Synthesis and characterization of new functional molecules and application studies in dye-sensitized and organic solar cells

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Synthesis and Characterization of New Functional Molecules and Application Studies in Dye-sensitized and Organic Solar Cells

LAI Lai Fan

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
October 2013
Declaration

I hereby declare that this thesis represents my own work except for those in collaboration with others which has been done after registration for the degree of Doctor of Philosophy 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 qualifications.

Signature:____________________

Date:    October 2013
Abstract

This thesis describes the synthesis and characterization of a series of photosensitizers, transition metal-containing polymers and small organic molecules for dye-sensitized solar cells and organic solar cells.

To begin with, a brief overview on the background of dye-sensitized solar cells (DSSCs) and organic solar cells was presented in Chapter 1.

In Chapter 2, a series of novel donor-acceptor-π-acceptor bithiazole-based and fluorenone-based organic dyes for dye-sensitized solar cells were successfully synthesized and fully characterized. We discovered that the performance of the photovoltaic devices depends significantly on the nature and strength of the electron-donating end group along the conjugated main. Some of the materials have been found to show higher power conversion efficiency of 4.71% ($V_{oc} = 565 \text{ mV}, J_{sc} = 11.71 \text{ mA cm}^{-2}, FF = 0.71$) under AM 1.5 irradiation (100 mW cm$^{-2}$).

In Chapter 3, ten novel donor-donor-π-acceptor organic dyes for dye-sensitized solar cells have been synthesized and applied for the fabrication of DSSCs, including six dibenzothiophene-based photosensitizers and carbazole-based photosensitizers. All the dyes have efficient charge injection from the excited sensitizer molecule to TiO$_2$ conduction band and can provide ample driving force for efficient dye regeneration.
and thus the charge separation. Among all the photosensitizers, DSSCs exhibited the best overall light to electricity conversion efficiency of 5.28% ($V_{oc} = 0.70$ V, $J_{sc} = 11.06$ mA cm$^{-2}$, $FF = 0.68$) under AM 1.5 irradiation, which reached 73% with respect to that of an N719-based device fabricated under similar fabrication conditions.

Besides, nine novel di-anchoring organic sensitizers employing two different electron-donating cores, which are the fluorene and carbazole units, and two symmetrical anchoring cyanoacrylic acid (acceptor) termini have been synthesized and studied for their applications in DSSCs in Chapter 4.

In Chapter 5, four new platinum polyyne polymers were prepared via the Sonogashira-type dehydrohalogenation reaction between the ethynyl precursor and $trans$-Pt(PBu$_3$)$_2$Cl$_2$. All of the polymers are air-stable and well characterized by different spectroscopic methods and photophysical measurements. Their photovoltaic behaviors were fully investigated. Their model compounds were also prepared and studied.

In Chapter 6, a series of new organic small molecules were designed and synthesized comprising head-to-head coupled heylthiophene, dithienosilole and dithienogermole units. They exhibited broad absorption peaks with favorable spectral overlap with the solar spectrum. These seven small molecules have been applied to
the bulk heterojunction solar cells and the corresponding photovoltaic properties were presented. Among these molecules, the highest PCE of 4.93% was achieved with a $V_{oc} = 0.79$ V, $J_{sc} = 1.22$ mA cm$^{-2}$ and $FF = 0.51$ under illumination of an AM 1.5 solar cell simulator.

Finally, Chapters 7 and 8 present the concluding remarks and the experimental details of the work described in Chapters 2–6.
Acknowledgements

I would like to express my profound gratitude and sincere thanks to my supervisor Prof. Raymond W. Y. Wong for his invaluable advice, encouragement and uninterrupted support throughout my study. He has been supportive since the days I began working on his research group as an undergraduate. He has been supporting me not only by providing precious comments and opinion, but also provided me academic and spiritual support for over almost four years. His erudite advices always open up new horizons for me and his devoted attitude in research has influenced me a lot and made my study a truly rewarding experience.

Wordless thanks also go to Prof. T. He and Dr. W. J. Wu (Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, China), Prof. J. T. Lin and Dr. Y. C. Chen (Institute of Chemistry, Academia Sinica, Taiwan), Dr. L. Y. Han, Dr. C. J. Qin (Photovoltaic Materials Unit and NIMS Saint-Gobain Center of Excellence for Advanced Materials, National Institute for Materials Science, Japan) for the fabrication and testing of DSSCs; Vinay Gupta (Center for Polymers and Organic Solids, Departments of Chemistry & Biochemistry and Materials, University of California, Santa Barbara) for the fabrication and testing of BHJ solar cells. Dr. F. R. Dai (Hong Kong Baptist
University), and M. S. Cheung (The Hong Kong University of Science and Technology) for density functional theory calculations; Dr. C. H. Chui (Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hong Kong) for cytotoxicity test.

Special thanks are given to Prof. Guillermo C. Bazan (Center for Polymers and Organic Solids, Departments of Chemistry & Biochemistry and Materials, University of California, Santa Barbara) for giving me an opportunity to do an exchange program in his group and Prof. T. He (Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, China) for giving me a chance to explore the fabrication of DSSCs.

I would like to show my kind gratitude to our research group members, Dr. C. L. Ho, Miss Qian Liu, Miss Hao Wu, Dr. G. P. Tan, Dr. F. R. Dai, Dr. Q. C. Dong, Dr. H. M. Zhan, Dr. L. Li, Dr. Q. W. Wang, Dr. X. L. Liu, Dr. Z. Xie and others, for their genuine care, guidance, support and encouragement. I am indebted to all clerical and scientific officers of the Department of Chemistry.

I would like to acknowledge the financial support from the Hong Kong Baptist University, Hong Kong Research Grants Council (HKBU203011), the University Grants Committee Areas of Excellence Scheme (AoE/P-03/08) and the National Natural Science Foundation of China (NSFC) (project number: 21029001) for
financial support of this work.

Significantly, I would like to thank my parents for their unconditional support throughout my study. In addition, the love and understanding shown by Michael Chan during the years is greatly appreciated.

Last but not least, I would like to thank God for his wisdom that he has been bestowed upon me during this research project and even my life. I would also like to thank my brothers and sisters in Christ, for their continuous support and encouragement throughout my life.
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<td>CHCl$_3$</td>
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<td>N,N-Dimethylformamide</td>
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<td>Dimethyl sulfoxide</td>
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<td>Methanol</td>
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<td>NBS</td>
<td>N-Bromosuccinimide</td>
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<td>NEt$_3$</td>
<td>Triethylamine</td>
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<td>PCBM</td>
<td>[6,6]-Phenyl C$_{61}$ butyric acid methyl ether</td>
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<td>THF</td>
<td>Tetrahydrofuran</td>
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<td>$E_g$</td>
<td>Energy gap</td>
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<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
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<tr>
<td>°C</td>
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<tr>
<td>δ</td>
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<td>λ</td>
<td>Wavelength</td>
</tr>
<tr>
<td>λ_{abs}</td>
<td>Absorption wavelength</td>
</tr>
<tr>
<td>λ_{em}</td>
<td>Emission wavelength</td>
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<tr>
<td>ε</td>
<td>Molar absorptivity/molar extinction coefficient</td>
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D3

D4

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n = 2 DT2
n = 3 DT3
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\[ \text{AT1} \]

\[ \text{AT2} \]

\[ \text{AT3} \]
Chapter 1 Introduction

1.1 Dye-sensitized Solar Cells (DSSCs)

1.1.1 Background

Energy crisis problem has become more and more internationally concerned because of the shortage for petroleum. Investigating alternative forms of renewable and sustainable energy sources become a significant issue today. Especially, solar energy is in the forefront of the fossil fuel alternatives as solar energy is the most abundant, inexhaustible and clean among all renewable energy resources. The energy of light can be directly converted into electricity by the photovoltaic effect using a solar cell device.

Photovoltaic devices have been dominated by solid-state junction devices which are usually made of silicon and profited from the good experience and material availability resulting from the semiconductor industry. The dominance of the inorganic solid-state junction devices is now being challenged by a third generation of cells such as nanocrystalline dye-sensitized solar cells and conducting polymer films. These offer very low-cost fabrication and show attractive features that facilitate market entry. Besides, nanocrystalline dye-sensitized solar cells have shown obviously high conversion efficiencies, which compete with those of the conventional
The history of the dye-sensitized solar cells has been chronicled.\cite{3,4} The silver halides used in photography have band gaps of the order of 2.7–3.2 eV, and hence they are insensitive to most of the visible light, just as is the TiO$_2$ nowadays used in the dye-sensitized solar cells. The first panchromatic film which was able to render the image of a scene realistically into black and white followed from the work of Vogel in Berlin after 1873 that he associated dyes with the halide semiconductor grains.\cite{5} Afterwards, the first sensitization of a photo-electrode followed shortly in which a similar chemistry was made.\cite{6} Then, the parallelism between the two procedures, a realization that the same dyes in principle could function in both\cite{7} and their operating mechanisms were clearly recognized by injection of electrons from the photo-excited dye molecules into the conduction band of the n-type semiconductor substrates in the late 1960s.\cite{8} In subsequent years, the idea expanded in that the dye could function most efficiently if it was chemisorbed on the surface of the semiconductor.\cite{9,10} The concept was visualized to use dispersed particles to provide a sufficient interface,\cite{11} and then photo-electrodes were employed.\cite{12} Titanium dioxide became the common choice of semiconductor. The material is good at sensitized photochemistry and photo-electrochemistry because it is a low cost, widely available, non-toxic and biocompatible material.\cite{13} Also, it can be even used in health care devices.
products as well as domestic applications such as paint pigmentation. The standard dye at that time was tris(2,2-bipyridyl-4,4-carboxylate)ruthenium(II), and the function of the carboxylate is to attach the chromophore to the oxide substrate by chemisorption. Afterwards, the sensitized electrochemical photovoltaic device had conversion efficiency at that time of 7.1% under solar illumination in 1991.\textsuperscript{[1, 2]} That evolution has continued progressively since then, with certified efficiency now over 12.3%.\textsuperscript{[14]}

1.1.2 Operation Principle of Organic Solar Cells

Various functionalized metal-free organic dyes have been designed and synthesized to replace expensive ruthenium(II) complexes. Although their performance in DSSCs is lower or close to the ruthenium complexes, these metal-free organic dyes can be considered as a new generation of sensitizers. It is therefore important to determine design rules for organic dyes to achieve enhanced properties and performance so that they may compete with ruthenium(II) sensitizers in the future. The efficiency of the solar cells does not only depend on the molecular structure of the dye, but sometimes even more on other solid-state properties, such as aggregation, morphology, self-assembly, type of photoelectrode, anchoring group of the dye, electrolyte, and mediating redox couple.
Therefore, only approximate trends are available for the design of organic dyes with respect to their device performance. The general design principle for a dye or sensitizer is illustrated in Figure 1.1. Generally, a dye or sensitizer consists of a donor, acceptor and substituted \( \pi \)-conjugated “bridge” to the anchoring group which is attached to the TiO\(_2\) at the periphery of the acceptor.

Analysis of the data concerning which type of donor (D), \( \pi \) bridge, and acceptor (A) leads to the most efficient organic dyes in DSSCs reveals that the best donors come from the family of electron-rich arylamines such as aminocoumarin, (difluorenyl)phenylamine, triphenylamine, and indoline. The best moieties for the \( \pi \)-conjugated bridge very frequently contain thiophene units, such as oligothiophenes, thienylenevinylene, dithienothiophene or phenyleinylene because of their excellent charge-transport properties.\(^{[14]}\) The variation on the acceptor side is rather small, and in most cases a cyanoacrylic acid group is used, with the anchoring carboxylic acid group elegantly incorporated into the acceptor moiety.\(^{[14]}\) Rhodamine-3-acetic acid among the rest was used as a second type of acceptor.

**Figure 1.1** Design principle of an organic dye for TiO\(_2\) photoanode in DSSCs.
1.1.2.1 Overview of the Different Electron-Transfer Processes

At the heart of the system is a mesoporous oxide layer composed of nanometer-sized particles which have been sintered together to allow for electronic conduction to take place. The choice of material is TiO$_2$, although alternative wide band gap oxides such as ZnO\textsuperscript{[15]} and Nb$_2$O$_5$ have also been investigated.\textsuperscript{[16]} Material attached to the surface of the nanocrystalline film is a monolayer of the charge transfer dye. Photo-excitation of the dyes injects an electron into the conduction band of the oxide. The original state of the dye is subsequently restored by electron donation from the electrolyte which is usually an organic solvent containing redox system, such as the iodide/triiodide couple. The regeneration of the sensitizer by iodide intercepts the recapture of the conduction band electron by the oxidized dye. The iodide is in turn regenerated by the reduction of triiodide at the counter electrode and the circuit is being completed via electron migration through the external load. The voltage generated under illumination corresponds to the difference between the Fermi level of the electron in the solid and the redox potential of the electrolyte. Overall the device generates electric power from light without suffering from any permanent chemical transformation.

The electron-transfer processes of the dye-sensitized solar cells involve reactions
1 and 2: electron injection and excited state decay; reaction 3: regeneration of the oxidized dyes; reaction 4: electron transport through the mesoporous oxide film; reactions 5 and 6: recombination of electrons in the semiconductor with oxidized dyes or electrolyte species; and reaction 7: reduction of electron acceptors in an electrolyte at the counter electrode.

**Figure 1.2** Fundamental processes in a dye-sensitized solar cell.

### 1.1.2.2 Reactions 1 and 2: Electron Injection and Excited State Decay

One of the most attractive findings in DSSC research is the ultrafast injection from the excited ruthenium(II) complexes in the TiO$_2$ conduction band (reaction 2).
Although the detailed mechanism of the injection process is still under debate, it is generally accepted that a fast femtosecond component is observed for this type of sensitizers directly attached to an oxide surface.\textsuperscript{[17–20]} For DSSC device performance, the time scales of the injection process should be compared with decay of the excited state of the dye to the ground state (reaction 1). This is given by the excited state lifetime of the dye, which for typical ruthenium(II) complexes used in DSSCs is 20–60 ns.\textsuperscript{[21]} Interestingly, Durrant and co-workers have observed a much slower electron injection in a complete DSSC device with a half-life of around 150 ps. This would then be slow enough for kinetic competition between electron injection and excited state decay of the dye with potential implications for the overall DSSC performance.\textsuperscript{[22]}

1.1.2.3 Reaction 3: Regeneration of the Oxidized Dyes

The interception of the oxidized dye by the electron donor, normally I\textsuperscript{−}, is in the microsecond time domain. For a turnover number, the cycle life of the sensitizer in the DSSC device is above 108 which is required for a DSSC lifetime of 20 years in outdoor conditions. The lifetime of the oxidized dye must be larger than 100 s if the regeneration time is 1 \( \mu \)s. This is achieved by the best-performing ruthenium(II) complexes.\textsuperscript{[23]}
1.1.2.4 Reaction 4: Electron Transport through the Mesoporous Oxide Film

The charge transport through the nanocrystalline TiO$_2$ layer is highly efficient. The mesoporous electrodes are very much different compared with their compact analogues because the inherent conductivity of the film is very low. Secondly, the small size of the individual colloidal particles does not support a built-in electrical field. Besides, the oxide particles and the electrolyte-containing pores form interpenetrating networks whose phase boundaries produce a junction of huge contact area. These films may be viewed as an ensemble of individual particles through which electrons can percolate by hopping from one crystallite to the next. The charge transport mechanisms in DSSC are still under keen debate today.

1.1.2.5 Reactions 5 and 6: Recombination of Electrons in the Semiconductor with Oxidized Dyes or Electrolyte Species

The kinetics of the back-electron-transfer reaction from the conduction band to the oxidized sensitizers follow a multiexponential time law, occurring on a microsecond to millisecond time scale depending on electron concentration in the semiconductor and thus the light intensity. Recombination of electrons in TiO$_2$ with acceptors in the electrolyte is normally referred to as the electron lifetime. Lifetimes
observed with the $I/\Gamma_{3}^-$ are very long which is about 1 to 20 ms under one sun light intensity compared with other redox systems used in hence DSSC, explaining the success of this redox couple.

1.1.2.6 Reaction 7: Reduction of Electron Acceptors in the Electrolyte at the Counter Electrode

Counter electrodes for DSSCs with $I/\Gamma_{3}^-$ electrolytes can be rather easily prepared by deposition of a thin catalytic layer of platinum onto a conducting glass substrate. Best performance and long-term stability have been achieved with nanoscale Pt clusters. Charge transfer resistances of less than $1 \ \Omega \ \text{cm}^2$ can be achieved.[24]

1.1.3 Efficiency Measurements

1.1.3.1 Measurement of $I-V$ Curve

The current-voltage ($I-V$) characteristics of a solar cell under illumination are used to determine the power conversion efficiency (PCE). Because dye-sensitized solar cells have a relatively slow electrical response due to their high interfacial capacity, the voltage scan should be sufficiently slow to avoid errors in the current measurement due to capacitive discharging. Alternatively, the currents from a rapid
forward and reverse voltage scan can be averaged.\textsuperscript{[25]} From the $I$–$V$ curve, the short-circuit current, $I_{sc}$ or short-circuit current density, $J_{sc}$, is determined at the $V = 0$ V intercept, while the open-circuit potential, $V_{oc}$, is found at the $I = 0$ intercept. The maximum output power of the solar cell is found where the product $|I \times V|$ reaches a maximum power point. The power conversion efficiency is given by

$$\eta = \frac{|J V|_{\text{max}}}{P_{\text{in}}} = \frac{J_{sc} V_{oc} FF}{P_{\text{in}}}$$

where $P_{\text{in}}$ is the power density of the incident light and $FF$ is the fill factor. The fill factor is a value between 0 and less than 1 that describes the shape of the $I$–$V$ curve, where a high value indicates a more preferable rectangular shape.

In a solar cell, power is dissipated through the resistance of the contacts, during charge transport, and through leakage currents within the device or around the sides of the device. These effects are electrically equivalent to resistances in series and in shunt and reduce the fill factor. Series resistance is particularly problematic at high current densities, whereas the shunt resistance is a problem in poorly rectifying devices.

It is a common practice to use white light from a solar simulator as the light source for efficiency measurements. The standard irradiance spectrum for the solar cell measurements is AM 1.5 G. As most solar simulators do not provide an ideal AM
1.5 G spectrum, a careful correction needs to be made to account for the spectral mismatch.\cite{26, 27}

1.1.3.2 Measurement of IPCE

The spectral response of dye-sensitized solar cells is determined by measuring the monochromatic incident photon-to-current conversion efficiency (IPCE). It is customary that the IPCE is measured under short-circuit conditions. There are two principal IPCE measurement methods namely the DC and the AC method. In the DC method, monochromatic light is obtained by passing white light through a monochromator or a bandpass filter, and the photocurrent is measured. In the AC method, the monochromatic light is usually mechanically chopped, and the AC-photocurrent response is measured using a lock-in amplifier. The latter method has the advantage that white bias light can be added, so that the solar cell is working under true operational conditions. It should be noted that DSSCs have slow response times compared with solid-state photovoltaics, so that a low chopping frequency must be chosen. In the DC method, the generated photocurrent may be 2–3 orders of magnitude lower than that in full sunlight. This method will therefore only give useful results if the photocurrent increases linearly with light intensity, which is usually the case for DSSCs. A very useful test is to calculate $J_{sc}$ in full sunlight from the obtained
IPCE spectrum:

\[ J_{sc} = \int \text{IPCE}(\lambda) e \phi_{\text{ph,AM1.5G}}(\lambda) d\lambda \]

where \( e \) is the elementary charge and \( \phi_{\text{ph,AM1.5G}} \) is the photon flux in AM 1.5 G, 100 mW cm\(^{-2}\).

The IPCE can be expressed as follows:

\[ \text{IPCE}(\lambda) = \text{LHE}(\lambda) \phi_{\text{inj}}(\lambda) \phi_{\text{reg}} \eta_{\text{CC}}(\lambda) \]

where LHE is the light-harvesting efficiency, \( \phi_{\text{inj}} \) and \( \phi_{\text{reg}} \) are the quantum yields for electron injection and dye regeneration, respectively, and \( \eta_{\text{CC}} \) is the charge collection efficiency (LHE) \((1 - 10^{-4})\), with \( A \) being the absorbance of the film.

### 1.2 Organic Solar Cells

#### 1.2.1 Background

Up to now, silicon-based solar cells such as monocrystalline, polycrystalline or amorphous silicon, which have reasonable and relatively higher power conversion efficiencies (PCE), about 13~17% in production and 18~24% in laboratory, are by far the most dominating type of photovoltaic cells. However, the silicon solar cells require highly pure silicon and skilled manufacturing techniques, such as high temperatures, high vacuum conditions, and many lithographic steps. As a consequence, the costs of these silicon-based solar cells are very high. The cost of
these solar cells needed to be reduced in order to motivate the prevalence of the use of photovoltaic cells.\textsuperscript{[28]}

In recent years, a lot of scientists have been paying attention to organic semiconductors because they are a less expensive alternative to silicon-based semiconductors and their weight is lighter than that of crystalline inorganic semiconductors. Organic solar cells are normally built from thin films of organic semiconductors such as polymers and small molecules and carbon-based fullerenes or fullerene derivatives such as methanofullerene [6,6]-phenyl-C\textsubscript{61}-butyric acid methyl ester (PCBM).

Anthracene was the first organic compound that possesses photoconductivity, which was discovered by Pochettino in 1906\textsuperscript{[29a]} and Volmer in 1913.\textsuperscript{[29b]} In the late 1950s to 1960s, the potential use of organic materials as photoreceptors in imaging systems was known.\textsuperscript{[29c]} Afterwards, the field of organic electronics based on conjugated materials has started in 1977 when A. G. MacDiarmid and H. Shirakawa discovered that the conjugated polymer polyacetylene shows conductivity, for which they were awarded the Nobel Prize in Chemistry in 2000.\textsuperscript{[30]} In 2007, metallated conjugated polymer based solar cells have been studied. The milestone in the development of organic solar cells is shown in Table 1.1.\textsuperscript{[31]}
Table 1.1. The important milestone in the development of organic solar cells.

<table>
<thead>
<tr>
<th>Year</th>
<th>Event Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1839</td>
<td>Becquerel discovered the photoelectrochemical process.</td>
</tr>
<tr>
<td>1906</td>
<td>Pochettino discovered photoconductivity in solid anthracene.</td>
</tr>
<tr>
<td>1950s</td>
<td>Chlorophyll and related organic dyes were studied; Keehns and Calvin worked with magnesium phthalocyanine.</td>
</tr>
<tr>
<td>1980s</td>
<td>First polymer based solar cells were developed.</td>
</tr>
<tr>
<td>1986</td>
<td>First solar cell with donor and acceptor was designed by Tang et al.</td>
</tr>
<tr>
<td>1991</td>
<td>First dye/dye based cell was set up by Hiramoto.</td>
</tr>
<tr>
<td>1993</td>
<td>First polymer/C₆₀ based cell was made by Sariciftci et al.</td>
</tr>
<tr>
<td>1995</td>
<td>First polymer/polymer based cell was done by Yu and Hall.</td>
</tr>
<tr>
<td>2000</td>
<td>Oligomer-C₆₀ dyad/triad as the active material was observed by Peters and Van Hal.</td>
</tr>
<tr>
<td>2007</td>
<td>Metallated conjugated polymer based solar cell</td>
</tr>
</tbody>
</table>

1.2.2 Structure and Operation Principle of Organic Solar Cells

The typical bilayer and the bulk heterojunction (BHJ) devices are shown in Figure 1.3. The active region of these devices consists of two materials, one acting as an electron donor and the other as an acceptor.
In a bilayer heterojunction device, p-type and n-type semiconductors are sequentially stacked on top of each other. In such devices, only excitons created within the distance of 10–20 nm from the interface can reach the heterojunction interface. This leads to the loss of absorbed photons further away from the interface and results in low quantum efficiencies.\(^{32}\) The efficiency of these bilayer solar cells is limited by the charge generation at 10–20 nm around the donor-acceptor interface.

