, 29.0, 22.6, 14.1 ppm. MALDI [M+1]$^+$: found: 517.17, calcd: 517.17.

*Synthesis of P7-alkyne:*

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.02$ (s, 1H), 7.85 (s, 1H), 7.66 (d, 1H, $J = 13.0$ Hz), 3.59 (s, 1H), 3.58 (s, 1H), 2.79 (t, 4H, $J = 7.6$ Hz), 1.72 (m, 4H), 1.41-1.33 (m, 12H), 0.89 (t, 6H, $J = 6.8$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$): 160.4, 157.8, 153.1, 152.9, 149.9, 149.4, 149.1, 137.5, 137.4, 132.6, 132.5, 131.1, 131.0, 129.1, 125.2, 125.1, 119.9, 119.8, 119.7, 116.7, 116.4, 111.0, 110.8, 85.6, 85.3, 31.7, 31.6, 30.3, 30.2, 29.6, 29.5, 29.0, 22.7, 22.6, 14.2 ppm. MALDI [M+1]$^+$: found: 535.17, calcd: 535.16.

*Synthesis of P8-alkyne:*

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$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.52$ (s, 2H), 3.58 (s, 2H) 2.75 (t, 4H, $J = 7.6$ Hz), 1.69 (m, 4H), 1.40-1.32 (m, 12H), 0.90 (t, 6H, $J = 6.8$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$): 152.4, 150.5, 148.9, 134.1, 131.9, 119.0, 116.8, 84.9, 31.7, 30.3, 29.7, 29.1, 22.7, 14.2 ppm. MALDI [M+1]$^+$: found: 553.14, calcd: 553.15.
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Biographical item on the thesis author, Mr. Liu Xinli:

1) Born on March 24, 1981

2) Received the degree of Bachelor from Chemistry Department of Jilin University, July 2002.

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