For BHJ, the active layer is a blend of the donor and acceptor components in a bulk volume. It exhibits a donor-acceptor phase separation in 10–20 nm length scale. In such a nanoscale interpenetrating network, each interface is within a distance less than the exciton diffusion length from the absorbing site. The BHJ concept has increased the interfacial area between the donor and acceptor phases and resulted in improved efficiency of solar cells.\(^{32}\) Polymer and small-molecule photovoltaic solar cells which can be processed in solution generally take the form of BHJ devices.
The process of light conversion into electricity in organic solar cell is shown in Figure 1.4. Generally, there are fundamental steps on how light energy is converted into electrical energy in the devices: 1) Absorption of light and generation of excitons, 2) Diffusion of the excitons, 3) Dissociation of the excitons with generation of charge, 4) Charge transport and charge collection.[33, 34]
Creation of charges is one of the key steps in photovoltaic devices in the conversion of solar light into electrical energy. The elementary steps involved in the pathway from photoexcitation to the generation of free charges are listed in Scheme 1.1. In most organic solar cells, charges are created by photoinduced electron transfer. In this reaction, an electron is transferred from a donor (D) which is a p-type semiconductor, to an acceptor (A) which is an n-type semiconductor, with the aid of the additional input energy of an absorbed photon ($h\nu$). In the photoinduced electron

Figure 1.4 General mechanism for photoenergy conversion in excitonic solar cells.\[34\]
transfer reaction, the first step is the generation of excition of the donor (D\(^{\ast}\)), followed by creation of the charge-separated state consisting of the radical cation of the donor (D\(^{\ast}\)) and the radical anion of the acceptor (A\(^{\ast}\)).\[^{34}\]

\[
\begin{array}{c}
D + A \leftrightarrow \text{hv} \rightarrow D^{\ast} + A \\
D^{\ast} + A \leftrightarrow [D^{\ast}, A] \\
[D^{\ast}, A] \leftrightarrow [D^{\ast}, A^{-}] \\
[D^{\ast}, A^{-}] \leftrightarrow [D^{\ast} + A^{-}]
\end{array}
\]

**Scheme 1.1** Elementary steps in the process of photoinduced charge separation for a donor (D) and an acceptor (A).\[^{34}\]

1.2.3 Conjugated Polymer Cells

Conjugated polymers are excellent candidates for use in low-cost electronics and photovoltaics as they can be deposited by screen printing, doctor blading, inkjet printing, and spray deposition due to their good solubility. One of the most studied photoconducting polymers is poly(N-vinylcarbazole) (PVK). The first report was in 1958 by Hoegel\[^{35}\] who suggested PVK can be used as an electrophotographic agent. In the 1970s, certain conjugated polymers such as poly(sulphur nitride) and polyacetylene could be highly conducting in the presence of certain dopants.\[^{36}\] In 1982, Weinberger discovered polyacetylene as the active material in an
The cell had a low open-circuit voltage of only 0.3 V and a low quantum efficiency (QE) of only 0.3%. Afterwards, Glenis made different polythiophenes. Again, the systems suffered from low efficiencies and low open-circuit voltages in the 0.4 V range. Followed by the poly(alkyl-thiophenes) (PATs), PPV and its derivatives are the most investigated conjugated polymer in PV cells. Karg was the first group to make PPV in ITO/PPV/Al LEDs and PV devices in 1993. His group measured $V_{oc}$ of 1 V and a PCE of 0.1% under white light illumination. In 1994, both Marks and Antoniad also investigated this system. Marks found that their cells were completely depleted while Antoniadis’ cells formed Schottky type barriers at the Al-interface. This divergent behaviour is probably related to the fact that PPV is very sensitive to atmospheric oxygen as an efficient dopant for PPV. Thus, in the presence of oxygen, electron abstraction from PPV increases the conductance orders of magnitude, due to the p-type behaviour of PPV.

Up to date, the most efficient example of a low-bandgap polymer for use in solar cells is based on benzothiadiazole (or its analogues) as the acceptor in combination with cyclopentabithiophene as the donor. Mulbacher et al. synthesized a copolymer of dialkyl-cyclopentabithiophene and benzothiadiazole (PCPDTBT, Figure 1.5). The polymer shows an absorption maximum at 705 nm in solution, shifting to 775 nm for
film, and a bandgap of 1.40 eV. Solar cells were realized by blending PCPDTBT with PCBM or its C$_{70}$ analogue in a 1:3 weight ratio. The action spectra demonstrated a photocurrent onset beyond 900 nm with a maximum EQE of approximately 30% for PCBM and 35% for the C$_{70}$ derivative. Under white-light irradiation (100 mW cm$^{-2}$) current densities of 9 and 11 mW cm$^{-2}$ with a $V_{oc}$ of 0.65 V were obtained, corresponding to PCE of 2.67 and 3.16%, respectively. Recently, Yang’s group demonstrated a single-junction device of PDDPDFBT which showed high external quantum efficiency of >60% and spectral response that was extended to 900 nm, with a PCE of 7.9%. The polymer enables a solution processed tandem solar cell with certified 10.6% which is a world record.$^{[43]}$

![Figure 1.5](image)

**Figure 1.5** Chemical structures of representative conjugated polymers.

In order to improve coverage of the solar spectrum and enhance the efficiency of...
polymer photovoltaic cells, polymer-based BHJ solar cells need to be optimized which are mainly focused on three areas: 1) developing better electron donor materials with low band-gap energy to serve as light absorbers and charge carriers; 2) developing new electron acceptor materials; 3) developing new technologies based on new solar cell architectural designs.

1.2.4 Small Molecules

Organic small-molecule solar cells (OSSCS) have attracted considerable attention due to the unique advantages of well-defined molecular structure, definite molecular weight, high purity and good batch-to-batch reproducibility. In addition, vacuum evaporation/sublimation is a very clean (no solvent) choice for the deposition of thin films based on small molecules.

The first relatively successful organic solar cells reported by Tang in 1986 was fabricated from copper phthalocyanine (CuPc) as the electron-donor material and a perylene tetracarboxylic derivative which worked as electron-acceptor material (Figure 1.6). A PCE of about 1% was achieved under simulated AM2 illumination. FF of 0.65 represents a substantial improvement over values previously obtained for organic solar cells. This kind of solar cells has accordingly been heavily investigated. Recent results reveal that a CuPc:C$_{60}$ bilayer device with a very
low resistance shows a significant improvement in $\eta$, especially at higher illumination intensity, achieving a maximum $\eta = (4.2 \pm 0.2)\%$.\textsuperscript{[47]} Afterwards, Zhan and co-workers reported a three-dimensional, star-shaped small molecule, S(TPA-BT-HTT) with a PCE of 4.3\%.\textsuperscript{[48]} Then, Bazan et al. synthesized a core A-D-A framework with end-capping donor units in a small molecule, DTS(PTTh$_2$)$_2$, which demonstrated a PCE as high as 6.7\%.\textsuperscript{[49]} Recently, Chen and co-workers designed and synthesized a linear small molecule, DR$_3$TBDT, which showed excellent photovoltaic performance with a PCE of 7.38\%, which is a high efficiency reported to date for small molecule based solar cells and approaches the value for polymer solar cells.\textsuperscript{[50]} Lately, Heeger et al. demonstrated solution-processed small molecule DTS(FBTTh$_2$)$_2$:PC$_{71}$BM BHJ solar cells with a PCE of 8.01\% that is the highest value reported for an organic solar cell.
Figure 1.6 Chemical structures of CuPc and perylene tetracarboxylic derivative.
1.3 Scope of the Thesis

In order to develop new materials with high efficiency for both dye-sensitized and organic solar cells, we plan to design and prepare a series of new photosensitizers, small organic molecules and \(\pi\)-conjugated platinum(II) polyyne polymers with different \(\pi\)-conjugated central cores which were fully characterized by different spectroscopic methods and also tested for their photovoltaic behavior in polymer solar cells. The photophysical, electrochemical and structural properties of these compounds have been extensively investigated. In this thesis, two different types of D-A-\(\pi\)-A organic dyes for dye-sensitized solar cells; two different types of D-D-\(\pi\)-A organic dyes for dye-sensitized solar cells; two different types of symmetrical di-anchoring organic photosensitizers for dye-sensitized solar cells; two different types of small molecules for bulk heterojunction solar cells; two different types of platinum(II) polyyne polymers for organic solar cells were studied.
References:


2.1 Synthesis and Characterization of Functionalized Bithiazole-Based Dye-sensitized Solar Cells

2.1.1 Introduction

The most abundant and clean source of energy on earth is solar energy to date. The solar energy reaching the earth in 1 h is almost equivalent to the current global annual energy consumption. To replace the use of fossil fuels and petroleum, the conversion of sunlight energy into electrical energy is, therefore, seen as one of the most promising solutions for the energy crisis problem. The energy of sunlight can be directly converted into electricity by the photovoltaic effect using a solar cell device.¹ Inorganic semiconductor solar cells, especially silicon in various forms,² have been developed over several decades and have important applications. However, silicon materials are not cost effective. In recent years, Ru(II)-polypyridyl photosensitizers such as N3,¹⁶ N719,¹¹c,³ N907,⁴ and black dye⁵ have achieved solar-to-electricity conversion efficiency higher than 10% under AM 1.5 simulator, a value close to an amorphous silicon-based photovoltaic cell.⁶ As compared to metal-based Ru(II) dyes,
organic compounds can also be used in the manufacture of dye-sensitized solar cells (DSSCs).\cite{7} Organic DSSCs are a low-cost alternative of our renewable energy sources in the past decades because they have potential to get high PCE and their devices are easy to fabricate.\cite{8} Their high molar extinction coefficients, ease of purification and flexible structural modifications render them attractive light-harvesting materials. Recently, Wang and co-workers reported an impressive PCE of 9.8% with excellent stability for a DSSC based on a metal-free sensitizer.\cite{9} The performance of DSSCs based on other metal-free organic dyes has also been remarkably improved recently by several groups.\cite{10} These researchers have applied various approaches to tune the HOMO and LUMO energy levels of the chromophores, where the donor, linker or acceptor moieties were altered independently. These results suggest that smartly designed metal-free organic dyes are also highly competitive candidates as photosensitizers for DSSCs.

The thiazole unit is one of the strongest electron-accepting aza-heterocycles because it contains one electron-withdrawing nitrogen atom of imine (C=N) in place of the carbon atom at the 3-position of thiophene. Therefore, a number of \( \pi \)-conjugated polymers incorporating bithiazole moieties have been demonstrated to be promising as new n-type transporting materials,\cite{11-13} and have also been used as an acceptor unit for photovoltaic application. Therefore, bithiazole-based materials are
conceived to be attractive photovoltaic materials. However, organic dyes containing the bithiazole moiety are still not very well studied. On the other hand, triarylamine-based dyes have been widely used because the arylamine groups can increase the electron density of donor moiety and hence improve the dye performance effectively. Also, compounds involving fluorene and carbazole moieties in the main chain have been extensively reported and used in photovoltaics research. Introduction of a thiophene moiety normally allows a red-shift of the absorption maximum and broadens the spectral profile of absorption of a particular dye.

Based on the above considerations, five new organic bithiazole-bridged dye photosensitizers D1–D5 were designed and synthesized with thiophene, triarylamine, carbazole and fluorene units as the electron donor, bithiazole as a π-conjugated bridge, and a cyanoacrylic acid moiety as the electron-withdrawing and anchoring group (Chart 2.1). The five new dyes have been applied to the sensitization of nanocrystalline TiO₂-based solar cells and the corresponding photovoltaic properties, electronic and optical properties are also presented in this chapter.
Chart 2.1 The chemical structures of organic dyes D1–D5 in this study.

2.1.2 Synthesis

All of the new dyes have been synthesized according to some classical organic transformations and the synthetic routes are outlined in Schemes 2.1–2.3. The dyes are composed of an aromatic donor moiety, a conjugated bridge of a bithiazole unit and 1-cyanoacrylic acid as the electron acceptor and anchoring group to the TiO₂. The key material 4,4’-dinonyl-2,2’-bithiazole was obtained firstly by bromination of
2-undecanone with bromine to form 1-bromo-undecan-2-one, which then underwent cycloaddition with dithiooxamide via the Hantzsch thiazole synthesis.[16] Subsequently, this compound was monobrominated by N-bromosuccinimide (NBS) to give D1-Br. Then, the key intermediate D1-CHO was obtained by Suzuki coupling reaction between D1-Br and 5-formylthiophen-2-yl-2-boronic acid. Knoevenagel condensation of the aldehyde D1-CHO and cyanoacetic acid in the presence of piperidine gave the desired dye D1. For the donor-substituted dyes D2–D5, bromination of compound D1-CHO gives the corresponding bromide which reacts with an appropriate arylboronic acid via Suzuki coupling to afford intermediates D2-CHO to D5-CHO. The syntheses of the dyes were then completed by the same procedure as that for D1 and they were isolated in moderate yields. The structures of all the dyes were verified by NMR spectroscopy and MALDI-TOF mass spectrometry. The dyes are orange or orange-red in color and are readily soluble in common organic solvents such as THF, CH₂Cl₂, CHCl₃ and DMSO.
Scheme 2.1 Synthetic routes for various boronic acid derivatives: i) $p$-toluenesulfonic acid, glycol, benzene; ii) $n$-BuLi, B(OMe)$_3$, HCl; iii) NBS, CHCl$_3$; iv) $n$-BuLi, B(OMe)$_3$; v) NaOH, DMSO; vi) $n$-BuLi, B(OMe)$_3$.

Scheme 2.2 Synthesis of D1: i) Br$_2$, methanol; ii) dithiooxamide, ethanol; iii) NBS, DMF; iv) Pd(PPh$_3$)$_4$, Na$_2$CO$_3$ (2 M, aq), THF; v) cyanoacetic acid, piperidine, dry CHCl$_3$. 
Scheme 2.3 Synthesis of D2–D5: i) NBS, CHCl₃/acetic acid, overnight; ii) Pd(PPh₃)₄, Na₂CO₃ (2 M, aq), THF; iii) cyanoacetic acid, piperidine, dry CHCl₃.
2.1.3 Results and Discussion

2.1.3.1 Spectroscopic Characterization

All the newly synthesized dyes were well characterized by common spectroscopic techniques such as NMR spectroscopy. All the dyes are air-stable and soluble in common organic solvents. All the compounds have shown characteristic $^1$H NMR spectra. All the NMR data of the intermediates and dyes are summarized in the experimental part of Chapter 8.

All the proton signals of aromatic rings of the photosensitizers are on the downfield region (above 6.80 ppm) and those of the butyl group are on the upfield region (below 2.30 ppm). The $^1$H NMR spectra of D2 and D4 are shown in Figures 2.1 and 2.2, respectively.
Figure 2.1 $^1$H NMR spectrum of dye D2 in $d_6$-DMSO.

Figure 2.2 $^1$H NMR spectrum of dye D4 in $d_6$-DMSO.
2.1.3.2 Photophysical Properties

The UV-Vis absorption spectra of the photosensitizers $D_1$–$D_5$ in THF at room temperature are displayed in Figure 2.3 and the data are collected in Table 2.1. All of the dyes give two distinct absorption bands: one relatively weak band in the near UV region at around 270 to 300 nm can be attributed to the $\pi-\pi^*$ transition and the other stronger band at around 400 to 450 nm is caused by the intramolecular charge transfer (ICT) between the different donors and the cyanoacrylic acid anchoring moiety,\textsuperscript{16,17} producing an efficient charge separated state. The spectra of all the dyes are quite similar, but those with stronger donor group $D_2$–$D_5$ are red-shifted in comparison to that of $D_1$, which could be ascribed to the presence of more electron-rich moieties to produce more extended $\pi$-conjugation system. The absorption peak maximum of the dye ranks in the order: $D_3$ (432 nm) > $D_4$ (428 nm) ≈ $D_5$ (427 nm) > $D_2$ (425 nm) > $D_1$ (413 nm). The increase in conjugation length and the increased electron density associated with the fluorenyl group in $D_5$, carbazolyl group in $D_4$ and triarylamine group in $D_3$ lead to a larger bathochromic shift of the absorption maximum.\textsuperscript{18} The molar extinction coefficients of the ICT bands for $D_1$–$D_5$ were also investigated in THF and increase in the order of $D_4$ > $D_5$ > $D_3$ > $D_2$ > $D_1$, which suggests that $D_4$ should have the best light-harvesting ability. Noticeably, the molar extinction coefficients of $D_3$–$D_5$ are even higher than that of the $N_3$ dye ($1.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$).\textsuperscript{19e}
The higher molar extinction coefficients of the organic dyes allow a correspondingly thinner nanocrystalline film so as to avoid the decrease of the film mechanical strength. This also benefits the electrolyte diffusion in the film and reduces the recombination possibility of the light-induced charges during transportation.\[19\]

![Normalized absorbance spectra](image)

**Figure 2.3** Normalized absorption spectra of the new dyes measured in THF at 298 K.

Figure 2.4 depicts the absorption spectra on TiO\(_2\) film and photoluminescence (PL) spectra in THF solution of the new dyes. Their absorption spectra on TiO\(_2\) film are broadened due to the interaction of the anchoring group of organic dyes with the TiO\(_2\) electrode which was commonly observed for other organic dyes.\[20,21\] In addition, all of the dyes exhibit a broadened absorption spectrum and a slight blue shift of 14
nm (D1), 19 nm (D2), 16 nm (D3), 8 nm (D4) and 14 nm (D5) in wavelength as compared to that measured in THF solution. This broadening favors the light harvesting of the solar cells and thus increases the photocurrent response region with a rise of short-circuit current density (J_sc). The blue shift is due to the formation of H-aggregate on the TiO₂ electrode. Such a slight shift indicates that the aggregates of dyes are not obvious which may be explained by the notion that the introduction of long alkyl chains of bithiazole unit inhibits the formation of aggregates to some extent. The dyes show emissions when they are being excited. Similar to their UV-Vis absorption spectra, the most red-shifted peak is shown at around 560 nm for D3 which has triarylamine as an electron-donating group while the most blue-shifted peak is shown at around 502 nm by the sensitizer D1 without an electron-donating group (Table 2.1).

All of the dyes are photoluminescent at room temperature (Table 2.1) and the fluorescence peak maximum ranges from 502 to 560 nm. Similar to the absorption spectra, the presence of electron-releasing groups would shift the emission maximum to the red and the most electron-donating triarylamine unit would give the most red-shifted peak at 560 nm for D3.
Figure 2.4 Absorption spectra in THF (solid line) and on TiO$_2$ film (dotted line), and PL spectra (dashed line) in THF of (a) D1, (b) D2, (c) D3, (d) D4 and (e) D5 at 298 K.
Table 2.1 Absorption and PL data of D1–D5 in THF at 298 K.

<table>
<thead>
<tr>
<th>Dye</th>
<th>λ(_{\text{max}}) in THF (nm)</th>
<th>Molar extinction coefficients (M(^{-1}) cm(^{-1}))</th>
<th>λ(_{\text{max}}) on TiO(_2) film (nm)</th>
<th>λ(_{\text{em}}) in THF (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>263, 413</td>
<td>1590, 5140</td>
<td>399</td>
<td>502</td>
</tr>
<tr>
<td>D2</td>
<td>289, 425</td>
<td>3490, 13450</td>
<td>406</td>
<td>534</td>
</tr>
<tr>
<td>D3</td>
<td>301, 432</td>
<td>17190, 25820</td>
<td>416</td>
<td>560</td>
</tr>
<tr>
<td>D4</td>
<td>265, 296, 428</td>
<td>19817, 26850, 36788</td>
<td>420</td>
<td>539</td>
</tr>
<tr>
<td>D5</td>
<td>264, 296, 427</td>
<td>8560, 8030, 28560</td>
<td>415</td>
<td>530</td>
</tr>
</tbody>
</table>

2.1.3.3 Electrochemical Properties

To investigate the electron transfer from the excited dye molecule to the conductive band (\(E_{\text{cb}}\) of TiO\(_2\), cyclic voltammetry was performed for the dyes in thin films on glassy carbon electrode measured in 0.1 M tetrabutylammonium hexafluorophosphate solution in acetonitrile at a scan rate of 50 mV s\(^{-1}\). Under these conditions, the \(E_{1/2}\) of ferrocene was 0.07 V vs Ag/AgCl. The results are summarized in Table 2.2. All of the dyes are redox stable and showed quasi-reversible oxidation and reduction waves.\(^{[24]}\) The HOMO and LUMO energy levels of the dyes were measured from the onset oxidation and reduction potentials. The negative shifts of the \(E_{\text{ox}}\) were observed for D2–D5 versus D1, leading to a decrease of their energy gaps.
between the HOMO and LUMO as compared to D1. That could be attributed to the increased electron density and the larger extension of their π-conjugated systems than that of D1. It is clear that the HOMO level of D3 is the highest among the dyes, which is in agreement with the order of the electron-donating ability of the triarylamine donor.[18]

From Table 2.2, both the HOMO and LUMO levels of these dyes match well with the energy requirement as efficient photosensitizers. Since the reduction waves correspond to the reduction of the anchoring cyanoacrylic acid group in each case, the LUMO levels of D1–D5 only span a narrow range of –3.50 to –3.72 eV. These values are much higher than the lower bound level of the conduction band of TiO₂ (–4.4 eV), indicating that the efficiency of charge injection from the excited sensitizer molecule to the TiO₂ conduction band is viable.[25] The HOMO energy levels of the sensitizers are calculated to be –5.43 to –5.98 eV. These values are lower than that of the I⁻/I₃⁻ pair (–4.9 eV), ensuring effective sensitizer regeneration process, so that the oxidized dyes could be regenerated by the reduced part (I⁻) in the electrolyte to guarantee an efficient charge separation in the photovoltaic devices.[26,27]
Table 2.2 Electrochemical properties of D1–D5.

<table>
<thead>
<tr>
<th>Dye</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>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>1.25</td>
<td>−5.98</td>
<td>−1.16</td>
<td>−3.57</td>
<td>2.41</td>
</tr>
<tr>
<td>D2</td>
<td>1.01</td>
<td>−5.74</td>
<td>−1.21</td>
<td>−3.72</td>
<td>2.02</td>
</tr>
<tr>
<td>D3</td>
<td>0.70</td>
<td>−5.43</td>
<td>−1.22</td>
<td>−3.51</td>
<td>1.92</td>
</tr>
<tr>
<td>D4</td>
<td>0.79</td>
<td>−5.52</td>
<td>−1.23</td>
<td>−3.50</td>
<td>2.02</td>
</tr>
<tr>
<td>D5</td>
<td>0.97</td>
<td>−5.70</td>
<td>−1.17</td>
<td>−3.56</td>
<td>2.14</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)

2.1.3.4 Computational Studies

Time-dependent density functional theory (TDDFT) calculations were carried out for D1–D5 in order to gain better insights into the electronic and spectroscopic properties as well as the nature of absorption bands for these complexes. The density functional theory (DFT) method at the gradient-corrected correlation functional level PBE1PBE$^{[28]}$ was used to optimize the ground state geometries of D1–D5. On the basis of the ground-state optimized geometry, 50 singlet excited states for D1–D5 were calculated at the PBE1PBE/6-31G (d, p) levels with the TDDFT approach.

As shown from the orbital profiles in Figures 2.5–2.9 and Table 2.3, the HOMOs of D1–D5 are mainly located at the $\pi$-conjugated thiazole ligands and the electron-donating group. Especially for D4, the HOMO level is highly located at the
triarylarnino unit. The LUMOs of D1–D5 have amplitudes mostly on the anchoring
2-cyano-3-(5-ethynylthiophen-2-yl)acrylic acid unit. As indicated from Table 2.3, the
calculated lowest-energy absorption (from the HOMO+1→LUMO transition (98–100%)) can be primarily assigned to the ICT transition from the
electron-donating group to the electron-accepting
2-cyano-3-(5-ethynylthiophen-2-yl)acrylic acid unit. It was revealed that the
HOMO→LUMO excitation transferring electrons from the electron-donating group to
the anchoring ligand can facilitate electron injection from the excited state of the
sensitizer to TiO2. The TDDFT calculations suggest that addition of the
electron-donating group, especially the triarylarnino group, can elevate the HOMO
energy level (D4 (HOMO: −5.20 eV) > D5 (−5.74 eV) ≈ D3 (−5.76 eV) > D2 (−5.88
eV) > D1 (−6.09 eV)), resulting in the enhancement of the absorption ability of the
responding compound by reducing the energy gap for the HOMO→LUMO
transition.
Table 2.3 Absorption transitions for D1–D5 calculated by the TDDFT method.

<table>
<thead>
<tr>
<th>state</th>
<th>transition</th>
<th>contribution (%)</th>
<th>$E$ (nm)</th>
<th>oscillator strength</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>D1</strong></td>
<td>S3 HOMO→LUMO</td>
<td>100</td>
<td>430</td>
<td>0.8637</td>
</tr>
<tr>
<td></td>
<td>S7 HOMO→LUMO+1</td>
<td>56</td>
<td>343</td>
<td>0.1579</td>
</tr>
<tr>
<td></td>
<td>HOMO−1→LUMO</td>
<td>42</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S9 HOMO−1→LUMO</td>
<td>56</td>
<td>317</td>
<td>0.1886</td>
</tr>
<tr>
<td></td>
<td>HOMO→LUMO+1</td>
<td>40</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>D2</strong></td>
<td>S3 HOMO→LUMO</td>
<td>98</td>
<td>466</td>
<td>0.9944</td>
</tr>
<tr>
<td></td>
<td>S6 HOMO−1→LUMO</td>
<td>56</td>
<td>371</td>
<td>0.3075</td>
</tr>
<tr>
<td></td>
<td>HOMO→LUMO+1</td>
<td>42</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S9 HOMO→LUMO+1</td>
<td>52</td>
<td>351</td>
<td>0.1429</td>
</tr>
<tr>
<td></td>
<td>HOMO−1→LUMO</td>
<td>42</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>D3</strong></td>
<td>S3 HOMO→LUMO</td>
<td>98</td>
<td>478</td>
<td>1.07</td>
</tr>
<tr>
<td></td>
<td>S7 HOMO−1→LUMO</td>
<td>90</td>
<td>387</td>
<td>0.3609</td>
</tr>
<tr>
<td></td>
<td>HOMO→LUMO+1</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S8 HOMO→LUMO+1</td>
<td>84</td>
<td>364</td>
<td>0.2966</td>
</tr>
<tr>
<td></td>
<td>Transition</td>
<td>Energy 1</td>
<td>Energy 2</td>
<td>Intensity</td>
</tr>
<tr>
<td>---</td>
<td>---------------------</td>
<td>----------</td>
<td>----------</td>
<td>-----------</td>
</tr>
<tr>
<td></td>
<td>HOMO−1→LUMO</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HOMO−2→LUMO</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S25</td>
<td>HOMO→LUMO+2</td>
<td>56</td>
<td>295</td>
<td>0.1217</td>
</tr>
<tr>
<td></td>
<td>HOMO−6→LUMO</td>
<td>28</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HOMO−5→LUMO</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D4</td>
<td>S3      HOMO→LUMO</td>
<td>98</td>
<td>568</td>
<td>0.428</td>
</tr>
<tr>
<td></td>
<td>S6      HOMO−1→LUMO</td>
<td>90</td>
<td>439</td>
<td>1.0189</td>
</tr>
<tr>
<td></td>
<td>HOMO→LUMO+1</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>S7      HOMO→LUMO+1</td>
<td>88</td>
<td>410</td>
<td>0.1112</td>
</tr>
<tr>
<td></td>
<td>HOMO−1→LUMO</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S14</td>
<td>HOMO−2→LUMO</td>
<td>58</td>
<td>349</td>
<td>0.1373</td>
</tr>
<tr>
<td></td>
<td>HOMO−1→LUMO+1</td>
<td>36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S17</td>
<td>HOMO−1→LUMO+1</td>
<td>54</td>
<td>329</td>
<td>0.1714</td>
</tr>
<tr>
<td></td>
<td>HOMO−2→LUMO</td>
<td>38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S22</td>
<td>HOMO→LUMO+2</td>
<td>76</td>
<td>312</td>
<td>0.2615</td>
</tr>
<tr>
<td></td>
<td>HOMO→LUMO+3</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S29</td>
<td>HOMO→LUMO+4</td>
<td>92</td>
<td>298</td>
<td>0.2314</td>
</tr>
</tbody>
</table>
Figure 2.5 Contour plots of selected frontier orbitals of D1.
Figure 2.6 Contour plots of selected frontier orbitals of D2.

Figure 2.7 Contour plots of selected frontier orbitals of D3.
Figure 2.8 Contour plots of selected frontier orbitals of D4.

Figure 2.9 Contour plots of selected frontier orbitals of D5.
2.1.4 Applications in DSSCs

2.1.4.1 Preparation of DSSC Devices

The TiO$_2$ nanoparticles and reference compound N719 were purchased from Solaronix, S.A., Switzerland. The photoanode used was the TiO$_2$ thin film (12 µm of 20 nm particles as the absorbing layer and 6 µm of 400 nm particles as the scattering layer) coated on FTO glass substrate with a dimension of 0.5 × 0.5 cm$^2$. The film thickness was measured by a profilometer (Dektak3, Veeco/Sloan Instruments Inc., USA). A platinized FTO produced by thermopyrolysis of H$_2$PtCl$_6$ was used as a counter electrode. The TiO$_2$ thin film was dipped into the THF solution containing 3×10$^{-4}$ M dye sensitizers for at least 12 h. After rinsing with THF, the photoanode adhered with a polyester tape of 60 µm in thickness and with a square aperture of 0.36 cm$^2$ was placed on top of the counter electrode and they were tightly clipped together to form a cell. Electrolyte was then injected into the space and then the cell was sealed with the Torr Seal cement (Varian, MA, USA). The electrolyte was composed of 0.5 M lithium iodide (LiI), 0.05 M iodine (I$_2$), and 0.5 M 4-tert-butylpyridine dissolved in acetonitrile.

The photoelectrochemical characterizations on the solar cells were carried out using an Oriel Class A solar simulator (Oriel 91195A, Newport Corp.). Photocurrent-voltage characteristics of the DSSCs were recorded with a
potentiostat/galvanostat (CHI650B, CH Instruments, Inc.) at a light intensity of 100 mW cm\(^{-2}\) calibrated by an Oriel reference solar cell (Oriel 91150, Newport Corp.). The monochromatic quantum efficiency was recorded through a monochromator (Oriel 74100, Newport Corp.) at short-circuit condition. The intensity of each wavelength was in the range of 1 to 3 mW cm\(^{-2}\). Electrochemical impedance spectra were recorded for DSSCs under illumination at open-circuit voltage (\(V_{oc}\)) at room temperature. The frequencies explored range from 10 mHz to 100 kHz.

### 2.1.4.2 Photovoltaic Performance of DSSCs

DSSCs with an effective area of 0.25 cm\(^2\) were fabricated by using our new compounds adsorbed on nanocrystalline TiO\(_2\) as the sensitizers. The DSSCs with different dyes were measured under AM 1.5 solar light condition. The losses of light reflection and absorption by the conducting glass were not corrected. The device performance statistics such as short-circuit current density (\(J_{sc}\)), open-circuit voltage (\(V_{oc}\)), fill factor (\(FF\)) and photovoltaic conversion efficiency (PCE) are summarized in Table 4.

Figure 2.10 shows the action spectra of IPCE for DSSCs using \textbf{D1–D5}. All of the dyes can efficiently convert visible light to photocurrent in the region from 400 nm to 600 nm. The IPCE performance of the DSSCs with \textbf{D4} is higher than the others.
due to its best light-harvesting ability. Its IPCE reaches a maximum 68.5% at 459 nm which is comparable to that of N719 (70.0%) in the region from 400–530 nm, although the IPCE of D4 is lower than N719 in the wavelength region of 530–700 nm, indicating that D4-sensitized TiO₂ electrode can generate the highest conversion yield among all the dyes studied.

**Figure 2.10** Photocurrent action spectra of the TiO₂ electrode sensitized by D1–D5.

Figure 2.11 shows the current-voltage (J–V) characteristics of DSSCs fabricated with these bithiazole-containing photosensitizing dyes (D1–D5) under simulated sunlight illumination. Relative to D1, the photovoltaic performance can be significantly improved by introducing an electron-donating group such as thiophene, triarylamine, carbazole and fluorene in the molecule for D2–D5. The J_{sc} is related to
the molar extinction coefficient of the dye molecule, in which a higher molar extinction coefficient has a better light-harvesting ability and yields a higher $J_{sc}$. **D4** has the highest light-harvesting efficiency and consequently an improved $J_{sc}$ (9.61 mA cm$^{-2}$) due to the largest molar extinction coefficient among all the dyes. The light-harvesting efficiency of **D5** is lower than that of **D4** and this may be attributed to the smaller molar extinction coefficient. Conversely, by comparing **D3** with **D4** and **D5**, there is a dramatic fall in both $J_{sc}$ and $V_{oc}$ values in **D3**, which is ascribed to the lower IPCE value of **D3**. The decreased IPCE values suggest that there is an inefficient regeneration of the oxidized dye and accordingly a lower $J_{sc}$ (6.85 mA cm$^{-2}$) value was observed. These results agree well with the corresponding IPCE spectra.

**Figure 2.11** $J$–$V$ curves of the DSSC devices under AM 1.5G simulated sunlight illumination.
For the overall light to electricity conversion efficiency of D1 to D5, dye D4 exhibited the best PCE of 4.65% under standard global AM 1.5 solar light condition, which reached 64% with respect to that of an N719-based device fabricated under similar fabrication conditions. The lower PCE is largely due to the lower $J_{sc}$ of the sensitizer as compared to N719.

**Table 2.4** Photovoltaic performance of DSSCs with D1–D5 and N719 under the AM 1.5 sunlight illumination.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$V_{oc}$ / mV</th>
<th>$J_{sc}$ / mA cm$^{-2}$</th>
<th>FF</th>
<th>PCE / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>605</td>
<td>2.57</td>
<td>0.76</td>
<td>1.18</td>
</tr>
<tr>
<td>D2</td>
<td>583</td>
<td>6.49</td>
<td>0.68</td>
<td>2.58</td>
</tr>
<tr>
<td>D3</td>
<td>625</td>
<td>6.85</td>
<td>0.70</td>
<td>2.98</td>
</tr>
<tr>
<td>D4</td>
<td>695</td>
<td>9.61</td>
<td>0.70</td>
<td>4.65</td>
</tr>
<tr>
<td>D5</td>
<td>655</td>
<td>7.08</td>
<td>0.67</td>
<td>3.12</td>
</tr>
<tr>
<td>N719</td>
<td>745</td>
<td>15.3</td>
<td>0.64</td>
<td>7.29</td>
</tr>
</tbody>
</table>

Electrochemical impedance spectroscopy (EIS) is a powerful technique of characterizing the important interfacial charge transfer processes in a DSSC. The EIS spectra were measured in the dark to elucidate correlation of $V_{oc}$ with charge transfer...
resistance \( (R_{ct}) \) of the devices. The EIS spectra of DSSCs based on \textbf{D3}, \textbf{D4}, \textbf{D5} and \textbf{N719} under a forward bias of 0.055 V in the dark are shown in Figure 2.12. The middle-frequency semicircle in the EIS spectra represents the charge transfer resistance between the TiO\(_2\) surface and the electrolyte. Efficient suppression of the charge transfer resistance leads to a larger semicircle. The charge transfer resistance is the largest for \textbf{N719} (648 Ω) and the smallest for \textbf{D3} (133 Ω), indicating that the charge recombination rate also decreases in the same order. The results obtained here are roughly consistent with the trend observed for the \( V_{oc} \) and PCE value.

The Nyquist plots of DSSCs with \textbf{D3}, \textbf{D4}, \textbf{D5} and \textbf{N719} under light illumination are depicted in Figure 2.13. All the measurements were carried out with an irradiation of AM 1.5 solar simulator at \( V_{oc} \) scanning the frequencies from 10 mHz to 100 kHz. Three semicircles were observed in the Nyquist plots. The small and large semicircles, located in the high- and middle frequency regions, are assigned to the charge transfer at the Pt/electrolyte and TiO\(_2\)/dye/electrolyte interfaces, respectively.\(^{[29]}\) Another small semicircle, which should have appeared at the low frequency region, is overlapped by the middle frequency large semicircle. The \( R_{ct} \) value on the TiO\(_2\) surface, which is related to the charge recombination rate between injected electron and electron acceptor \( (I_3^-) \) in the electrolyte, is estimated by the large semicircle width. A large \( R_{ct} \) means the small charge recombination rate and vice versa. As found in Figure 6, the
values of $R_{ct}$ of $\text{D3–D5}$ based DSSCs (33 $\Omega$ for $\text{D3}$, 19 $\Omega$ for $\text{D4}$ and 32 $\Omega$ for $\text{D5}$, respectively) are larger than that in the case of $\text{N719}$ (16 $\Omega$). This means that the $\text{D3–D5}$ based DSSCs have less efficient electron collection than that of $\text{N719}$, meanwhile, the $\text{D3}$ based DSSC is the least efficient among $\text{D3–D5}$. The result appears to be consistent with the aforementioned variation trend of $V_{oc}$ values in the cells of $\text{D3–D5}$.

Figure 2.12 Impedance plots of the DSSCs based on photosensitizers $\text{D3}$, $\text{D4}$, $\text{D5}$ and $\text{N719}$ (measured at 55 mV in the dark).
Figure 2.13 Impedance plots of the DSSCs based on photosensitizers D3, D4, D5 and N719 (measured at $V_{oc}$ potentials under AM 1.5G illumination).
2.1.5 Cytotoxicity Test of Dye-sensitizers on Human Cells

All the five tested compounds did not possess any significant variation in the optical absorbance when compared with the vehicle control (0.5% dimethyl sulfoxide) as well as the untreated control (data not shown). As shown in Figure 2.14, we further concluded that all of them did not exert any observable cytotoxicity towards the HaCaT cells of up to a maximum concentration of 100 µg mL\(^{-1}\) for 24 hours of incubation. Doxorubicin at 4 µg mL\(^{-1}\), on the other hand, executed a significant cell death phenomenon which included the detachment from the substratum, cell rounding and cell shrinkage.
Figure 2.14 Human cell line HaCaT normal human skin keratinocytes were incubated

(A) D4, (B) D3, (C) D2, (D) D1, (E) D5, (F) 0.5% dimethyl sulfoxide, (G) untreated
and (H) 4 µg mL⁻¹ of doxorubicin for 24 hours and their effects on cell growth were
determined by sulforhodamine B assay. Cells were then fixed with trichloroacetic acid, washed and stained with sulforhodamine B. HaCaT cells did not show any growth inhibitory phenomenon from (A) to (G). Doxorubicin executed a significant cell death phenomenon which included the detachment from the substratum, cell rounding and cell shrinkage (H).
2.2 Synthesis and Characterization of Fluorenone-containing Organic Photosensitizers for Dye-sensitized Solar Cells

2.2.1 Introduction

In recent years, to overcome one of the topmost problems – energy that human faces, many researchers have already started working on various issues by generating energy from renewable alternatives. Solar energy conversion has become the major alternative to the conventional fossil fuels, considering their drastic depletion over the last few decades and the environmental issues caused by their heavy utilization. DSSCs have attracted considerable scientific and industrial interest as a promising candidate for a new renewable energy source in the past decades.\textsuperscript{[12]} Especially, the extensively used charge-transfer Ru(II)-polypyridyl photosensitizers in DSSCs have achieved solar-to-electricity conversion efficiency higher than 10% under AM 1.5 simulator, which is a value close to an amorphous silicon-based photovoltaic cell.\textsuperscript{[6]} However, the rarity of the Ru(II) metal, lack of good absorption in the red region of the visible spectrum and tricky purification steps all pose certain limitations in the practical application of these complexes for DSSCs.\textsuperscript{[7]} Despite the superiority of the Ru(II)-based dyes, there is a rapid progress in the development of the metal-free organic dyes.\textsuperscript{[8]} To date, the metal-free organic dyes are on a par with the benchmark Ru(II)-polypyridyl complexes since they are a low-cost alternative of our renewable
energy sources. Moreover, they were shown to have great potential to get high PCE and show good ease of device fabrication.\textsuperscript{[8]} Also, their high molar extinction coefficients, ease of purification and flexible structural modifications render them to be attractive light-harvesting materials.\textsuperscript{[32]}

Fluorenone and their derivatives are generally regarded as one of the most promising candidates for photonic and optoelectronic devices due to their high thermal stability, ease of preparation and good electron-transporting property.\textsuperscript{[33]} They are also widely used in the preparation and investigation of charge-transfer complexes,\textsuperscript{[34]} activation of photoconductivity of organic semiconductors\textsuperscript{[35]} and as electron transport materials. When these 9-oxo-substituted fluorenes (i.e. fluorenones) have been extensively studied,\textsuperscript{[36]} many research groups tempted to prepare copolymers of fluorenone with the goal of tuning the resulting electronic and optical properties.\textsuperscript{[37]} Therefore, fluorenone-based materials are conceived to be attractive photovoltaic materials, especially because their weakly electron-accepting property may result in a broader absorption profile and hence a much better match between the solar radiation and absorption, leading in turn to a much better device efficiency as compared to the fluorene-derived counterparts. However, organic dyes containing the fluorenone moiety are still not very well studied to date.\textsuperscript{[38]} On the other hand, the excellent stability, electron-donating ability and inhibition of aggregation due to a
non-planar molecular configuration of triphenylamine-based sensitizers have made them a prospective chromophore for DSSC applications.\textsuperscript{[39]} As a continuation of our efforts to develop functional materials suitable for DSSCs,\textsuperscript{[40–42]} four new fluorenone-functionalized organic photosensitizers F1–F4 of the type D-A-\pi-A (D = donor, A = acceptor) were designed and synthesized here with triarylamine or fluorene unit as the electron donor, an additional fluorenone unit as a mild electron-withdrawing linkage and a cyanoacrylic acid moiety as the electron-withdrawing and anchoring group (Chart 2.2).

\textbf{Chart 2.2} The chemical structures of new organic dyes F1–F4 in this study.
2.2.2 Synthesis

The synthetic routes of the target dyes are outlined in Schemes 2.4–2.6. The key materials 2-bromofluoren-9-one and 2,7-dibromofluoren-9-one were firstly obtained by oxidation of 2-bromofluorene and 2,7-dibromofluorene with potassium dichromate in acetic acid, respectively.[43] These two compounds then reacted with the corresponding arylboronic acid derivatives by the Suzuki coupling reaction. Then, monobromination of these compounds by N-bromosuccinimide (NBS) gave $F1-\text{Br}$ and $F3-\text{Br}$ to $F4-\text{Br}$. The intermediates $F1-\text{CHO}$ to $F4-\text{CHO}$ were subsequently made by the Suzuki coupling reaction of $F1-\text{Br}$ to $F4-\text{Br}$ with 5-formylthiophenyl-2-boronic acid. The final step involved a Knoevenagel condensation with cyanoacetic acid in the presence of piperidine to convert the carbaldehydes to cyanoacrylic acids.[44] Purification of the reaction mixtures by silica gel chromatography furnished $F1$–$F4$ as air-stable powders with high purity. The structures of all the dyes were verified by NMR spectroscopy and MALDI-TOF mass spectrometry. The dyes are orange or red in color and are readily soluble in common organic solvents such as THF, CH$_2$Cl$_2$, CHCl$_3$ and DMSO.
Scheme 2.4 Synthesis of F1: i) K$_2$Cr$_2$O$_7$, acetic acid; ii) Pd(PPh$_3$)$_4$, Na$_2$CO$_3$ (2 M, aq), THF; iii) NBS, CHCl$_3$/acetic acid; iv) Pd(PPh$_3$)$_4$, Na$_2$CO$_3$ (2 M, aq), toluene/EtOH; v) Cyanoacetic acid, piperidine, dry CHCl$_3$.

Scheme 2.5 Synthesis of F2: i) K$_2$Cr$_2$O$_7$, acetic acid; ii) Pd(PPh$_3$)$_4$, Na$_2$CO$_3$ (2 M, aq), THF; iii) Pd(PPh$_3$)$_4$, Na$_2$CO$_3$ (2 M, aq), toluene/EtOH; iv) Cyanoacetic acid, piperidine, dry CHCl$_3$. 
Scheme 2.6 Synthesis of F3 and F4: i) Pd(PPh$_3$)$_4$, Na$_2$CO$_3$ (2 M, aq), THF; ii) Pd(PPh$_3$)$_4$, Na$_2$CO$_3$ (2 M, aq), THF; iii) NBS, CHCl$_3$/acetic acid; iv) Pd(PPh$_3$)$_4$, Na$_2$CO$_3$ (2 M, aq), toluene/EtOH; v) Cyanoacetic acid, piperidine, dry CHCl$_3$. 

F3-Br: Ar = \[
\begin{array}{c}
\text{C}_4\text{H}_9 \\
\text{C}_4\text{H}_9
\end{array}
\]
F3-CHO: Ar = \[
\begin{array}{c}
\text{C}_4\text{H}_9 \\
\text{C}_4\text{H}_9
\end{array}
\]
F4-Br: Ar = \[
\begin{array}{c}
\text{C}_4\text{H}_9 \\
\text{C}_4\text{H}_9
\end{array}
\]
F4-CHO: Ar = \[
\begin{array}{c}
\text{C}_4\text{H}_9 \\
\text{C}_4\text{H}_9
\end{array}
\]
2.2.3 Results and Discussion

2.2.3.1 Photophysical Properties

The UV-Vis absorption spectra of the photosensitizers F1–F4 in THF at room temperature are displayed in Figure 2.15 and the data are collected in Table 2.5. The more intense absorption band located in the range of 365 to 398 nm corresponds to the π-π* transition of the conjugated aromatic rings. The other weaker low-energy bands appeared as a shoulder between 450 and 550 nm which are attributed to the intramolecular charge transfer (ICT). The lowest energy transition in fluorenone possesses n-π* or π-π* character with a contribution from ICT which gives rise to a shoulder band in the absorption spectrum. The spectra of all the dyes are quite similar, but those with two thiophene groups F1, F3 and F4 are red-shifted in comparison to that of F2, which is mainly due to the effective conjugation caused by the introduction of one more thiophene unit. In addition, F3 and F4 are more red-shifted than that of F1, which could be ascribed to the presence of one more electron-rich moieties to produce more extended π-conjugation system. The molar extinction coefficients of the π-π* bands for F1–F4 were also investigated in THF and increase in the order of F4 > F3 > F2 > F1, which indicates that F4 should possess the best light-harvesting ability. The high molar extinction coefficients of the organic dyes allow a correspondingly thinner nanocrystalline film so as to avoid the decrease of the
film mechanical strength. This also benefits the electrolyte diffusion in the film and reduces the recombination possibility of the light-induced charges during transportation.\cite{19}

![Normalized absorption spectra of F1–F4 measured in THF.](image)

**Figure 2.15** Normalized absorption spectra of F1–F4 measured in THF.

As shown in Figure 2.16, the absorption bands of photosensitizers F1–F4 attached to the transparent TiO$_2$ electrode (4 mm thickness) are broadened significantly as compared to those in THF solution, indicating that aggregation of the photosensitizers occurs commonly on the TiO$_2$ surface.\cite{20,21} In addition, the entire dyes exhibit a slight red shift of 29 nm (F1), 13 nm (F2), 23 nm (F3), and 11 nm (F4) in wavelength as compared to that measured in THF solution. The red shifts of the
absorption spectra on TiO$_2$ of F1–F4 are probably due to the $J$-aggregation of the dyes on the TiO$_2$ surface in the presence of the carboxyl moiety in the molecules.$^{[49]}$ This may also be due to the increased delocalization of the $\pi^*$ orbital of the conjugated framework caused by the interaction between the carboxylate group and the Ti$^{4+}$ ions that directly decreases the energy of the $\pi^*$ level.$^{[50]}$

All of the dyes display photoluminescence at room temperature (Figure 2.17) when they are excited at their respective absorption bands and the fluorescence peak maximum ranges from 547 to 620 nm. Similar to the absorption spectra, the presence of electron-donating groups and extension of the conjugation by thiophene group would shift the emission maximum to the red. The most electron-donating triarylamine unit gave the most red-shifted peak at 620 nm for F4.

![Normalized Absorption Spectra](image)

**Figure 2.16** Normalized absorption spectra of F1–F4 measured on TiO$_2$ film.
Figure 2.17 Normalized PL spectra of F1–F4 in THF at 298 K.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$\lambda_{\text{max}}$ in THF (nm)</th>
<th>Molar extinction coefficients (M$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{\text{max}}$ on TiO$_2$ film (nm)</th>
<th>$\lambda_{\text{em}}$ in THF (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>376</td>
<td>3980</td>
<td>405</td>
<td>574</td>
</tr>
<tr>
<td>F2</td>
<td>301, 366</td>
<td>11260, 10220</td>
<td>379</td>
<td>547</td>
</tr>
<tr>
<td>F3</td>
<td>297, 365, 398</td>
<td>23170, 18010, 20260</td>
<td>421</td>
<td>572</td>
</tr>
<tr>
<td>F4</td>
<td>304, 393</td>
<td>19090, 25620</td>
<td>404</td>
<td>620</td>
</tr>
</tbody>
</table>
2.2.3.2 Electrochemical Properties

To investigate the electron transfer from the excited dye molecule to the conductive band ($E_{cb}$) of TiO$_2$ and understand the molecular orbital energy levels, cyclic voltammetry (CV) was performed for the dyes in thin films on glassy carbon electrode measured in 0.1 M tetrabutylammonium hexafluorophosphate solution in acetonitrile at a scan rate of 50 mV s$^{-1}$. The reference electrode was Ag/AgCl calibrated with ferrocene-ferrocenium (Fc$^+/Fc$, 0.07 V) as an internal reference. The results are summarized in Table 2.6. All of the dyes are redox stable and show irreversible oxidation and reduction waves.$^{[24]}$ The HOMO and LUMO energy levels of the dyes were measured from the first onset oxidation ($E_{ox}$) and reduction potentials ($E_{red}$).

As shown in Figure 2.18 and Table 2.6, the HOMO levels of F1–F4 are calculated to be –5.40 to –5.21 eV. These values are lower than that of the I$^-$/I$_3^-$ electrolyte (–4.95 eV), thereby ensuring an effective sensitizer regeneration process to give an efficient charge separation.$^{[25]}$ The LUMO levels of these sensitizers are –3.48 to –3.55 eV. These values are much higher than the bottom level of the conduction band of TiO$_2$ (–4.4 eV), and hence indicate that the dyes provide sufficient driving forces for electron injection and the charge injection from the excited photosensitizer molecule to the TiO$_2$ conduction band is viable.$^{[18]}$ In addition, it is clear that the
HOMO level of F4 is the highest among the dyes, which is in agreement with the order of the electron-donating ability of the triarylamino donor.\textsuperscript{[28]}

\textbf{Figure 2.18} Cyclic voltammograms of the thin films of F1–F4 on glassy carbon electrode measured in 0.1 M Bu\textsubscript{4}NPF\textsubscript{6} acetonitrile solutions at a scan rate of 50 mV s\textsuperscript{-1}.
Table 2.6 Electrochemical properties of F1–F4.

<table>
<thead>
<tr>
<th>Dye</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>F1</td>
<td>0.65</td>
<td>−5.38</td>
<td>−1.18</td>
<td>−3.55</td>
<td>1.83</td>
</tr>
<tr>
<td>F2</td>
<td>0.67</td>
<td>−5.40</td>
<td>−1.20</td>
<td>−3.53</td>
<td>1.87</td>
</tr>
<tr>
<td>F3</td>
<td>0.64</td>
<td>−5.37</td>
<td>−1.21</td>
<td>−3.52</td>
<td>1.85</td>
</tr>
<tr>
<td>F4</td>
<td>0.48</td>
<td>−5.21</td>
<td>−1.25</td>
<td>−3.48</td>
<td>1.73</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)

2.2.3.3 Computational Studies

DFT was used to optimize the ground state geometries as well as gain better insights into the electronic and spectroscopic properties of F1–F4 (Figure 2.19). For F1, the electron density in HOMO is equally distributed all along the molecule, which is also observable for F2 and F3. Porzio et al. also reported a similar fluorenone-based molecule TFT that can be compared to F1 by removing the cyanoacrylic acid moiety.<sup>[51]</sup> Both F1 and TFT have almost the same HOMO characters. For F4, the electron density is mainly delocalized on the triphenylamine moiety in the HOMO which indicates that delocalization of the electrons on the triphenylamine moiety may facilitate redox reaction with liquid electrolyte, making the dye suitable for highly efficient solar cells. The LUMO electron densities of F1–F4 are all located predominantly on the cyanoacetic acid units and extended to the fluorenone moieties.
These kinds of electron distributions facilitate electron injection from the photoexcited dye into the conduction band of the TiO$_2$ oxide. As a consequence, it was revealed that the HOMO→LUMO excitation transferring electrons from the electron-donating group through the π-framework to the anchoring ligand via the acceptor-fluorenone moiety can facilitate electron injection from the excited state of the photosensitizer to TiO$_2$.

<table>
<thead>
<tr>
<th>HOMO</th>
<th>LUMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) F1</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>HOMO</th>
<th>LUMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>b) F2</td>
<td></td>
</tr>
</tbody>
</table>
2.2.4 Applications in DSSCs

2.2.4.1 Preparation of DSSC Devices

A double-layer TiO$_2$ photoelectrode (thickness 15 µm; area 0.25 cm$^2$) was used as a working electrode. A 10 µm main transparent layer with titania particles (~20 nm) and a 5 µm scattering layer with titania particles (~400 nm) were screen-printed on the fluorine-doped tin oxide conducting glass substrate. A solution of F$_1$–F$_4$ ($3 \times 10^{-4}$ M) in acetonitrile/tert-butyl alcohol (1/1, v/v) was used to coat the TiO$_2$ film with the
dye. Deoxycholic acid (20 mM) was added to the dye solution as a co-adsorbent to prevent aggregation of the dye molecules. The electrodes were immersed in the dye solutions and then kept at 25 °C for 24 h to adsorb the dye onto the TiO$_2$ surface. The dye-coated TiO$_2$ film was used as the working electrode, and platinum-coated conducting glass was used as the counter-electrode. The two electrodes were separated by a Surlyn spacer (50 µm thick) and sealed up by heating the polymer frame. The electrolyte was composed of 0.6 M dimethylpropylimidazolium iodide, 0.05 M I$_2$, 0.1 M LiI and 0.5 M tert-butylpyridine in acetonitrile. The current-voltage characteristics were measured using a black metal mask and edge with an aperture area of 0.25 cm$^2$ under standard AM 1.5 sunlight (100 mW cm$^{-2}$, WXS−155S−10: Wacom Denso Co. Japan). Monochromatic incident photon-to-current conversion efficiency spectra were measured with monochromatic incident light of $1 \times 10^{16}$ photons cm$^{-2}$ under 100 mW cm$^{-2}$ in direct current mode (CEP-2000BX, Bunko-Keiki). The electrochemical impedance spectra (EIS) were measured with an impedance analyzer (Solartron Analytical, 1255B) connected with a potentiostat (Solartron Analytical, 1287) under illumination using a solar simulator (WXS-155S-10: Wacom Denso Co. Japan). The frequency range was 0.1 Hz–100 kHz at 298 K. The magnitude of the alternative signal was 10 mV. The applied voltage bias was $-0.55$ V. The electrical impedance spectra were characterized using Z-View
2.2.4.2 Photovoltaic Performance of DSSCs

DSSCs photosensitized by F1–F4 were measured under standard AM 1.5 irradiation (100 mW cm\(^{-2}\)) using a black metal mask with an aperture area of 0.25 cm\(^2\) and an electrolyte composed of 0.6 M dimethylpropylimidazolium iodide, 0.05 M I\(_2\) and 0.1 M LiI in acetonitrile.

Fig. 2.20 shows the photocurrent action spectra of incident photon-to-current conversion efficiency (IPCE) for DSSCs using F1–F4. The losses of light reflection and absorption by the conducting glass were not corrected for. All of the dyes can efficiently convert the visible light to photocurrent in the region from 300 nm to 600 nm. Generally, the IPCE values of DSSCs depend on a number of factors, including the molar absorptivity of the molecule, the amount of materials being absorbed by the TiO\(_2\), the efficiency of charge injection, transportation and collection.\(^{[52]}\) Charge transfer kinetics calculations are needed in each step in order to establish the relationship between the structure of dye and IPCE. It is known from the equation \(\text{IPCE} = (1240 \times J_{sc} 100/(\lambda \times P_{in}) \text{ (in %)}\) that the IPCE value is closely related to \(J_{sc}\) at a specific wavelength and fixed input power \(P_{in}\), and the IPCE values of our dyes are in line with the order of \(J_{sc}\) values observed (F1 < F2 < F3 < F4). Their IPCE
reaches a maximum of 80% in the range of 450 to 600 nm. F4 exhibits a broader photocurrent action spectrum than that of F3, which is attributed to the lower bandgap of F4 in the presence of the electron-donating triphenylamine groups. Also, as the IPCE value is a function of the wavelength, it is difficult to make an accurate comparison here for the performance among the dyes, and we can only compare them at a fixed wavelength. Hence, the extinction coefficient becomes a major factor in governing the IPCE at a particular wavelength, which is in agreement with the trend for the molar extinction coefficient of our dyes (F1 < F2 < F3 < F4). Moreover, for the issue on dye regeneration, it depends mainly on the composition of the electrolyte. As all of the DSSCs are working in the I-/I₃⁻ redox couple as the active component in the electrolyte, the dye regeneration rate (dye regeneration charge kinetics) should be similar for each case. This factor would not contribute significantly to the variation of the IPCE of the dyes. More detailed studies are currently underway to establish the correlation between the dye structure and IPCE.
Fig. 2.20 Photocurrent action spectra of the TiO$_2$ electrode sensitized with F1–F4.

Fig. 2.21 shows the photocurrent-voltage (J–V) characteristics of DSSCs fabricated with these fluorenone-based photosensitizing dyes (F1–F4) under simulated sunlight illumination. Compared with the control molecule F1, the photovoltaic performance can be significantly improved by introducing an electron-donating group such as triarylamine and fluorene in the molecule for F2–F4. A high molar extinction coefficient of the dye molecule as well as a broad absorption spectrum can help enhance the light-harvesting ability, thus yielding a higher $J_{sc}$. F4 has the highest light-harvesting efficiency and consequently an improved $J_{sc}$ (11.71 mA cm$^{-2}$) due to its largest molar extinction coefficient, broader absorption spectrum
and highest IPCE value among all the dyes. The light-harvesting efficiency of F3 is slightly lower than that of F4 and this may be attributed to the smaller molar extinction coefficient.

**Figure 2.21** J–V curves of the DSSC devices under AM 1.5G simulated sunlight illumination.

The device photovoltaic statistics $J_{sc}$, $V_{oc}$, $FF$ and PCE are summarized in Table 2.7. For the overall light to electricity conversion efficiency of F1–F4, dye F4 exhibited the best PCE of 4.71%, with $V_{oc}$ of 565 mV and a $FF$ of 0.71. The PCE of F4 is higher than the reported fluorenone-based organic dyes. Under the same device
operating conditions, F3 shows a slightly poorer device performance with fluorene in place of triarylamine as the donor with PCE of 4.06%, $J_{sc}$ 10.90 mA cm$^{-2}$, $V_{oc}$ of 549 mV and a $FF$ of 0.68. The incorporation of additional thiophene ring as the conjugated bridge between F2 and F3 shows distinct characteristics which broaden the light-harvesting capacity and hence higher efficiency was obtained for F3. In addition, the $V_{oc}$ value of F3 is higher than that of F2. This may be due to the increasing length of the π-bridge of F3. It would be more difficult for the injected electron in the TiO$_2$ conduction band to recombine with the redox electrolyte due to the formation of a thicker dye block layer. Additionally, electron recombination with the photooxidized adsorbed sensitizers could also be reduced with increasing the length of the π-bridge because the more extended charge delocalized HOMO is more far away from the TiO$_2$ substrate.$^{[53]}$

The electrochemical impedance spectroscopy (EIS) technique was applied to study the electron recombination process in DSSCs based on these four dyes under open circuit and illuminated conditions. As shown in the Nyquist plots in Fig. 2.22 under light illumination, the Nyquist plots exhibited three semicircles, the largest semicircle (intermediate frequencies, 1–100 Hz) represents the electron transfer resistance ($R_{ct}$) at the TiO$_2$/dye/electrolyte interface. The radius of the largest semicircle increased in the order F1 < F2 < F3 < F4, indicating that the electron
recombination resistance increases from F1 to F4. This result is also in good agreement with the $V_{oc}$ results above and suggests that the electron recombination rate between the TiO$_2$ film and the electrolyte has strong relationships with their structures in this series of fluorenone-based dyes.

**Table 2.7** Photovoltaic performance of DSSCs sensitized with F1–F4 under the AM 1.5 sunlight illumination.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$V_{oc}$ / mV</th>
<th>$J_{sc}$ / mA cm$^{-2}$</th>
<th>FF</th>
<th>PCE / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>453</td>
<td>5.62</td>
<td>0.70</td>
<td>1.79</td>
</tr>
<tr>
<td>F2</td>
<td>512</td>
<td>6.88</td>
<td>0.72</td>
<td>2.54</td>
</tr>
<tr>
<td>F3</td>
<td>549</td>
<td>10.90</td>
<td>0.68</td>
<td>4.06</td>
</tr>
<tr>
<td>F4</td>
<td>565</td>
<td>11.71</td>
<td>0.71</td>
<td>4.71</td>
</tr>
</tbody>
</table>
Figure 2.22 The EIS Nyquist plots for DSSCs sensitized with F1–F4 under light illumination.

2.3 Concluding Remarks

In section 2.1, five metal-free organic dyes (D1–D5) comprising triarylamine, fluorene, carbazole or thiophene moiety as the electron donor, a cyanoacrylic acid as the anchoring group, and a less common bithiazole ring as the bridge were synthesized and used for the fabrication of DSSCs. The performance of the photovoltaic devices depend significantly on the nature and strength of the electron-donating end group along the conjugated main. Among all of the dyes examined, DSSCs based on D4 exhibited the best overall light to electricity
conversion efficiency of 4.65% under AM 1.5 irradiation (100 mW cm\(^{-2}\)). Although the PCE of those DSSCs are lower than that of the reported DSSCs\(^{[13]}\), the \( FF \) are higher than them. The optimization of the device is in progress to further improve their energy conversion efficiency.

In section 2.2, four new metal-free organic dyes (F1–F4) containing triarylamine or fluorene moiety as the electron donor, cyanoacrylic acid as the anchoring group, and fluorenone group as the linkage were synthesized. All of the dyes were fully characterized by spectroscopic and photophysical measurements. Their photovoltaic behaviors have also been fully investigated. The power conversion efficiency of the DSSCs depend significantly on the nature and strength of the electron-donating end group along the conjugated main as well as the length of the thienyl rings. Among all of the dyes examined, DSSCs based on F4 exhibited the best overall light to electricity conversion efficiency of 4.71\% \((V_{oc} = 565 \text{ mV}, J_{sc} = 11.71 \text{ mA cm}^{-2}, FF = 0.71)\) under AM 1.5 irradiation (100 mW cm\(^{-2}\)). Although the PCE of F4 is lower than that of the reported DSSCs\(^{[39]}\), it is still promising in the development of high-performance DSSCs because it is both stable and inexpensive.
References:


Chapter 3 New Donor-Donor-π-Acceptor Organic Dyes for Dye-sensitized Solar Cells

3.1 Synthesis and Characterization of Functionalized Dibenzothiophene-based Dye-sensitized Solar Cells

3.1.1 Introduction

As renewable energy resources become an important issue, the use of solar energy for electricity generation has been an attractive research subject.[1] DSSCs based on highly porous nanocrystalline films of TiO$_2$ have attracted considerable scientific and industrial attention as a promising candidate for a new renewable energy source during the past decades.[2] To date, two kinds of photosensitizers, ruthenium dyes and metal-free organic dyes,[3] were developed for DSSCs. The inexpensive and ease of synthesis features together with the high molar extinction coefficients are advantageous of metal free organic dyes over metallic organic dyes which are rather expensive and hard to purify. Recently, novel organic dyes based on porphyrin,[4] perylene,[5] cyanine,[6] xanthene,[7] merocyanine,[8] coumarin,[9] hemicyaine,[10] indoline,[11] diketopyrrolopyrrole[12] and ethylenedioxythiophene[13] have been investigated as photosensitizers for DSSCs and great progress has been
made in this field.

The development of DSSCs is concentrated on the structure of donor-π-bridge-acceptor (D-π-A). Electron acceptors such as cyanoacrylic acid which can attach to the TiO$_2$ have been widely studied. The nature of photosensitizers, such as redox potential, structure and photophysical properties, etc., plays an important role in determining the overall cell efficiencies.$^{[14-20]}$ By carefully choosing the appropriate combination of donor, π-bridge and acceptor moieties, the light harvesting capabilities and electron injection properties of the dyes can be altered. Dibenzothiophene unit with the coplanar fused benzene rings has excellent hole-injection/transportation characteristics, and the dibenzothiophene derivatives are potentially high mobility semiconductor materials.$^{[21]}$ Macromolecules incorporated with benzothiophene units have higher electronic conductivity as compared to the other π-conjugated aromatic polymers.$^{[22]}$ Moreover, the sulfur atoms in dibenzothiophene can enhance intermolecular overlap, which facilitates charge migration. In addition, dibenzothiophene is a good conjugated unit for organic semiconductors, which is cheap and will improve the stability and mobility of materials.$^{[23]}$

Triphenylamine-based dyes have been widely used in organic photovoltaic functional materials and have become the focus of intensive research in the field of solar cells.$^{[24]}$ In addition, fluorene-based dyes exhibit very high molar extinction
coefficients in the electronic absorption spectra. Also, the introduction of a thiophene moiety was expected to allow a red-shift of the spectrum, and broaden the spectral region of absorption. Until now, there is no report on using dibenzothiophene as donor unit in synthesizing photosensitizer for DSSC application. Six new dibenzothiophene based organic dye-sensitized solar cells DT1–DT6 (Chart 3.1) have been designed and synthesized; their photovoltaic properties were also examined.

![Chart 3.1 The chemical structures of organic dyes DT1–DT6 in this study.](image)

**3.1.2 Synthesis**

The synthetic routes for all new dyes containing dibenzothiophene functionalities are outlined in Schemes 3.1–3.3. The key materials 2-bromodibenzothiophene and 2,8-dibromodibenzothiophene were obtained firstly by
bromination with bromine. Then, the brominated precursors underwent Suzuki coupling reaction with different functionalized arylboronic acid to give the corresponding products. Subsequently, these compounds were monobrominated by N-bromosuccinimide (NBS) to give DT1-Br to DT6-Br. Two different methods were applied to afford the aldehydes. For aldehydes DT1-CHO and DT2-CHO, they were obtained by putting n-BuLi and DMF into the brominated precursors DT1-Br and DT2-Br, respectively. For the other aldehydes DT3-CHO to DT6-CHO, they were obtained by Suzuki coupling reaction between DT2-Br, DT4-Br to DT6-Br with 5-formylthiophen-2-yl-2-boronic acid, respectively. Comparing the methods of synthesis of the aldehydes by using n-BuLi followed by DMF and Suzuki coupling reaction with 5-formylthiophen-2-yl-2-boronic acid, the overall yield is higher with easier purification procedure for the formaer. Finally, Knoevenagel condensation between the aldehyde precursors and cyanoacetic acid in the presence of piperidine gave the desired dyes DT1–DT6 after conventional purification by column chromatography. All the structures of the compounds and dyes were thoroughly verified by NMR spectroscopy and MALDI-TOF mass spectrometry and the spectral data are consistent with the formulated structures. The dyes are orange or red in color and readily soluble in common organic solvents such as THF, CH2Cl2, CHCl3 and DMSO.
Scheme 3.1 Synthesis of DT1–DT2: i) Br₂, CHCl₃; ii) Pd(PPh₃)₄, Na₂CO₃ (2 M, aq), THF; iii) NBS, CHCl₃; iv) n-BuLi, DMF; v) cyanoacetic acid, piperidine, dry CHCl₃.

Scheme 3.2 Synthesis of DT3: i) Pd(PPh₃)₄, Na₂CO₃ (2 M, aq), THF; ii) cyanoacetic acid, piperidine, dry CHCl₃.
Scheme 3.3 Synthesis of DT4–DT6: i) Br₂, CHCl₃; ii) Pd(PPh₃)₄, Na₂CO₃ (2 M, aq), THF; iii) Pd(PPh₃)₄, Na₂CO₃ (2 M, aq), THF; iv) NBS, CHCl₃; v) Pd(PPh₃)₄, Na₂CO₃ (2 M, aq), THF; vi) cyanoacetic acid, piperidine, dry CHCl₃.
3.1.3 Results and Discussion

3.1.3.1 Spectroscopic Characterization

All the newly synthesized dyes were characterized by common spectroscopic techniques such as NMR spectroscopy. All the dyes are air-stable and soluble in common organic solvents. All the compounds showed characteristic $^1$H NMR spectra. All the NMR data of intermediates and dyes are summarized in the experimental part of Chapter 8.

For dye photosensitizers DT1 to DT6, all the proton signals of aromatic rings are in the downfield (above 6.80 ppm) region, carbaldehyde group in the more downfield position (above 10 ppm) and those of the butyl groups in the upfield region (below 2.30 ppm). The $^1$H NMR spectra of DT2 and DT6 are shown in Figures 3.1 and 3.2. Due to the poor solubility of some dyes and long acquisition time for a $^{13}$C NMR spectrum, only data for DT1 was obtained. In the downfield region, the aromatic carbons and pyridyl ring are shown above 100 ppm. In the upfield region, the signals of butyl groups are shown below 55 ppm. (Figures 3.3)
Figure 3.1 $^1$H NMR spectrum of dye DT2 in $d_6$-DMSO.

Figure 3.2 $^1$H NMR spectrum of dye DT6 in $d_6$-DMSO.
3.1.3.2 Photophysical Properties

The electronic absorption spectra of photosensitizers DT1–DT6 were investigated in THF solution at room temperature. Figure 3.4 shows the absorption spectra of DT1–DT6 and their photophysical data are summarized in Table 3.1. Dyes DT1–DT6 showed a strong absorption in the ultraviolet and visible regions with absorption maxima between 389 nm to 452 nm. Generally, DT1–DT3 demonstrated a single absorption peak, but when an extra donor, fluorene, triarylamine or dibenzothiophene was added in DT4–DT6, two distinct absorption bands were observed. The shorter wavelength absorption bands at ca. 320 nm are assigned as π-π*
transition in DT4–DT6. The bands at the lower energy may originate from an electronic excitation resulting in charge transfer from different donor to the cyanoacrylic acid acceptor in all these dyes. In DT1–DT3, DT2 exhibited an obvious red shift when compared to DT1 because of the enhanced electronic communication after an extra thiophene ring was added which can lower the energy of the charge transfer in the molecules. Although the absorption maximum of DT3 was observed to be blue-shifted as compared to DT2, its spectrum was found to be much broader than that of DT2, this may be attributed to the increment of intramolecular charge transfer (ICT) characters within the molecule. The edge of absorption band in DT3 was also extended, implying that narrower bandgap was detected in DT3 as compared to DT2. The same phenomenon from DT1 to DT2 supports this assignment. The elongation of π-conjugation by the addition of fluorene or dibenzothiophene donor in DT4 and DT6 did not show significant red-shift in their absorption spectra as compared to DT2. It is probably due to the interrupted conjugation of 2,8-dibromodibenzothiophene unit which is detrimental for the transmission of the conjugation effects. Among all the dyes, the most red-shifted peak is shown at around 452 nm for the dye DT5 which has a triarylamine as an electron-donating group in the structure. Our results, we indicated that addition of thiophene rings beyond three in the system would not lead to much bathochromic effect in their absorption, but the ICT transition can be greatly enhanced
by the introduction of triarylamine donor group which results in a broader absorption band.

The molar extinction coefficients of dyes DT1–DT6 were also investigated. Their molar extinction coefficients increase in the order of DT4 > DT5 > DT6 > DT3 > DT2 > DT1. The higher molar extinction coefficients of the organic dyes allow a correspondingly thinner nanocrystalline film so as to avoid the decrease of the film mechanical strength. This also benefits the electrolyte diffusion in the film and reduces the recombination possibility of the light-induced charges during transportation.[27] The absorptivites were increased along the trend in DT1–DT3 of 5960, 10630 and 11890 M\(^{-1}\) cm\(^{-1}\), respectively, owing to the increase in their absorption ability imparted by the thiophene ring. The highest molar extinction coefficient was measured for DT4 which may potentially possess the best light-harvesting ability.

As illustrated in Figure 3.5, all the photosensitizers are emissive in their solution state. Similar to their electronic absorption spectra, DT2 to DT6 show red shifts in the emission wavelength relative to DT1. The most electron-donating triarylamine unit in DT5 gives the most red-shifted emission peak at 542 nm.
**Figure 3.4** Normalized absorption spectra of dyes DT1–DT6 measured in THF at 298 K.

**Table 3.1** Photophysical data of DT1–DT6 in THF at 298 K.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$\lambda_{\text{abs}}$ in THF (nm)</th>
<th>Molar extinction coefficient (M$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{\text{em}}$ in THF (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DT1</td>
<td>389</td>
<td>5960</td>
<td>474</td>
</tr>
<tr>
<td>DT2</td>
<td>426</td>
<td>10630</td>
<td>489</td>
</tr>
<tr>
<td>DT3</td>
<td>422</td>
<td>11890</td>
<td>489</td>
</tr>
<tr>
<td>DT4</td>
<td>318, 421</td>
<td>45330, 33840</td>
<td>505</td>
</tr>
<tr>
<td>DT5</td>
<td>319, 452</td>
<td>16460, 23340</td>
<td>434, 542</td>
</tr>
<tr>
<td>DT6</td>
<td>294, 422</td>
<td>6220, 14690</td>
<td>462, 487</td>
</tr>
</tbody>
</table>
Figure 3.5 Normalized photoluminescence spectra of dyes DT1–DT6 in THF at 298 K.

3.1.3.3 Electrochemical Properties

To evaluate the thermodynamic basis of these electron transfer processes, cyclic voltammetric technique has been used to assess the energy levels of the photosensitizers. Cyclic voltammograms obtained by this technique are shown in Figure 3.6 and the data are summarized in Table 3.2. The cyclic voltammetry was performed in thin films of the dyes on glassy carbon electrode measured in 0.1 M tetrabutylammonium hexafluorophosphate solution in acetonitrile at a scan rate of 50 mV s⁻¹. Under these conditions, the $E_{1/2}$ of ferrocene was 0.07 V vs Ag/AgCl. All of
the dyes are redox stable and showed quasi-reversible oxidation and reduction waves.\textsuperscript{[28]} It is clear that the HOMO level of DT5 is the highest among the dyes, which is in agreement with the order of the electron-donating ability of the triarylamine donor in the series.

For efficient electron injection, the LUMO of the dye should be above the conduction band edge of TiO\textsubscript{2}, and for efficient dye regeneration the HOMO of the dye should lie below the energy level of redox (iodine/iodide) system.\textsuperscript{[29]} The LUMO levels of the photosensitizers DT1–DT6 are in the range of −3.35 to −3.57 eV. These values are much higher than the bottom of the conduction band of TiO\textsubscript{2} (−4.4 eV), indicating electron can be energetically injected into the TiO\textsubscript{2} conduction band from the excited dyes.\textsuperscript{[30]} The HOMO levels of DT1–DT6 were found to be −5.39, −5.37, −5.28, −5.34, −5.25 and −5.37 eV, respectively. These values are lower than that of the iodide/tri-iodide pair (−4.9 eV), thereby indicating the dyes have enough driving force for electron injection from their excited states.\textsuperscript{[31]}
Figure 3.6 Cyclic voltammograms of the DT1–DT6 thin films on glassy carbon electrode measured in 0.1 mol L$^{-1}$ Bu$_4$NPF$_6$ acetonitrile solutions at a scan rate of 50 mV s$^{-1}$. 
Table 3.2 Electrochemical properties of photosensitizers DT1–DT6.

<table>
<thead>
<tr>
<th>Dye</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>DT1</td>
<td>0.56</td>
<td>−5.35</td>
<td>−1.20</td>
<td>−3.35</td>
<td>2.04</td>
</tr>
<tr>
<td>DT2</td>
<td>0.64</td>
<td>−5.37</td>
<td>−1.18</td>
<td>−3.55</td>
<td>1.82</td>
</tr>
<tr>
<td>DT3</td>
<td>0.55</td>
<td>−5.28</td>
<td>−1.24</td>
<td>−3.49</td>
<td>1.79</td>
</tr>
<tr>
<td>DT4</td>
<td>0.61</td>
<td>−5.34</td>
<td>−1.20</td>
<td>−3.53</td>
<td>1.81</td>
</tr>
<tr>
<td>DT5</td>
<td>0.52</td>
<td>−5.25</td>
<td>−1.26</td>
<td>−3.47</td>
<td>1.78</td>
</tr>
<tr>
<td>DT6</td>
<td>0.64</td>
<td>−5.37</td>
<td>−1.16</td>
<td>−3.57</td>
<td>1.80</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)

3.1.3.4 Computational Studies

Molecular geometries were optimized at the Becke3LYP (B3LYP) level of DFT. Time-dependent Density functional theory (TDDFT) was performed based on the optimized structures to obtain the excitation energies. The effective core potentials (ECPs) of Hay and Wadt with the double-$\zeta$ valence basis sets (LanL2DZ) were used to describe S atoms. The standard 6-31G basis set was used for all other atoms. Polarization functions were added for S($\zeta_d = 0.503$). All the calculations were carried out using the Gaussian 03 program.

The calculation results show that the HOMO is generally evenly delocalized on the whole molecule, except DT5 where the HOMO is mainly localized on the
electron-donating amine structural moiety, while the LUMO is mainly localized on the thiophene rings. For **DT1–DT3**, their HOMO-LUMO gaps decrease with the increasing number of thiophene rings, due to the more extensive electronic delocalization. By comparing **DT4–DT6** with **DT1**, their HOMO-LUMO gaps are smaller, also due to the more extensive electronic delocalization. **DT5** has the smallest HOMO-LUMO gap, reflecting that it has the most extensive electronic delocalization and the electron-donating amine moiety further raises the HOMO energy level.

The TDDFT results indicate that the wavelength required for the HOMO-LUMO transition (S₀→S₁) is consistent with the magnitudes of the HOMO-LUMO gaps.
Table 3.3 TDDFT calculation results of the compounds DT1–DT6.

<table>
<thead>
<tr>
<th>Dye</th>
<th>H→L: 0.68 (679.1 nm)</th>
<th>H→L: 0.64 (428.3 nm)</th>
<th>0.7477</th>
<th>3.11</th>
</tr>
</thead>
<tbody>
<tr>
<td>DT1</td>
<td>H→L: 0.71</td>
<td>H→L: 0.64</td>
<td>1.1217</td>
<td>2.76</td>
</tr>
<tr>
<td>DT2</td>
<td>H→L: 0.70</td>
<td>H→L: 0.64</td>
<td>1.0977</td>
<td>2.54</td>
</tr>
<tr>
<td>DT3</td>
<td>H→L: 0.53</td>
<td>H→L: 0.68</td>
<td>0.5139</td>
<td>2.66</td>
</tr>
<tr>
<td>DT4</td>
<td>H→L: 0.69</td>
<td>H→L: 0.71</td>
<td>0.0150</td>
<td>2.02</td>
</tr>
<tr>
<td>DT5</td>
<td>H→L: 0.61</td>
<td>H→L: 0.66</td>
<td>0.7008</td>
<td>2.72</td>
</tr>
</tbody>
</table>

aH→L represents the HOMO to LUMO transition. CI stands for configuration interaction.
LUMO+1: –1.41 eV  
LUMO: –2.87 eV

HOMO: –5.98 eV  
HOMO-1: –6.54 eV

**Figure 3.7** Contour plots of the frontier molecular orbitals for DT1.

LUMO+1: –1.61 eV  
LUMO: –2.94 eV

HOMO: –5.70 eV  
HOMO-1: –6.35 eV

**Figure 3.8** Contour plots of the frontier molecular orbitals for DT2.
**Figure 3.9** Contour plots of the frontier molecular orbitals for DT3.

**Figure 3.10** Contour plots of the frontier molecular orbitals for DT4.
Figure 3.11 Contour plots of the frontier molecular orbitals for DT5.

LUMO+1: $-1.58$ eV
LUMO: $-2.92$ eV
HOMO: $-4.94$ eV
HOMO-1: $-5.66$ eV

Figure 3.12 Contour plots of the frontier molecular orbitals for DT6.

LUMO+1: $-1.63$ eV
LUMO: $-2.96$ eV
HOMO: $-5.67$ eV
HOMO-1: $-5.89$ eV
3.1.4 Applications in DSSCs

3.1.4.1 Preparation of DSSC Devices

TiO$_2$ nanoparticles and the reference compound N719 were purchased from Solaronix SA, Switzerland. A TiO$_2$ thin film (12 mm of 20 nm particles as the absorbing layer and 6 mm of 400 nm particles as the scattering layer) coated on FTO glass substrate with a dimension of 0.5 × 0.5 cm$^2$ was used as the photoanode.$^{[32]}$ The film thickness was measured by using a profilometer (Dektak3, Veeco/Sloan Instruments Inc., USA). A platinized FTO produced by thermopyrolysis of H$_2$PtCl$_6$ was used as a counter electrode. The TiO$_2$ thin film was dipped into a THF solution containing 3 × 10$^4$ M dye sensitizer for at least 12 h. After rinsing with THF, the photoanode adhered with a polyester tape of 60 mm in thickness and with a square aperture of 0.36 cm$^2$ was placed on top of the counter electrode and both were tightly clipped together to form a cell. Electrolyte was then injected into the space and then the cell was sealed with Torr Seal cement (Varian, MA, USA). The electrolyte was composed of 0.5 M lithium iodide (LiI), 0.05 M iodine (I$_2$), and 0.5 M 4-tert-butylpyridine dissolved in acetonitrile.

The photoelectrochemical characterizations on the solar cells were carried out using an Oriel Class A solar simulator (Oriel 91195A, Newport Corp.). Photocurrent-voltage characteristics of the DSSCs were recorded with a
potentiostat/galvanostat (CHI650B, CH Instruments, Inc.) at a light intensity of 100 mW cm\(^{-2}\) calibrated by an Oriel reference solar cell (Oriel 91150, Newport Corp.). The monochromatic quantum efficiency was recorded through a monochromator (Oriel 74100, Newport Corp.) at short-circuit condition. The intensity of each wavelength was in the range of 1 to 3 mW cm\(^{-2}\). Electrochemical impedance spectra (EIS) were recorded for DSSCs under illumination at \(V_{oc}\) at room temperature. The frequencies explored range from 10 mHz to 100 kHz.

### 3.1.4.2 Photovoltaic Performance of DSSCs

DSSCs sensitized by DT1–DT6 were fabricated under standard AM 1.5 irradiation (100 mW cm\(^{-2}\)). Figure 3.11 shows the action spectra of incident photon-to-current conversion efficiency (IPCE) for DSSCs using DT1–DT6. The losses of light reflection and absorption by the conducting glass were not corrected. All of the dyes can efficiently convert the visible light to photocurrent in the region from 400 nm to 700 nm. The IPCE of DT1–DT6 reached a maximum 48.4% at 440 nm, 57.1% at 420 nm, 63.6% at 442 nm, 92.5% at 458 nm, 66.5% at 460 nm and 66.1% at 460 nm, respectively. The IPCE performance of the DSSCs with DT4 is higher than the others and even higher than that of N719 in the region from 400 nm to 530 nm, indicating DT4 sensitized TiO\(_2\) electrode would generate the higher
conversion yield with better light-harvesting ability in this region.

![Photocurrent action spectra (IPCE) of the TiO₂ electrode sensitized by DT1–DT6 and N719.](image)

**Figure 3.13** Photocurrent action spectra (IPCE) of the TiO₂ electrode sensitized by DT1–DT6 and N719.

The device performance data such as $J_{sc}$, $V_{oc}$, $FF$ and PCE are summarized in Table 3.4. For the overall light to electricity conversion efficiency of DT1–DT6, dye DT4 exhibited the best PCE of 4.87% ($V_{oc} = 0.70$ V, $J_{sc} = 9.94$ mA cm$^{-2}$, $FF = 0.70$), which reached 68% with respect to N719-based device fabricated under similar conditions. Figure 3.14 shows the $J$–$V$ characteristics of DSSCs fabricated with these dibenzothiophene-based photosensitizing dyes (DT1–DT6) under simulated sunlight illumination. As compared with DT1, the photovoltaic performance can be enhanced
by introducing more thiophene groups for DT2–DT3. On the other hand, the photovoltaic performance can also be improved by adding an electron-donating group, such as triarylamine, dibenzothiophene and fluorene in the molecule in DT4–DT6. The $J_{sc}$ is related to the molar extinction coefficient of the dye molecule, in which a higher molar extinction coefficient has a better light-harvesting ability and thus a higher $J_{sc}$. DT4 has the largest molar extinction coefficient and consequently an improved $J_{sc}$ (9.94 mA cm$^{-2}$).

![Figure 3.14]$J–V$ curves of the DT1–DT6 DSSC devices under AM 1.5G simulated sunlight illumination.
Table 3.4 Photovoltaic performance of DSSCs with DT1–DT6 and N719 under the AM 1.5 sunlight illumination.

<table>
<thead>
<tr>
<th>Dyes</th>
<th>$V_{oc}$ / V</th>
<th>$J_{sc}$ / mA cm$^{-2}$</th>
<th>FF</th>
<th>PCE / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>N719</td>
<td>14.09</td>
<td>0.77</td>
<td>0.66</td>
<td>7.14</td>
</tr>
<tr>
<td>DT1</td>
<td>3.34</td>
<td>0.57</td>
<td>0.66</td>
<td>1.25</td>
</tr>
<tr>
<td>DT2</td>
<td>3.00</td>
<td>0.68</td>
<td>0.66</td>
<td>1.34</td>
</tr>
<tr>
<td>DT3</td>
<td>5.08</td>
<td>0.59</td>
<td>0.56</td>
<td>1.68</td>
</tr>
<tr>
<td>DT4</td>
<td>9.94</td>
<td>0.70</td>
<td>0.70</td>
<td>4.87</td>
</tr>
<tr>
<td>DT5</td>
<td>7.37</td>
<td>0.64</td>
<td>0.68</td>
<td>3.20</td>
</tr>
<tr>
<td>DT6</td>
<td>4.74</td>
<td>0.61</td>
<td>0.67</td>
<td>1.95</td>
</tr>
</tbody>
</table>

Electrochemical impedance spectroscopy (EIS) analysis was performed to elucidate correlation of $V_{oc}$ with charge transfer resistance ($R_{ct}$) of the devices. Figure 3.15 shows the electrochemical impedance spectra for the DSSCs made with TiO$_2$ electrodes dipped with the six dyes (DT1–DT6) in the dark under a forward bias of −0.55 V. The middle-frequency semicircle in the EIS spectra represents the charge transfer resistance between the TiO$_2$ surface and the electrolyte. The charge transfer resistance decreases in the order DT4 > DT5 > DT6 > DT3 > DT2 > DT1, and hence indicates that the charge recombination rate of DT4 is the highest while DT1 is the
lowest.

The Nyquist plots of DSSCs with DT1–DT6 were measured on the same cells measured at $V_{oc}$ potentials under AM 1.5G solar illumination by scanning the frequencies from 10 mHz to 100 kHz (Figure 3.16) to elucidate the electronic and ionic transport processes in DSSCs. Three semicircles were observed in the Nyquist plots. The small and large semicircles, located in the high and middle frequency regions, are assigned to the charge transfer at the Pt/electrolyte and TiO$_2$/dye/electrolyte interfaces, respectively.[33] Another small semicircle, which should appear at the low frequency region is overlapped by the middle frequency large semicircle. The $R_{ct}$ value on the TiO$_2$ surface, which is related to the charge recombination rate between injected electron and electron acceptor ($I_3^-$) in the electrolyte, is estimated by the large semicircle width. A large $R_{ct}$ means a smaller charge recombination rate and vice versa. As shown in Figure 3.16, the values of $R_{ct}$ of DSSCs based on DT1–DT6 (77 Ω for DT1, 66 Ω for DT2, 43 Ω for DT3, and 20 Ω for DT4, 29 Ω for DT5, and 42 Ω for DT6, respectively) are larger than that of N719 (19 Ω). This means that DT1–DT6 based DSSCs have less efficient electron collection than N719. However, the rate of electron collection of DT4 is close to N719.
Figure 3.15 Impedance plots of the DSSCs based on photosensitizers DT1–DT6 and N719 (measured at 55 mV in the dark).

Figure 3.16 Impedance plots of the DSSCs based on photosensitizers DT1–DT6 and N719 (measured at \( V_{oc} \) potentials under AM 1.5G illumination).
3.2 Synthesis and Characterization of Functionalized Carbazole-based Dye-sensitized Solar Cells

3.2.1 Introduction

DSSC has attracted much attention as a promising technology for low-cost photovoltaics in the past two decades. After the first report of DSSC by Grätzel and O’Regan in 1991,[34] much effort has been put to develop better photovoltaic materials to improve the device performance.[18] Especially, Ru(II)-polypyridyl photosensitizers such as N3,[35] N719,[36] N907,[37] and black dye[38] have achieved solar-to-electricity conversion efficiency higher than 10% under AM 1.5 simulator, which is a value close to an amorphous silicon-based photovoltaic cell.[39] However, the cost of these ruthenium dyes is high because of the expensive ruthenium metal, and these dyes require careful synthesis and tricky purification steps. As compared with the ruthenium dyes, organic dyes can be fabricated rather inexpensively, possess high extinction coefficients by suitable molecular modifications,[40] are flexible at the molecular level,[41] have tunable optical properties,[42] exhibit lower degree of aggregation and have potentially higher dye loadings.[43]

Carbazole has a strong absorption in the near-UV region and a low redox potential, and is also an excellent hole-transporting material. Thus, the
electrochemical and spectroscopic properties of carbazole and its derivatives have been extensively studied.\textsuperscript{[44]} Carbazole moiety has been widely used in nonlinear optical,\textsuperscript{[37]} photorefractive materials,\textsuperscript{[36]} and organic light-emitting diodes (OLEDs).\textsuperscript{[45]} Also, organic dyes possessing carbazole\textsuperscript{[39, 46-49]} moiety have achieved good photovoltaic performances in the application of DSSCs.

Introduction of thiophene spacer could be beneficial to obtain higher molar extinction coefficients for the absorption.\textsuperscript{[50]} 9-Phenylcarbazole so far is not widely used in the design and synthesis of organic dyes. Therefore, we have developed and synthesized a series of dyes bearing 9-phenylcarbazole or dibenzothiophene donor, carbazole-thiophene linker and cyanoacrylic acid as electron-withdrawing group. Based on the above consideration, four new carbazole-based organic dye sensitizers \textbf{C1–C4} have been designed and synthesized (Chart 3.2).
Chart 3.2 The chemical structures of organic dyes C1–C4 in this study.

3.2.2 Synthesis

The routes to compounds C1–C4 are shown in Scheme 3.4–3.6. The starting 2-bromodibenzothiophene, dibenzothiophen-2-ylboronic acid, 3-bromo-9-phenyl-9H-carbazole and 9-phenyl-9H-carbazol-3-yl-3-boronic acid were prepared according to the reported procedures.[45, 51–52] Then, the intermediates were obtained by Suzuki coupling reaction with the corresponding boronic acids. Subsequently, these compounds were monobrominated by N-bromosuccinimide (NBS) to give C1-Br and C3-Br. Knoevenagel condensation of the aldehyde intermediate (C1-CHO to C4-CHO) and cyanoacetic acid in the presence of piperidine gave the desired dyes
C1–C4. The structures of all the dyes were verified by NMR spectroscopy and MALDI-TOF mass spectrometry. The dyes are red in color and are readily soluble in common organic solvents such as THF, CHCl₃ and DMSO.

Scheme 3.4 Synthetic routes for various boronic acid derivatives: i) Br₂, CHCl₃; ii) nBuLi, B(OMe)₃; iii) NBS, CHCl₃; iv) nBuLi, B(OMe)₃.
Scheme 3.5 Synthetic route for C1 and C2: i) Pd(PPh₃)₄, Na₂CO₃ (2 M, aq), THF; ii) NBS, CHCl₃/acetic acid, overnight; iii) Pd(PPh₃)₄, Na₂CO₃ (2 M, aq), THF; iv) cyanoacetic acid, piperidine, dry CHCl₃.
Scheme 3.6 Synthetic route for C3 and C4: i) Pd(PPh₃)₄, Na₂CO₃ (2 M, aq), THF; ii) NBS, CHCl₃/acetic acid, overnight; iii) Pd(PPh₃)₄, Na₂CO₃ (2 M, aq), THF; iv) NBS, CHCl₃/acetic acid, overnight; v) Pd(PPh₃)₄, Na₂CO₃ (2 M, aq), THF; vi) cyanoacetic acid, piperidine, dry CHCl₃.
3.2.3 Results and Discussion

3.2.3.1 Spectroscopic Characterization

All the newly synthesized dyes were well characterized by common spectroscopic techniques. All the dyes are air-stable and soluble in common organic solvents. All the compounds showed characteristic $^1$H NMR spectra. All the NMR data of the intermediates and dyes are summarized in the experimental part of Chapter 5. All the proton signals of aromatic rings of the dyes are on the downfield region (above 6.80 ppm) and those of the butyl group are on the upfield region (below 2.30 ppm). The $^1$H NMR spectra of C1 and C3 are shown in Figures 3.17 and 3.18.

![Figure 3.17 $^1$H NMR spectrum of dye C1 in $d_6$-DMSO.](image)
3.2.3.2 Photophysical Properties

The electronic absorption spectra of photosensitizers C1–C4 were investigated in THF solution at room temperature. Figure 3.19 shows the absorption spectra of C1–C4. Generally, all the dyes exhibit two distinct absorption bands. The absorption bands in the UV region at about 300 nm correspond to the π to π* electron transition. The other absorption bands which located in the range from 430 nm to 457 nm are attributed to the intramolecular charge transfer excitation.[53–55] The red-shift of C3 and C4 from C1 and C2 is mainly due to the effective conjugation caused by the introduction of one more thiophene unit.[37]
The molar extinction coefficients of photosensitizers $\text{C1–C4}$ were investigated in THF solution at room temperature. Relevant data are summarized in Table 3.5. The dyes which have two substituted thiophene ($\text{C3 and C4}$) have higher molar extinction coefficients than the dyes which have only one substituted thiophene ($\text{C1 and C2}$) at the ICT absorption band. This is because of the introduction of more thiophene units.\textsuperscript{[53]} In addition, the molar extinction coefficients of the dyes which have electron-donating 9-phenylcarbazole group ($\text{C2 and C4}$) are higher than those with dibenzothiophene as the electron-donating group ($\text{C1 and C3}$). These results indicate that the dyes $\text{C2 and C4}$ have better light harvesting ability.

From Figure 3.20, emission bands were observed for all dyes. All of these dyes exhibited emissions with a Stokes shift of about 100 nm in THF solutions. Similar to the electronic absorption spectra, the dyes also displayed consistently red-shifted absorptions and emissions upon increasing the number of thiophene units. The dyes with two substituted thiophene ($\text{C3 and C4}$) are more red-shifted than the dyes which have only one substituted thiophene ($\text{C1 and C2}$). The bathochromic shift is due to the extension of the $\pi$ system.\textsuperscript{[55]}
Figure 3.19 Normalized absorption spectra of the new dyes measured in THF at 298 K.

Figure 3.20 Normalized photoluminescence (PL) spectra of dyes in THF at 298 K.
Table 3.5 Absorption and PL data of C1–C4 in THF at 298 K.

<table>
<thead>
<tr>
<th>Dye</th>
<th>λ_{abs} in THF (nm)</th>
<th>Molar extinction coefficient (M^{-1} cm^{-1})</th>
<th>λ_{em} in THF (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>299, 430</td>
<td>25800, 12510</td>
<td>537</td>
</tr>
<tr>
<td>C2</td>
<td>303, 436</td>
<td>28140, 15470</td>
<td>548</td>
</tr>
<tr>
<td>C3</td>
<td>303, 452</td>
<td>25160, 16460</td>
<td>571</td>
</tr>
<tr>
<td>C4</td>
<td>300, 457</td>
<td>25190, 18340</td>
<td>588</td>
</tr>
</tbody>
</table>

3.2.3.3 Electrochemical Properties

To evaluate the thermodynamic basis of these electron transfer processes, cyclic voltammetric technique has been used to assess the energy levels of the dyes. Cyclic voltammograms of C1–C4 are shown in Figure 3.21 and the data are listed in Table 3.6. To investigate the electron transfer from the excited dye molecule to the conductive band (E_{cb}) of TiO_2, cyclic voltammetry was performed for the dyes in thin films on glassy carbon electrode measured in 0.1 M tetrabutylammonium hexafluorophosphate solution in acetonitrile at a scan rate of 50 mV s^{-1}. Under these conditions, the E_{1/2} of ferrocene was 0.07 V vs Ag/AgCl. All of the dyes are redox stable and showed irreversible oxidation and reduction waves.\textsuperscript{[28]} The HOMO and LUMO energy levels of the dyes were measured from the onset oxidation and
reduction potentials.

The LUMO levels of C1–C4 are –3.49 to –3.56 eV. These values are much higher than the bottom of the conduction band of TiO₂ (–4.4 eV), indicating that the efficient charge injection from the excited sensitizer molecule to TiO₂ conduction band is viable. The HOMO energy levels of the four dyes are calculated to be –5.12 to –5.32 eV. These values are lower than that of the I⁺/I₃⁻ pair (–4.9 eV), which indicate that the oxidized dyes may be efficiently regenerated by the electrolyte. It is worthy to note that the HOMO levels of conelectron-donating phenylcarbazole dyes are higher than that of the dibenzothiophene dyes.

Table 3.6 Electrochemical properties of sensitizers.

<table>
<thead>
<tr>
<th>Dye</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>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0.59</td>
<td>–5.32</td>
<td>–1.17</td>
<td>–3.56</td>
<td>1.76</td>
</tr>
<tr>
<td>C2</td>
<td>0.51</td>
<td>–5.24</td>
<td>–1.18</td>
<td>–3.55</td>
<td>1.69</td>
</tr>
<tr>
<td>C3</td>
<td>0.42</td>
<td>–5.15</td>
<td>–1.24</td>
<td>–3.49</td>
<td>1.66</td>
</tr>
<tr>
<td>C4</td>
<td>0.39</td>
<td>–5.12</td>
<td>–1.23</td>
<td>–3.50</td>
<td>1.62</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)
Figure 3.21 Cyclic voltammograms of the thin films on glassy carbon electrode measured in 0.1 mol L$^{-1}$ Bu$_4$NPF$_6$ acetonitrile solutions at a scan rate of 50 mV s$^{-1}$. 
3.2.3.4 Computational Studies

Molecular geometries were optimized at the Becke3LYP (B3LYP) level of DFT. Time-dependent DFT was performed based on the optimized structures to obtain the excitation energies. The effective core potentials (ECPs) of Hay and Wadt with the double-$\zeta$ valence basis sets (LanL2DZ) were used to describe S atoms. The standard 6-31G basis set was used for all other atoms. Polarization functions were added for S($\zeta_d = 0.503$). All the calculations were carried out using the Gaussian 03 program.

As shown from the orbital profiles in Figures 3.22–3.25 and Table 3.7 the calculation results show that for each of the four compounds, the HOMO is mainly localized on the phenylcarbazole moieties while the LUMO is mainly localized on the thiophene rings. In the LUMO, orbital mixing from the cyanoacrylic acid moiety is also quite significant.

$\textbf{C}_3$ has a smaller HOMO–LUMO gap (2.55 eV) than $\textbf{C}_1$ (2.83 eV), reflecting that $\textbf{C}_3$ is more delocalized due to an additional thiophene ring. Similarly, we see that $\textbf{C}_4$ has a smaller HOMO–LUMO gap (2.41 eV) than $\textbf{C}_2$ (2.64 eV). $\textbf{C}_2$ and $\textbf{C}_4$ have smaller HOMO–LUMO gaps than $\textbf{C}_1$ and $\textbf{C}_3$, respectively, indicating that a phenylcarbazole moiety is more electron-rich than that of a dibenzothiophene moiety. The TDDFT results indicate that the HOMO–LUMO transition is responsible for the lowest electronic excitation.
Figure 3.22 Contour plots of the frontier molecular orbitals for C1.

Figure 3.23 Contour plots of the frontier molecular orbitals for C2.
Figure 3.24 Contour plots of the frontier molecular orbitals for C3.

Figure 3.25 Contour plots of the frontier molecular orbitals for C4.
Table 3.7 TDDFT calculation results of the four compounds C1–C4.

<table>
<thead>
<tr>
<th>Dyes</th>
<th>The largest coefficient in the CI expansion of the T&lt;sub&gt;1&lt;/sub&gt; state&lt;sup&gt;a&lt;/sup&gt; (S&lt;sub&gt;0&lt;/sub&gt;→T&lt;sub&gt;1&lt;/sub&gt; excitation energy)</th>
<th>The largest coefficient in the CI expansion of the S&lt;sub&gt;1&lt;/sub&gt; state&lt;sup&gt;a&lt;/sup&gt; (S&lt;sub&gt;0&lt;/sub&gt;→S&lt;sub&gt;1&lt;/sub&gt; excitation energy)</th>
<th>The oscillator strength (f) of the S&lt;sub&gt;0&lt;/sub&gt;→S&lt;sub&gt;1&lt;/sub&gt; transition</th>
<th>HOMO-LUMO gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>H→L: 0.53 (688.1nm)</td>
<td>H→L: 0.67 (481.7nm)</td>
<td>0.4328</td>
<td>2.84</td>
</tr>
<tr>
<td>C2</td>
<td>H→L: 0.55 (694.3nm)</td>
<td>H→L: 0.69 (522.0nm)</td>
<td>0.2196</td>
<td>2.64</td>
</tr>
<tr>
<td>C3</td>
<td>H→L: 0.60 (809.0nm)</td>
<td>H→L: 0.66 (531.0nm)</td>
<td>0.7303</td>
<td>2.54</td>
</tr>
<tr>
<td>C4</td>
<td>H→L: 0.54 (815.7nm)</td>
<td>H→L: 0.68 (565.9nm)</td>
<td>0.3907</td>
<td>2.41</td>
</tr>
</tbody>
</table>

<sup>a</sup>H→L represents the HOMO to LUMO transition. CI stands for configuration interaction.

3.2.4 Applications in DSSCs

3.2.4.1 Preparation of DSSC Devices

TiO<sub>2</sub> nanoparticles and the reference compound N719 were purchased from Solaronix SA, Switzerland. A TiO<sub>2</sub> thin film (12 µm of 20 nm particles as the absorbing layer and 6 µm of 400 nm particles as the scattering layer) coated on FTO glass substrate with a dimension of 0.5 × 0.5 cm<sup>2</sup> was used as the photoanode. The film thickness was measured by using a profilometer (Dektak3, Veeco/Sloan Instruments Inc., USA). A platinized FTO produced by thermopyrolysis of H<sub>2</sub>PtCl<sub>6</sub> was used as a counter electrode. The TiO<sub>2</sub> thin film was dipped into a THF solution containing 3 × 10<sup>−4</sup> M dye sensitizer for at least 12 h. After rinsing with THF, the
photoanode adhered with a polyester tape of 60 mm in thickness and with a square aperture of 0.36 cm$^2$ was placed on top of the counter electrode and both were tightly clipped together to form a cell. Electrolyte was then injected into the space and then the cell was sealed with Torr Seal cement (Varian, MA, USA). The electrolyte was composed of 0.5 M lithium iodide (LiI), 0.05 M iodine (I$_2$), and 0.5 M 4-tert-butylpyridine dissolved in acetonitrile.

The photoelectrochemical characterizations on the solar cells were carried out using an Oriel Class A solar simulator (Oriel 91195A, Newport Corp.). Photocurrent-voltage characteristics of the DSSCs were recorded with a potentiostat/galvanostat (CHI650B, CH Instruments, Inc.) at a light intensity of 100 mW cm$^{-2}$ calibrated by an Oriel reference solar cell (Oriel 91150, Newport Corp.). The monochromatic quantum efficiency was recorded through a monochromator (Oriel 74100, Newport Corp.) at short-circuit condition. The intensity of each wavelength was in the range of 1 to 3 mW cm$^{-2}$. Electrochemical impedance spectra (EIS) were recorded for DSSCs under illumination at open-circuit voltage ($V_{oc}$) at room temperature. The frequencies explored range from 10 mHz to 100 kHz.
3.2.4.2 Photovoltaic Performance of DSSCs

DSSCs with an effective area of 0.25 cm$^2$ were fabricated by using C1–C4 adsorbed on nanocrystalline TiO$_2$ as the sensitizers. The DSSCs with different dyes were measured under AM 1.5 solar light condition. The losses of light reflection and absorption by the conducting glass were not corrected. The device performance data such as $J_{sc}$, $V_{oc}$, FF and PCE are summarized in Table 3.8.

Figure 3.26 shows the action spectra of IPCE for DSSCs using C1–C4. The IPCE curves cover almost the entire visible spectrum, with maximum IPCE values of 52% to 72% for C1–C4 sensitized solar cells. The IPCE values of more than 70% were observed in the range of 450–550 nm for the DSSC based on dyes C3–C4, while the maximum values of IPCE for dyes C1–C2 were significantly decreased. C3 has the highest value of IPCE. Although the IPCE performance of the DSSCs with C3 is slightly higher than that of C4 (~1%), C4 is shifted to the longer wavelength indicating that C4-sensitized TiO$_2$ electrode can generate the highest conversion yield among all the dyes studied.

Figure 3.27 shows the $J$–$V$ characteristics of DSSCs fabricated with these carbazole-containing photosensitizing dyes (C1–C4) under simulated sunlight illumination. The $J_{sc}$ is related to the molar extinction coefficient of the dye molecule, in which a higher molar extinction coefficient has a better light-harvesting ability and
yields a higher $J_{sc}$. C4 has the highest light-harvesting efficiency and consequently an improved $J_{sc}$ (11.06 mA cm$^{-2}$) due to the largest molar extinction coefficient among all the dyes. The light-harvesting efficiency of the dyes which have only one substituted thiophene (C1 and C2) are lower than the dyes which have two substituted thiophene (C3 and C4) due to the smaller molar extinction coefficients of C1 and C2. In addition, the light-harvesting efficiency of the electron-donating 9-phenylcarbazole group in dyes C2 and C4 are higher than that in C1 and C3 with the dibenzothiophene electron-donating group. This is attributed to the higher molar extinction coefficients of C2 and C4.

For the overall light to electricity conversion efficiency of C1–C4, dye C4 exhibited the best PCE of 5.28% ($V_{oc} = 0.70$ V, $J_{sc} = 11.06$ mA cm$^{-2}$, $FF = 0.68$) under standard global AM 1.5 solar light condition, which reached 73% with respect to that of an N719-based device fabricated under similar fabrication conditions.
Figure 3.26 Photocurrent action spectra of the TiO₂ electrode sensitized by C₁–C₄.

Figure 3.27 J–V curves of the DSSC devices under AM 1.5G simulated sunlight illumination.
Electrochemical impedance spectroscopy (EIS) analysis was performed to elucidate correlation of $V_{oc}$ with charge transfer resistance ($R_{ct}$) of the devices. Figure 3.28 shows the electrochemical impedance spectra for the DSSCs made with TiO$_2$ electrodes dipped with the C1–C4 in the dark under a forward bias of −0.55 V. The middle-frequency semicircle in the EIS spectra represents the charge transfer resistance between the TiO$_2$ surface and the electrolyte. The charge transfer resistance decreases in the order C4 > C3 > C2 > C1, indicating that the charge recombination rate decreases in the order C4 > C3 > C2 > C1.
The Nyquist plots of DSSCs with C1–C4 were measured on the same cells measured at $V_{oc}$ potentials under AM 1.5G solar illumination by scanning the frequencies from 10 mHz to 100 kHz (Figure 3.28) to elucidate the electronic and ionic transport processes in DSSCs. Three semicircles were observed in the Nyquist plots. The small and large semicircles, respectively located in the high- and middle frequency regions, are assigned to the charge transfer at the Pt/electrolyte and TiO$_2$/dye/electrolyte interfaces, respectively.$^{[33]}$ Another small semicircle, which should have appeared at the low frequency region, is overlapped by the middle frequency large semicircle. The $R_{ct}$ value on the TiO$_2$ surface, which is related to the charge recombination rate between injected electron and electron acceptor ($I_3^-$) in the electrolyte, is estimated by the large semicircle width. A large $R_{ct}$ means a smaller charge recombination rate and vice versa. As shown in Figure 3.29, the values of $R_{ct}$ of DSSCs based on C1–C4 (42 Ω for C1, 40 Ω for C2, 33 Ω for C3, and 31 Ω for C4, respectively) are larger than that of N719 (27 Ω). This means that DSSCs based on C1–C4 have less efficient electron collection than N719.
Figure 3.28 Impedance plots of the DSSCs based on sensitizers C1–C4 and N719 (measured at 55 mV in the dark).

Figure 3.29 Impedance plots of the DSSCs based on sensitizers C1–C4 and N719 (measured at $V_{oc}$ potentials under AM 1.5G illumination).
3.3 Concluding Remarks

In chapter 3.1, a series of new organic dyes based on dibenzothiophene have been synthesized and applied for the fabrication of DSSCs. The results indicated that addition of thiophene rings beyond three in the system would not lead to much bathochromic effect in their absorption. All the dyes have efficient charge injection from the excited dye molecule to TiO₂ conduction band and can provide suitable driving force for efficient dye regeneration and thus the charge separation. Among all of the dyes examined, DSSCs based on DT₄ exhibited the best overall light to electricity conversion efficiency of 4.87% (Vₗ₉ = 0.70 V, Jₛₙ = 9.94 mA cm⁻², FF = 0.70) under AM 1.5 irradiation, which reached 68% with respect to that of an N719-based device fabricated under similar fabrication conditions.

In chapter 3.2, we have designed and synthesized four novel carbazole-based dye sensitizers (C₁ to C₄) which contain 9-phenylcarbazole and dibenzothiophene as their electron-donating group, and cyanoacrylic acid group as an electron-withdrawing and anchoring group. The molar extinction coefficients of electron-donating 9-phenylcarbazole dyes are higher than those with dibenzothiophene. These results indicate that the electron-donating 9-phenylcarbazole dyes have better light harvesting ability. Among all of the dyes examined, DSSCs based on C₄ exhibited the best
overall light to electricity conversion efficiency of 5.28% ($V_{oc} = 0.70$ V, $J_{sc} = 11.06$ mA cm$^{-2}$, $FF = 0.68$) under AM 1.5 irradiation, which reached 73% with respect to that of an N719-based device fabricated under similar fabrication conditions. Comparing with those developed carbazole DSSCs$^{39, 46-49}$, the optimization of the chemical structures needs to be done to further improve their energy conversion efficiency.
References:


Chapter 4 Novel Symmetrical Di-anchoring Organic Photosensitizers for Dye-sensitized Solar Cells

4.1 Introduction

DSSCs have attracted considerable attention since the first report by Grätzel in 1991.\cite{1} Several groups have developed metal-free organic photosensitizers containing two anchoring groups that can double the light absorption efficiency and minimize dye aggregation.\cite{2} Wong and co-workers recently introduced two electron donor-acceptor branches into the rigid cross-shaped molecular structure to improve dye adsorption, enhance direct photoinduced electron injection, and achieve an overall PCE of 3.75%.\cite{3}

Carbazole moiety which is an excellent hole-transporting material has been widely used in nonlinear optical,\cite{4} photorefractive materials,\cite{5} and organic light-emitting diodes (OLEDs)\cite{6}. Also, organic dyes possessing carbazole\cite{7-11} moiety have achieved good photovoltaic performances in the application of DSSCs. Although 3,6-carbazole moieties have become promising units for organic dyes in practical DSSC applications in recent years,\cite{12-13} 2,7-functionalized carbazole unit has been neglected for use in DSSC design. Making 2,7-functionalized carbazole unit is much more difficult as compared to 3,6-substituted compounds, since the 3- and 6-positions...
of the carbazole are activated by the nitrogen atom. All kinds of electrophilic substitution reactions will take place in these positions. In this study, we integrated central 2,7-functionalized carbazole donors with two terminal anchoring groups for the design of organic DSSC dyes.

Due to the efficient light harvesting and high molar extinction coefficients, fluorene-based compounds exhibited some significant power conversion efficiencies both in DSSC and polymer solar cell applications.\textsuperscript{[14–15]} Therefore, 2,7-functionalized fluorene unit can be a good candidate for DSSCs.

In this chapter, we report two sets of novel symmetrical acceptor-donor-acceptor organic sensitizers (Chart 4.1) possessing 2,7-functionalized carbazole and 2,7-functionalized fluorene cores which are linked through \pi-conjugated thiophene bridge or benzene bridge to two electron-accepting cyanoacrylic acid terminal anchoring groups. The nine dyes synthesized have been applied to the sensitization of nanocrystalline TiO\textsubscript{2}-based solar cells and the corresponding photovoltaic properties, electronic and optical properties are also presented in this chapter.
Chart 4.1 The chemical structures of organic dyes B1–B9 in this study.

4.2 Synthesis

All of the new dyes have been synthesized according to some classical organic transformations and the synthetic routes are outlined in Schemes 4.1–4.4. Scheme 4.1 shows the synthetic routes for various boronic acid derivatives. For the synthesis of
N-alkylated 2,7-dibromofluorene boronic acid, 2,7-dibromofluorene underwent N-alkylation to give 2,7-dibromo-9,9-dihexyl-9H-fluorene. Then, 2,7-dibromo-9,9-dihexyl-9H-fluorene reacted with n-BuLi and B(OMe)₃ to yield the boronic acid product. For the synthesis of N-alkylated 2,7-dibromocarbazole boronic acid, the first step consists of an Ullmann coupling reaction of 2,5-dibromonitrobenzene with activated copper.¹⁶⁻¹⁷ Before the ring closure, the nitro groups had to be reduced to the amines. The reduction was carried out with tin/HCl. The ring closure was made by heating 4,4′-dibromo-2,2′-diaminobiphenyl in concentrated H₃PO₄ to 190 °C for 24 h to yield 2,7-dibromocarbazole. In the next step, carbazole was N-alkylated with 1-bromooctane. The reactions were carried out in acetone/KOH with benzylthiethylammonium chloride as phase-transfer catalyst. Finally, 2,7-dibromo-9-octyl-9H-carbazole reacted with n-BuLi and B(OMe)₃ to yield the product.

Scheme 4.2 shows the synthetic routes for various halide precursors. B₁-Br and B₃-Br were obtained by reactions between 2-bromothiophene, POCl₃ and DMF. B₂-Br was achieved by Suzuki coupling reaction between B₁-Br and 9-phenyl-9H-carbazol-3-yl-3-boronic acid, followed by monobromination with N-bromosuccinimide (NBS). B₂-Br was obtained by charging n-BuLi and DMF into the brominated precursors.
The intermediates **B1-CHO** to **B9-CHO** were subsequently made by the Suzuki coupling reaction of various halide precursors with 9,9-dihexyl-9H-fluoren-2,7-diyl-2,7-diboronic acid and 9-octyl-9H-carbazol-2,7-diyl-2,7-diboronic acid. The final step involved a Knoevenagel condensation with cyanoacetic acid in the presence of piperidine to convert the carbaldehydes to cyanoacrylic acids.\[^{18}\] Purification of the reaction mixtures by silica gel chromatography furnished **B1–B9** as air-stable powders with high purity (Schemes 4.3–4.4). The structures of all the dyes were verified by NMR spectroscopy and MALDI-TOF mass spectrometry. The dyes are orange or red in color and are readily soluble in common organic solvents such as THF, CH$_2$Cl$_2$, CHCl$_3$ and DMSO.

![Scheme 4.1 Synthesis of boronic acid derivatives](image)

**Scheme 4.1** Synthetic routes for various boronic acid derivatives: i) C$_6$H$_{13}$Br, NaOH, DMSO; ii) n-BuLi, B(OMe)$_3$, HCl; iii) Cu powder, DMF; iv) Sn/HCl, ethanol; v) H$_3$PO$_4$; vi) benzylthiethylammonium chloride, 1-bromooctane, 50% wt NaOH, toluene; vii) n-BuLi, B(OMe)$_3$, HCl.
Scheme 4.2 Synthetic routes for various halide precursors: i) POCl₃, DMF; ii) Pd(PPh₃)₄, Na₂CO₃ (2 M, aq), THF; iii) NBS, DMF/acetic acid; iv) POCl₃, DMF; v) n-BuLi, DMF.

Scheme 4.3 Synthesis of B₁–B₄: i) Pd(PPh₃)₄, Na₂CO₃ (2 M, aq), THF; ii) cyanoacetic acid, piperidine, dry CHCl₃.
Scheme 4.4 Synthesis of B5–B9: i) Pd(PPh₃)₄, Na₂CO₃ (2 M, aq), THF; ii) cyanoacetic acid, piperidine, dry CHCl₃.

4.3 Results and Discussion

4.3.1 Spectroscopic Characterization

All the newly synthesized dyes were well characterized by common spectroscopic techniques. All the dyes are air-stable and soluble in common organic solvents. All the compounds showed characteristic ¹H NMR spectra. All the NMR data of the intermediates and dyes are summarized in the experimental part of Chapter 8.

All the proton signals of aromatic rings of the dyes are on the downfield region (above 7.10 ppm) and those of the butyl groups are on the upfield region (below 4.50 ppm).
ppm). The $^1$H NMR spectra of B1 and B5 are shown in Figures 4.1 and 4.2, respectively.

**Figure 4.1** $^1$H NMR spectrum of dye B1 in $d_6$-DMSO.

**Figure 4.2** $^1$H NMR spectrum of dye B5 in $d_6$-DMSO.
4.3.2 Photophysical Properties

The UV-Vis absorption spectra of the photosensitizers \textbf{B1–B9} in THF at room temperature are displayed in Figure 4.3 and Figure 4.4 and the data are collected in Table 4.1. For \textbf{B1–B4}, generally, \textbf{B4} demonstrates a single absorption peak, but when an extra donor, carbazole or thiophene, was added in \textbf{B1–B3}, two distinct absorption bands were observed. A strong absorption band at $\lambda_{\text{max}}$ of 337–344 nm is attributed to the localized $\pi-\pi^*$ transition and a weak absorption band in the visible region corresponds to an ICT transition from the central electron-donating fluorene unit to both electron-accepting cyanoacrylic acid termini.\[^{[19]}\] Because of their structural similarities, \textbf{B1–B3} exhibited similar ICT transition peaks located in the range ($\lambda_{\text{max}}$) from 400 to 444 nm. The absorption peak maximum of the dye ranks in the order: \textbf{B2} (444 nm) > \textbf{B3} (413 nm) > \textbf{B1} (400 nm) > \textbf{B4} (373 nm). \textbf{B2} is red-shifted in comparison to that of \textbf{B1}, which is mainly due to the effective conjugation caused by the introduction of one more thiophene unit (Figure 4.3).\[^{[20]}\] For the carbazole based dyes \textbf{B5–B9}, \textbf{B5–B8} demonstrates a single absorption peak whereas only \textbf{B9} shows two distinct absorption bands. The absorption peak maximum of the dye ranks in the order: \textbf{B6} (446 nm) > \textbf{B9} (443 nm) > \textbf{B5} (430 nm) > \textbf{B8} (398 nm) > \textbf{B7} (333 nm). \textbf{B6} exhibits an obvious red shift when compared to \textbf{B5} due to the enhanced electronic communication after an extra thiophene ring is added which can lower the energy of
the charge transfer in the molecule.\textsuperscript{[20]}

The molar extinction coefficients of $\text{B1-B9}$ were also investigated. The molar extinction coefficients of fluorene based photosensitizers $\text{B1-B4}$ increase in the order of $\text{B3} > \text{B2} > \text{B1} > \text{B4}$; and the carbazole based dyes $\text{B5-B9}$ increase in the order of $\text{B9} > \text{B6} > \text{B8} > \text{B7} > \text{B5}$. The higher molar extinction coefficients of the organic dyes allow a correspondingly thinner nanocrystalline film so as to avoid the decrease of the film mechanical strength. This also benefits the electrolyte diffusion in the film and reduces the recombination possibility of the light-induced charges during transportation.\textsuperscript{[21]} The highest molar extinction coefficients were measured in $\text{B4}$ and $\text{B9}$ which indicate that they should possess the best light-harvesting ability (Table 4.1).

All of the dyes display photoluminescence at room temperature (Figures 4.5 and 4.6) when they are excited at their respective absorption bands and the fluorescence peak maximum ranges from 450 to 750 nm. Similar to the absorption spectra, the presence of electron-donating groups and extension of the conjugation by thiophene group would shift the emission maximum to the red.
Figure 4.3 Normalized absorption spectra of B1–B4 measured in THF.

Figure 4.4 Normalized absorption spectra of B5–B9 measured in THF.
Figure 4.5 Normalized PL spectra of B1–B4 in THF at 298 K.

Figure 4.6 Normalized PL spectra of B5–B9 in THF at 298 K.
Table 4.1 Absorption and PL data of B1–B9 in THF at 298 K.

<table>
<thead>
<tr>
<th>Dye</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; in THF (nm)</th>
<th>Molar extinction coefficient (M&lt;sup&gt;-1&lt;/sup&gt; cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>λ&lt;sub&gt;em&lt;/sub&gt; in THF (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>335, 400</td>
<td>46690, 33300</td>
<td>519</td>
</tr>
<tr>
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</tr>
<tr>
<td>B9</td>
<td>347, 443</td>
<td>46960, 29010</td>
<td>557</td>
</tr>
</tbody>
</table>

4.3.3 Electrochemical Properties

To investigate the electron transfer from the excited dye molecule to the conductive band (<i>E<sub>cb</sub></i>) of TiO<sub>2</sub> and understand the molecular orbital energy levels, cyclic voltammetry (CV) was performed for the dyes in thin films on glassy carbon electrode measured in 0.1 M tetrabutylammonium hexafluorophosphate solution in acetonitrile at a scan rate of 50 mV s<sup>-1</sup>. The reference electrode was Ag/AgCl.
calibrated with ferrocene-ferrocenium (Fc⁺/Fc, 0.07 V) as an internal reference. The HOMO and LUMO energy levels of the dyes were measured from the first onset oxidation ($E_{ox}$) and reduction potentials ($E_{red}$).

As shown in Figure 4.7 and Table 4.2, the HOMO levels of B1–B9 are calculated to be in the range of –5.66 to –5.24 eV. These values are lower than that of iodide/tri-iodide redox potential value (–4.9 eV), thereby ensuring an effective sensitizer regeneration process to give an efficient charge separation. The LUMO levels of these photosensitizers are –3.54 to –3.45 eV. These values are much higher than the bottom level of the conduction band of TiO₂ (–4.4 eV), and hence indicate that the electron can be energetically injected into the TiO₂ conduction band from the excited dyes.
Figure 4.7 Cyclic voltammograms of the thin films of B1–B4 on glassy carbon electrode measured in 0.1 M Bu₄NPF₆ acetonitrile solutions at a scan rate of 50 mV s⁻¹.
Table 4.2 Electrochemical properties of B1–B9.

<table>
<thead>
<tr>
<th>Dye</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>B1</td>
<td>0.79</td>
<td>-5.52</td>
<td>-1.20</td>
<td>-3.53</td>
<td>1.99</td>
</tr>
<tr>
<td>B2</td>
<td>0.60</td>
<td>-5.33</td>
<td>-1.22</td>
<td>-3.51</td>
<td>1.82</td>
</tr>
<tr>
<td>B3</td>
<td>0.93</td>
<td>-5.66</td>
<td>-1.26</td>
<td>-3.47</td>
<td>2.19</td>
</tr>
<tr>
<td>B4</td>
<td>0.88</td>
<td>-5.61</td>
<td>-1.19</td>
<td>-3.54</td>
<td>2.07</td>
</tr>
<tr>
<td>B5</td>
<td>0.61</td>
<td>-5.34</td>
<td>-1.19</td>
<td>-3.54</td>
<td>1.80</td>
</tr>
<tr>
<td>B6</td>
<td>0.51</td>
<td>-5.24</td>
<td>-1.19</td>
<td>-3.54</td>
<td>1.70</td>
</tr>
<tr>
<td>B7</td>
<td>0.66</td>
<td>-5.39</td>
<td>-1.20</td>
<td>-3.53</td>
<td>1.86</td>
</tr>
<tr>
<td>B8</td>
<td>0.69</td>
<td>-5.42</td>
<td>-1.21</td>
<td>-3.52</td>
<td>1.90</td>
</tr>
<tr>
<td>B9</td>
<td>0.56</td>
<td>-5.29</td>
<td>-1.28</td>
<td>-3.45</td>
<td>1.84</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)

4.4 Applications in DSSCs

4.4.1 Preparation of DSSC Devices

A double-layer TiO$_2$ photoelectrode (thickness 15 µm; area 0.25 cm$^2$) was used as a working electrode. A 10 µm main transparent layer with titania particles (~20 nm) and a 5 µm scattering layer with titania particles (~400 nm) were screen-printed on the fluorine-doped tin oxide conducting glass substrate. A solution of B1–B9 (3 × 10$^{-4}$ M) in acetonitrile/tert-butyl alcohol (1/1, v/v) was used to coat the TiO$_2$ film with the dye. Deoxycholic acid (20 mM) was added to the dye solution as a co-adsorbent to
prevent aggregation of the dye molecules. The electrodes were immersed in the dye solutions and then kept at 25 °C for 24 h to adsorb the dye onto the TiO₂ surface. The dye-coated TiO₂ film was used as the working electrode, and platinum-coated conducting glass was used as the counter-electrode. The two electrodes were separated by a Surlyn spacer (50 µm thick) and sealed up by heating the polymer frame. The electrolyte was composed of 0.6 M dimethylpropylimidazolium iodide, 0.05 M I₂, 0.1 M LiI and 0.5 M tert-butyl pyridine in acetonitrile. The current-voltage characteristics were measured using a black metal mask and edge with an aperture area of 0.25 cm² under standard AM 1.5 sunlight (100 mW cm⁻², WXS–155S–10: Wacom Denso Co. Japan). Monochromatic incident photon-to-current conversion efficiency spectra were measured with monochromatic incident light of 1 × 10¹⁶ photons cm⁻² under 100 mW cm⁻² in direct current mode (CEP-2000BX, Bunko-Keiki). The electrochemical impedance spectra (EIS) were measured with an impedance analyzer (Solartron Analytical, 1255B) connected with a potentiostat (Solartron Analytical, 1287) under illumination using a solar simulator (WXS-155S-10: Wacom Denso Co. Japan). The frequency range was 0.1 Hz–100 kHz at 298 K. The magnitude of the alternative signal was 10 mV. The applied voltage bias was −0.55 V. The electrical impedance spectra were characterized using Z-View software (Solartron Analytical).
4.4.2 Photovoltaic Performance of DSSCs

DSSCs with an effective area of 0.25 cm$^2$ were fabricated by using our new compounds adsorbed on nanocrystalline TiO$_2$ as the photosensitizers. The DSSCs with different dyes were measured under AM 1.5 solar light condition. The losses of light reflection and absorption by the conducting glass were not corrected. The device performance data such as $J_{sc}$, $V_{oc}$, $FF$ and PCE are summarized in Table 4.3.

Figure 4.8 shows the photocurrent action spectra of IPCE for DSSCs using B1–B4. The IPCE spectra of B1–B2 are higher than that of B3–B4. The decreased IPCE values suggest that there are poor injections of electrons from excited dyes to the TiO$_2$ conduction bands in B3–B4. The IPCE spectrum of B2 shows a broader response in the range of 300–700 nm and the maximum value exhibits a strikingly high plateau at 71%, but smaller maximum values of IPCE spectra than the B1 dye (76%). The smaller IPCE value of B2 is attributed to the highest HOMO level of B2 dye (see Table 4.2), which leads to a slower regeneration of the oxidized dye and higher recombination of photo-injected electrons.\[^{24}\] Figure 4.9 shows the photocurrent action spectra of IPCE for DSSCs using B5–B9. The DSSC devices based on the dyes exhibit maximum IPCEs of approximately 28–60%. The IPCE values of more than 50% were observed in the range of 450–550 nm for the DSSCs based on the dyes B6, B8 and B9, while the maximum values of IPCE for dyes B5
and B7 were significantly decreased. B6 has the highest maximum values of IPCE. Although the IPCE performance of the DSSCs with B6 is slightly higher than that of B9 (~3%), the IPCE maximum is shifted to the longer wavelength for B9, indicating that B9-sensitized TiO₂ electrode can generate the highest conversion yield among all the dyes studied.

Figure 4.10 shows the $J-V$ characteristics of DSSCs fabricated with these fluorene based photosensitizing dyes (B1–B4) under simulated sunlight illumination. The $J_{sc}$ is related to the molar extinction coefficient of the dye molecule, in which a higher molar extinction coefficient has a better light-harvesting ability and yields a higher $J_{sc}$. The higher molar extinction coefficient of B1 and B3 than B4 reflected an enhanced light harvesting in B1 and B3 dye, and accordingly improved $J_{sc}$ values were observed. B2 has the highest light-harvesting efficiency and consequently an improved $J_{sc}$ (9.42 mA cm⁻²) due to its largest molar extinction coefficient, broader absorption spectrum and highest IPCE value among all the dyes. Figure 4.11 shows the $J-V$ characteristics of DSSCs fabricated with these carbazole based photosensitizing dyes (B5–B9) under simulated sunlight illumination. B9 has the highest light-harvesting efficiency so that it yields the highest $J_{sc}$ (8.91 mA cm⁻²) because of its largest molar extinction coefficient and broader absorption spectrum and highest IPCE value among all the dyes.
For the overall light to electricity conversion efficiency of B1 to B4, dye B2 exhibited the best PCE of 3.73% \( (V_{oc} = 0.69 \, V, J_{sc} = 9.43 \, mA \, cm^{-2}, FF = 0.56) \) under standard global AM 1.5 solar light condition, which reached 71% under similar fabrication conditions. Under the same device operating conditions, B3 shows a slightly poorer device performance with 9-butylcarbazole in place of 9-phenylcarbazole as the donor with PCE of 2.44%, \( J_{sc} \) 6.00 mA cm\(^{-2}\), \( V_{oc} \) of 0.57 mV and a FF of 0.71. For B5 to B9, dye B9 exhibited the best PCE of 4.00% \( (V_{oc} = 0.71 \, V, J_{sc} = 8.91 \, mA \, cm^{-2}, FF = 0.63) \) under standard global AM 1.5 solar light condition, which reached 47% under similar fabrication conditions. The incorporation of additional thiophene ring as the conjugated bridge between B5 and B6 shows distinct characteristics which broaden the light-harvesting capacity and hence higher efficiency was obtained for B6 (Table 4.3).
Figure 4.8 Photocurrent action spectra of the TiO$_2$ electrode sensitized by B1–B4.

Figure 4.9 Photocurrent action spectra of the TiO$_2$ electrode sensitized by B5–B9.
Figure 4.10 $J–V$ curves of B1–B4 under AM 1.5G simulated sunlight illumination.

Figure 4.11 $J–V$ curves of B5–B9 under AM 1.5G simulated sunlight illumination.
Table 4.3 Photovoltaic performance of DSSCs with B1–B9 and N719 under the AM 1.5 sunlight illumination.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$V_{oc} / V$</th>
<th>$J_{sc} / mA cm^{-2}$</th>
<th>$FF$</th>
<th>PCE / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>0.60</td>
<td>6.08</td>
<td>0.70</td>
<td>2.61</td>
</tr>
<tr>
<td>B2</td>
<td>0.56</td>
<td>9.43</td>
<td>0.69</td>
<td>3.73</td>
</tr>
<tr>
<td>B3</td>
<td>0.57</td>
<td>6.00</td>
<td>0.71</td>
<td>2.44</td>
</tr>
<tr>
<td>B4</td>
<td>0.54</td>
<td>3.92</td>
<td>0.66</td>
<td>1.42</td>
</tr>
<tr>
<td>B5</td>
<td>0.56</td>
<td>3.78</td>
<td>0.70</td>
<td>1.51</td>
</tr>
<tr>
<td>B6</td>
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<td>0.68</td>
<td>2.69</td>
</tr>
<tr>
<td>B7</td>
<td>0.64</td>
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<td>0.70</td>
<td>1.19</td>
</tr>
<tr>
<td>B8</td>
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<td>4.21</td>
<td>0.66</td>
<td>2.02</td>
</tr>
<tr>
<td>B9</td>
<td>0.71</td>
<td>8.91</td>
<td>0.63</td>
<td>4.00</td>
</tr>
</tbody>
</table>

4.5 Concluding Remarks

In summary, nine novel di-anchoring organic sensitizers (B1–B9) employing two different electron-donating cores, which are the fluorene (B1–B4) and carbazole (B5–B9) units, and two symmetrical anchoring cyanoacrylic acid (acceptor) termini linked via various number of thiophene ring, phenylcarbazole, carbazole, benzene and fluorene units were synthesized and studied for their applications in DSSCs. For the
fluorene based dyes, B2 dye (containing electron-donating 9-butylcarbazole units) showed the highest molar extinction coefficient, as a result it produced the highest PCE value of 3.73% \( (V_{oc} = 0.69 \, V, \, J_{sc} = 9.43 \, mA \, cm^{-2}, \, FF = 0.56) \) under standard AM 1.5 sunlight with a IPCE plateau of 71%. The symmetrical carbazole based dye showed PCE of 2.44%, \( J_{sc} \) of 6.00 mA cm\(^{-2}\), \( V_{oc} \) of 0.57 mV and a \( FF \) of 0.71.
References:


Chapter 5 Synthesis and Characterization of Novel Metallopolyyne Polymers as New Functional Materials for Application in Solar Cells

5.1 Introduction

Since the mid-1990s, many of the barriers to the development of the metallopolymers have been overcome through the discovery of new synthetic approaches. Polymerization protocols of soluble and stable high molecular weight metallopolymers have become readily available. Afterwards, the realm of metallopolymers has been rapidly expanding as the polymers have provided access to new properties and applications and have shown a wide variety of state-of-the-art characterization tools. Up to the present, moment metallopolymers still intrigue most scientists because they possess a linear combination of unique redox, electronic, magnetic, optical, and catalytic properties, and they are easily processed and fabricated into thin films, fibers, and other forms.

Among the metallopolymers, rigid rod transition metal acetylide polymers or polymetallaynes are one of the most popularly studied polymers. The alkynyl unit has a linear geometry as well as an unsaturated character. As a consequence, they can possess unique properties, such as electrical conductivities, luminescence properties, nonlinear optical properties, liquid crystallinity, and photovoltaic behavior. In the
1970s, Hagihara et al. developed the first synthetic methodologies of transition metal acetylide oligomers based on the synthesis of polymeric Pt and Pd acetylides.\textsuperscript{[2–5]} The development has aroused scientist’s interest because metal acetylide polymers possess a wide range of applications in molecular electronics and materials science.\textsuperscript{[6, 7]}

Especially, the platinum alkyne organometallic units have attracted a great deal of interest. They can be incorporated into the conjugated polymers as a result of the fact that the d-orbital of the Pt can overlap with the p-orbital of the alkyne unit, leading to an enhancement in electronic conjugation and delocalization along the polymer chain. Moreover, due to the strong spin-orbital coupling, efficient intersystem crossing in such organometallic species facilitates the formation of triplet excited states which have longer lifetimes and thus allow extended exciton diffusion lengths.\textsuperscript{[11]} On the basis of this consideration, platinum alkynyl conjugated organic polymers have been a good candidate for inclusion into such a polymeric backbone.\textsuperscript{[12]} Recently, efficient solar cells based on platinum metallopolyyne:PCBM bulk heterojunctions has been reported by our research group.\textsuperscript{[13]}

1,2,3-Benzotriazole (BTz), which is similar to 2,1,3-benzothiadiazole, is a known heteroaromatic compound with a strong electron-accepting feature because of two electron-withdrawing imine nitrogen atoms. Also, the ease of modification of the N–H bond of BTz unit can allow tuning of its structural and electronic properties to
achieve processable BTz-containing polymers. Several groups have used BTz-based homopolymers and copolymers in light emitting or electrochromic devices. For instance, Cao group synthesized copolymers from fluorene and BTz units, which emitted a blue electroluminescence.\cite{11} Gong and Cao groups copolymerized BTz segments with phenothiazine vinylene units to obtain orange-red light-emitting copolymers.\cite{12} Recently, Toppare et al. copolymerized BTz units with 3,4-ethylenedioxythiophene or thiophene segments to construct some copolymers which showed some interesting electrochromic properties.\cite{13} Therefore, our group was interested in further investigating the potential of this unit specifically for applications in solar cells.

In addition, benzodithiophene (BDT) unit and the polymers show broad absorption, low energy bandgap, tunable electronic energy levels and promising photovoltaic properties.\cite{14} By now, the copolymers composed of BDT unit and thieno[3,4-\textit{b}]thiophene unit show high photovoltaic efficiency of 5 to 7%.\cite{15,16} Also, BDT has a large planar conjugated structure and easily forms \(\pi\)-\(\pi\) stacking, which improves mobility.\cite{17} These results indicate that BDT could be a good candidate in constructing new conjugated polymer donors for solar cells.

The general structure for the platinum polyyne polymers in this chapter is shown in Figure 5.1. The metal polyyne polymer has a linear backbone which consists of
platinum metal center Pt, spacer or electron-donating group R and auxiliary ligands L.

The polymers are generally soluble in organic solvents and the solubility as well as polymer length can be modified by an appropriate selection of R or L units. Consequently, we chose BTz and BDT as the electron-donating group R in this chapter.

![Figure 5.1 General skeleton of the platinum polyyne polymer.](image)

### 5.2 Synthesis

Generally, the methods for preparing the new platinum(II) acetylide polymers P1–P4 and their corresponding model compounds M1–M4 are outlined in Schemes 5.1 to 5.3. The dibromo precursors L1-Br and L2-Br were synthesized as follows: starting from 1,2,3-benzotriazole, an alkylation reaction was performed to get 2-hexyl-2H-benzo[\(d\)][1,2,3]triazole, in this reaction by using KOH as base instead of \(t\)-BuOK as reported in the literature.\(^{[18]}\)

Because of the two possible alkylation positions of the benzotriazole, the desired isomer was isolated in 30% yield in the first step of the reaction sequence. This step was then followed by a dibromination reaction using a \(\text{Br}_2/\text{HBr}\) system to yield 4,7-dibromo-2-hexyl-2H-benzo[\(d\)][1,2,3]triazole.
Then, it reacted by a Suzuki coupling reaction with 2-thiophene boronic acid and a dibromination reaction using NBS as the brominating agent gave **L1-Br** and **L2-Br**.

Other dibromo precursors **L3-Br** and **L4-Br** were synthesized as follows: the acid chloride was prepared from the corresponding carboxylic acids by a milder selective reagent oxalyl chloride. Then, \( N, N \)-diethylthiophene-3-carboxamidem was prepared from thiophene-3-carbonyl chloride and diethylamine. Afterwards, \( N, N \)-diethylthiophene-3-carboxamide reacted with \( n \)-butyllithium in THF at 0 °C to produce the benzo[1,2-\( b:4,5-b' \)]dithiophene-4,8-dione. Subsequently, benzo[1,2-\( b:4,5-b' \)]dithiophene-4,8-dione was reduced by zinc dust in aqueous sodium hydroxide solution. When the reduction reaction was complete, 2-ethylhexyl bromide was added with a catalytic amount of tetrabutylammonium bromide. After being refluxed for 12 h, 4,8-bis(ethylhexyloxy)benzo[1,2-\( b:4,5-b' \)]dithiophene was obtained, and then it was brominated to give **L3-Br**. **L3-Br** then reacted via a Suzuki coupling reaction with 2-thiophene boronic acid followed by a dibromination reaction using NBS as the brominating agent to obtain **L4-Br**.

Conversion of the dibromide compounds (**L1-Br** to **L4-Br**) to their corresponding diethynyl congeners (**L1**–**L4**) can be readily achieved following the typical organic synthetic protocols for alkynylation of aromatic halides.\(^{[19]}\) Polymers **P1–P4** and model compounds **M1–M4** were prepared by the Sonogashira-type
dehydrohalogenation reaction between the diethynyl precursors (L1–L4) and platinum chloro precursor (trans-Pt(PBu₃)₂Cl₂). The feed mole ratio of the platinum precursor and the diethynyl ligands was 1:1. P1–P4 and M1–M4 were carefully purified to remove ionic impurities and catalyst residues, followed by repeated precipitation and isolation.

**Scheme 5.1** Synthesis of P1–P2: i) C₆H₅Br, KOH, CH₃OH; ii) Br₂/HBr; iii) Pd(PPh₃)₄, K₂CO₃ (2 M, aq), THF; iv) NBS, THF; v) CuI, Pd(OAc)₂, PPh₃; vi) K₂CO₃, CH₂Cl₂/CH₃OH; vii) trans-[Pt(PBu₃)₂Cl₂], CuI, Et₃N/CH₂Cl₂.
Scheme 5.2 Synthesis of P3–P4: i) Oxalyl chloride, CH₂Cl₂; ii) (C₂H₅)₂NH, CH₂Cl₂; iii) n-BuLi, THF; iv) Zn, NaOH, H₂O, 2-ethylhexyl bromide, TBAB; v) Br₂, CH₂Cl₂; vi) thiophen-2-yl-2-boronic acid, Pd(PPh₃)₄, K₂CO₃ (2 M, aq), THF; vii) NBS, CH₂Cl₂; viii) CuI, Pd(OAc)₂, PPh₃; ix) K₂CO₃, CH₂Cl₂/CH₃OH; x) trans-[Pt(PBu₃)₂Cl₂], CuI, Et₃N/CH₂Cl₂.
**Scheme 5.3** Synthesis of M1–M4: i) trans-[Pt(PPh₃)₂Cl₂], CuI, Et₃N/CH₂Cl₂.

5.3 Results and Discussion

5.3.1 Spectroscopic Characterization

All of the ligands, platinum(II) polymers and model complexes were fully characterized by common spectroscopic techniques including ¹H, ¹³C and ³¹P NMR spectroscopy and infrared spectroscopy. All the NMR data of the intermediates and dyes are summarized in the experimental part of Chapter 8.

¹H, ¹³C and ³¹P NMR analyses clearly demonstrate a well-defined structure for each of the compounds. All the proton signals of aromatic rings are in the downfield region (δ, above 6.70 ppm), and alkyl groups are in the upfield region (δ, below 4.3 ppm), and the sharp signals of C=C-H of ligands are located at around 3.5 ppm, which disappeared in the spectra of polymers and model complexes, indicating the two Pt
centers were capped by ligands. The strong single $^{31}\text{P}$ signals flanked with two satellites for the platinum units are consistent with a *trans*-geometry of the square-planar Pt unit. The $^1J_{\text{P-Pt}}$ values are around 2300 Hz for the PBu$_3$ moieties, which are typical of those for related *trans*-PtP$_2$ systems.$^{20}$ The $^1\text{H}$ NMR spectra of L$_2$, P$_1$ and M$_3$ are shown in Figures 5.2, 5.3 and 5.4 respectively. The $^{13}\text{C}$ NMR spectra of L$_2$ and M$_3$ are shown in Figures 5.5 and 5.6, respectively. Also, the $^{31}\text{P}$ NMR spectra of P$_3$ and M$_3$ are shown in Figures 5.7 and 5.8, respectively.

**Figure 5.2** $^1\text{H}$ NMR spectrum of L$_2$ in CDCl$_3$. 
Figure 5.3 $^1$H NMR spectrum of P1 in CDCl$_3$.

Figure 5.4 $^1$H NMR spectrum of M3 in CDCl$_3$. 
Figure 5.5 $^{13}$C NMR spectrum of L2 in CDCl$_3$.

Figure 5.6 $^{13}$C NMR spectrum of M3 in CDCl$_3$. 
Figure 5.7 $^{31}$P NMR spectrum of P3 in CDCl$_3$.

Figure 5.8 $^{31}$P NMR spectrum of M3 in CDCl$_3$. 
5.3.2 Photophysical Properties

The UV-Vis absorption spectra of the ligands L1–L4, polymers P1–P4 and model complexes M1–M4 in CH2Cl2 at room temperature are displayed in Figure 5.9 to Figure 5.12 and the relevant data are collected in Table 5.1.

For the series of BTz based molecules, the UV/Vis absorption spectra of L1, M1 and P1 are shown in Figure 5.9. And those of L2, M2 and P2 are shown in Figure 5.10. Both of the L1 and L2 show strong absorption bands at 412 nm and 458 nm, respectively, which can be assigned to the π-π* transitions.[23] The small red shift (46 nm) of L2 is due to the additional thiophene rings, which extend the π-conjugation of L2 as compared to L1. The absorption of M1–M2 and P1–P2 have a significant red shift as compared to those of the corresponding ligands, which is attributed to the extension of metal-organic π-conjugation in the presence of electron-rich heavy platinum unit.

For the series of BDT based molecules, the UV/Vis absorption spectra of L3, M3 and P3 are shown in Figure 5.11, and those of L4, M4 and P4 are shown in Figure 5.12. As a result of the characteristic of heavy platinum complexes, a slight red shift was observed in the platinum complexes M3–M4, and polymers P3–P4 show a larger red shift than the platinum complexes due to their longer conjugation length. From the results, it can be clearly observed that by increasing the conjugation length of the
polymer chain with an electron-rich thiophene ring, a reduction in the HOMO-LUMO gap appears.\cite{41} By incorporating the thiophene-containing ligand with platinum metal center, a more extended $\pi$-electron delocalized system is expected through the rigid organometallic and oligothienyl chain.

All of the ligands $L_1$–$L_4$ and polymers $P_1$–$P_4$ displayed photoluminescence at room temperature (Figure 5.13 and Table 5.2) when they are excited at their respective absorption bands and the fluorescence peak maximum ranges from 456 to 567 nm. Similar to the absorption spectra, the presence of electron-donating groups and extension of the conjugation by thiophene group would shift the emission maximum to the red.

![Normalized absorption spectra of $L_1$, $P_1$ and $M_1$ measured in $\text{CH}_2\text{Cl}_2$.](image)

**Figure 5.9** Normalized absorption spectra of $L_1$, $P_1$ and $M_1$ measured in $\text{CH}_2\text{Cl}_2$. 
Figure 5.10 Normalized absorption spectra of L2, P2 and M2 measured in CH₂Cl₂.

Figure 5.11 Normalized absorption spectra of L3, P3 and M3 measured in CH₂Cl₂.
Figure 5.12 Normalized absorption spectra of L4, P4 and M4 measured in CH₂Cl₂.

Table 5.1 Absorption data for ligands, polymers and model complexes in CH₂Cl₂.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>λ_{abs} (nm)</th>
<th>Polymer</th>
<th>λ_{abs} (nm)</th>
<th>Model complex</th>
<th>λ_{abs} (nm)</th>
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</thead>
<tbody>
<tr>
<td>L1</td>
<td>412</td>
<td>P1</td>
<td>474, 499</td>
<td>M1</td>
<td>462</td>
</tr>
<tr>
<td>L2</td>
<td>458</td>
<td>P2</td>
<td>495</td>
<td>M2</td>
<td>487</td>
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<tr>
<td>L3</td>
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<td>P3</td>
<td>374, 428</td>
<td>M3</td>
<td>362, 384, 404</td>
</tr>
<tr>
<td>L4</td>
<td>382, 417</td>
<td>P4</td>
<td>445, 474</td>
<td>M4</td>
<td>439, 465</td>
</tr>
</tbody>
</table>
Figure 5.13 Normalized emission spectra of L1–L4 and P1–P4 measured in CH$_2$Cl$_2$.

Table 5.2 Emission data for ligands and polymers in CH$_2$Cl$_2$.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>$\lambda_{em}$ (nm)</th>
<th>Polymer</th>
<th>$\lambda_{em}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>456, 479</td>
<td>P1</td>
<td>532</td>
</tr>
<tr>
<td>L2</td>
<td>515, 548</td>
<td>P2</td>
<td>567</td>
</tr>
<tr>
<td>L3</td>
<td>458</td>
<td>P3</td>
<td>448, 464</td>
</tr>
<tr>
<td>L4</td>
<td>517</td>
<td>P4</td>
<td>492, 523</td>
</tr>
</tbody>
</table>
5.3.3 Electrochemical Properties

To investigate the electron transfer from the excited dye molecule to the conductive band ($E_{cb}$) of TiO$_2$ and understand the molecular orbital energy levels, cyclic voltammetry (CV) was performed for the dyes in thin films on glassy carbon electrode measured in 0.1 M tetrabutylammonium hexafluorophosphate solution in acetonitrile at a scan rate of 50 mV s$^{-1}$. The reference electrode was Ag/AgCl calibrated with ferrocene-ferrocenium ($\text{Fc}^+/\text{Fc}$, 0.07 V) as an internal reference. The results are summarized in Table 5.3.

The polymers have different LUMO energy levels of $-3.44 \text{ eV}$ to $-3.49 \text{ eV}$, and HOMO energy levels of $-5.17 \text{ eV}$ to $-5.37 \text{ eV}$. As described in the literature, with increasing number of the thiophene ring, their oxidation potentials become smaller and their HOMO energy levels are elevated.$^{[21, 22]}$ This phenomenon was also observed in polymers $\text{P1-P2}$, and $\text{P3-P4}$. 
Figure 5.14 Cyclic voltammograms of the thin films of P1–P4 on glassy carbon electrode measured in 0.1 M Bu4NPF6 acetonitrile solution at a scan rate of 50 mV s⁻¹.
Table 5.3 Electrochemical properties of P1–P4.

<table>
<thead>
<tr>
<th>Polymer</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>P1</td>
<td>0.50</td>
<td>-5.23</td>
<td>-1.27</td>
<td>-3.46</td>
<td>1.76</td>
</tr>
<tr>
<td>P2</td>
<td>0.44</td>
<td>-5.17</td>
<td>-1.28</td>
<td>-3.45</td>
<td>1.72</td>
</tr>
<tr>
<td>P3</td>
<td>0.64</td>
<td>-5.37</td>
<td>-1.24</td>
<td>-3.49</td>
<td>1.88</td>
</tr>
<tr>
<td>P4</td>
<td>0.51</td>
<td>-5.24</td>
<td>-1.29</td>
<td>-3.44</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)

5.3.4 Molecular Weight Determination of Metallopolyyne Polymers

For the Gel Permeation Chromatography (GPC) results, the molecular weights of the metallopolymers (P1–P4) were obtained. The number average molecular weight ($M_n$), the weight average molecular weight ($M_w$), the polydispersity index (PDI) as well as the degree of polymerization are tabulated in Table 5.4. The highest number-average molecular weight of the polymer reached 27780 g mol$^{-1}$ for P3. Degree of polymerization (DP) indicates the repeating unit of heterocyclic rings along the polymer chain. The highest DP of up to 21 heterocyclic rings was obtained for P1.
Table 5.4 GPC data for P1–P4.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$\textsuperscript{a}</th>
<th>$M_w$\textsuperscript{b}</th>
<th>PDI\textsuperscript{c}</th>
<th>DP\textsuperscript{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>22960</td>
<td>34000</td>
<td>1.35</td>
<td>21</td>
</tr>
<tr>
<td>P2</td>
<td>14150</td>
<td>23070</td>
<td>1.63</td>
<td>12</td>
</tr>
<tr>
<td>P3</td>
<td>27780</td>
<td>48741</td>
<td>1.75</td>
<td>21</td>
</tr>
<tr>
<td>P4</td>
<td>26850</td>
<td>42190</td>
<td>1.57</td>
<td>19</td>
</tr>
</tbody>
</table>

\textsuperscript{a} $M_n$ = Number-average molecular weight  
\textsuperscript{b} $M_w$ = Weight-average molecular weight  
\textsuperscript{c} PDI = Polydispersity index  
\textsuperscript{d} DP = Degree of polymerization (calculated from $M_n$ values)

5.5 Applications in Polymer Solar Cells (PSCs)

Polymer solar cells (PSCs) were fabricated with the structure of ITO/PEDOT:PSS/polymer:PCBM/Mg/Al. The ITO glass was pre-cleaned and modified by a thin layer of PEDOT:PSS (Bayer) which was spin-cast from a PEDOT:PSS aqueous solution on the ITO substrate, and was dried subsequently at 150 °C for 10 min in a vacuum oven. The thickness of the PEDOT:PSS layer was about 30 nm. The photosensitive blend layer of polymer and PCBM was prepared by spin-coating the chlorobenzene solution of the polymers and PCBM (1:1, w/w) with the polymer concentration of 10 mg mL\textsuperscript{-1} on the ITO/PEDOT:PSS electrode, and dried at 80 °C for 30 min. The thickness of the photosensitive layer was controlled to
ca. 80 nm by adjusting the rotating speed of the spin-coating, and was measured on an Ambios Tech. XP-2 profilometer. Then the metal cathode, which is made up of Ca and Al, was deposited on the polymer layer by vacuum evaporation under $5 \times 10^{-5}$ Pa. The Ca layer was deposited by a speed of 0.03–0.05 nm per second, and the thickness of which is 20 nm. Then, the Al layer was deposited by a speed of 0.1–0.3 nm per second, and the thickness of which is 160 nm. The PSC devices were fabricated and the effective area of one cell is 4 mm$^2$.

The current-voltage ($I-V$) measurement of the devices was conducted on a computer-controlled Keithley 236 Source Measure Unit. A Xenon lamp with AM 1.5 filter was used as the white light source, and the optical power at the sample was 100 mW cm$^{-2}$. The input photon to converted current efficiency (IPCE) was measured using a Keithley 2000 DMM coupled with WDG3 monochromator and 500 W Xenon lamp. The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell.

Polymer solar cells (PSCs) were fabricated by using the metallopolymers developed in this section as an electron donor and PCBM as an electron acceptor. Relevant data are summarized in Table 5.5.

Figure 5.15 shows the $I-V$ curves of solar cells with $P1-P2:PCBM$ (1:3 w/w) active layers under simulated AM 1.5 solar irradiation, and photocurrent action
spectra of solar cells with P1–P2 are shown in Figure 5.16. A considerable increase in the short-circuit current density ($J_{sc}$) and PCE can be observed in P2 relative to P1 due to an increase of the conjugation length of the chain with thiophene rings. The PCE of 1.95% was achieved for P2 with a $V_{oc} = 0.80$ V, $J_{sc} = 2.47$ mA cm$^{-2}$ and $FF = 0.56$ under illumination of an AM 1.5 solar cell simulator in a 1:3 (P2:PCBM) blend ratio.

PSCs with P3:PCBM (1:1 w/w) and P4:PCBM (1:1 w/w) active layers were prepared at different spin-casting speed under simulated AM 1.5 solar irradiation (Figure 5.17 to 5.20). A higher PCE of 0.21% can be obtained for P3 with $V_{oc} = 0.73$ V, $J_{sc} = 0.75$ mA cm$^{-2}$ and $FF = 0.38$ under illumination of an AM 1.5 solar cell simulator in a 1:1 (P3:PCBM) blend ratio at 2500 rpm. Also, a higher PCE of 0.21% can be obtained for P3 with $V_{oc} = 0.87$ V, $J_{sc} = 2.59$ mA cm$^{-2}$ and $FF = 0.38$ under illumination of an AM 1.5 solar cell simulator in a 1:1 (P4:PCBM) blend ratio at 3000 rpm. The PCE of P4 is slightly higher than that of P3 due to the additional thiophene unit of P4.

PSCs were prepared with different weight ratios of P4 to PCBM at 3000 rpm. The blend ratio is an important parameter in controlling the morphology and phase separation of the film. In addition, different weight ratios affected all photovoltaic parameters [open-circuit voltage ($V_{oc}$), short-circuit current density ($J_{sc}$) and the fill
factor ($FF$). A higher PCE of 1.74% can be achieved for P4 with $V_{oc} = 0.84$ V, $J_{sc} = 4.62$ mA cm$^{-2}$ and $FF = 0.44$ under illumination of an AM 1.5 solar cell simulator in a 1:1.5 (P4:PCBM) blend ratio.

Table 5.5 Solar cell performance of the devices with P1–P4.

<table>
<thead>
<tr>
<th>PSCs$^a$</th>
<th>$V_{oc}$ / V</th>
<th>$J_{sc}$ / mA cm$^{-2}$</th>
<th>$FF$</th>
<th>PCE / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1:PCBM (1:3, 1000)</td>
<td>0.80</td>
<td>2.47</td>
<td>0.56</td>
<td>1.11</td>
</tr>
<tr>
<td>P2:PCBM (1:3, 1000)</td>
<td>0.81</td>
<td>4.24</td>
<td>0.57</td>
<td>1.95</td>
</tr>
<tr>
<td>P3:PCBM (1:1, 1000)</td>
<td>0.69</td>
<td>0.71</td>
<td>0.36</td>
<td>0.18</td>
</tr>
<tr>
<td>P3:PCBM (1:1, 1500)</td>
<td>0.69</td>
<td>0.70</td>
<td>0.37</td>
<td>0.18</td>
</tr>
<tr>
<td>P3:PCBM (1:1, 2000)</td>
<td>0.73</td>
<td>0.64</td>
<td>0.37</td>
<td>0.18</td>
</tr>
<tr>
<td>P3:PCBM (1:1, 2500)</td>
<td>0.73</td>
<td>0.75</td>
<td>0.38</td>
<td>0.21</td>
</tr>
<tr>
<td>P3:PCBM (1:1, 3000)</td>
<td>0.71</td>
<td>0.65</td>
<td>0.37</td>
<td>0.17</td>
</tr>
<tr>
<td>P3:PCBM (1:1, 3500)</td>
<td>0.58</td>
<td>0.50</td>
<td>0.34</td>
<td>0.10</td>
</tr>
<tr>
<td>P4:PCBM (1:1, 1000)</td>
<td>0.83</td>
<td>0.35</td>
<td>0.23</td>
<td>0.07</td>
</tr>
<tr>
<td>P4:PCBM (1:1, 1500)</td>
<td>0.82</td>
<td>2.02</td>
<td>0.31</td>
<td>0.53</td>
</tr>
<tr>
<td>P4:PCBM (1:1, 2000)</td>
<td>0.85</td>
<td>2.43</td>
<td>0.35</td>
<td>0.74</td>
</tr>
<tr>
<td>P4:PCBM (1:1, 2500)</td>
<td>0.86</td>
<td>2.58</td>
<td>0.35</td>
<td>0.78</td>
</tr>
<tr>
<td>P4:PCBM (1:1, 3000)</td>
<td>0.87</td>
<td>2.59</td>
<td>0.35</td>
<td>0.81</td>
</tr>
<tr>
<td>Composition</td>
<td>V1</td>
<td>V2</td>
<td>V3</td>
<td>V4</td>
</tr>
<tr>
<td>------------------------</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>P4:PCBM (1:1, 3500)</td>
<td>0.87</td>
<td>2.43</td>
<td>0.35</td>
<td>0.76</td>
</tr>
<tr>
<td>P4:PCBM (1:0.8, 3000)</td>
<td>0.41</td>
<td>1.32</td>
<td>0.30</td>
<td>0.16</td>
</tr>
<tr>
<td>P4:PCBM (1:1, 3000)</td>
<td>0.81</td>
<td>2.80</td>
<td>0.36</td>
<td>0.83</td>
</tr>
<tr>
<td>P4:PCBM (1:1.5, 3000)</td>
<td>0.84</td>
<td>4.62</td>
<td>0.44</td>
<td>1.74</td>
</tr>
<tr>
<td>P4:PCBM (1:2, 3000)</td>
<td>0.83</td>
<td>3.58</td>
<td>0.43</td>
<td>1.30</td>
</tr>
<tr>
<td>P4:PCBM (1:3, 3000)</td>
<td>0.78</td>
<td>2.65</td>
<td>0.36</td>
<td>0.76</td>
</tr>
<tr>
<td>P4:PCBM (1:4, 3000)</td>
<td>0.83</td>
<td>3.17</td>
<td>0.39</td>
<td>1.03</td>
</tr>
</tbody>
</table>

*The numbers in parentheses denote the ratio of polymer/PCBM (w/w) and the spinning speed, respectively.*
Figure 5.15 $J-V$ curves of solar cells with P1–P2:PCBM (1:3 w/w) active layers under simulated AM 1.5 solar irradiation.

Figure 5.16 Photocurrent action spectra of solar cells with P1–P2.
**Figure 5.17** $J-V$ curves of solar cells with P3:PCBM (1:1 w/w) active layers at different spin-casting speed under simulated AM 1.5 solar irradiation.

**Figure 5.18** Photocurrent action spectra of solar cells with P3 at different spin-casting speed.
Figure 5.19 $J–V$ curves of solar cells with P4:PCBM (1:1 w/w) active layers at different spin-casting speed under simulated AM 1.5 solar irradiation.

Figure 5.20 Photocurrent action spectra of solar cells with P4 at different spin-casting speed.
Figure 5.21 $J-V$ curves of solar cells with different $P4$:PCBM ratios in the active layers under simulated AM 1.5 solar irradiation.

Figure 5.22 Photocurrent action spectra of solar cells with different $P4$:PCBM ratios.
5.6 Concluding Remarks

In order to achieve the goal of improving PCE of solar cells, four new platinum polyyne polymers were prepared via the Sonogashira-type dehydrohalogenation reaction between the ethynyl precursor and trans-Pt(PBu$_3$)$_2$Cl$_2$. All the polymers were carefully purified by column chromatography over silica gel and repeated precipitation, leading to the polymers in good yields and high purity. All of them are air-stable and well characterized by different spectroscopic methods and photophysical measurements. Their photovoltaic behaviors were fully investigated. Their model compounds were also prepared and studied. The highest PCE of 1.95% was achieved from solar cell based on P2 with a $V_{oc} = 0.81$ V, $J_{sc} = 4.24$ mA cm$^{-2}$ and $FF = 0.57$ under illumination of an AM 1.5 solar cell simulator in a 1:3 (P2:PCBM) blend ratio.
References:


Chapter 6 Novel Small Molecules for Bulk Heterojunction Solar Cells

6.1 Introduction

Organic solar cell research has demonstrated significant accomplishments in the past few years with the use of low band gap polymers as the donor material blended with a fullerene to form the bulk-heterojunction (BHJ) solar cell. PCE in excess of 9% has recently been achieved.\(^1\) However, organic materials that can enhance the efficiency beyond 10% required for commercial application are still out of sight. The recent report of solution processable small molecules with PCE about 7% has generated tremendous hope for achieving PCE higher than 10% because the evolution of conjugated polymers started from less than 1% PCE.\(^2\) Solution processable small molecule donors offer relatively simple synthesis and purification, mono-dispersion and well-defined structures, no end group contaminants, relatively high charge carrier mobility, and better batch-to-batch reproducibility. Moreover, small molecules offer a rich variety of chemical structures.\(^3\) Solution processable small molecule solar cells with \(p\)-DTS(PTTh\(_2\))\(_2\)/PC\(_{71}\)BM blend as the photo-active layer demonstrated PCE of 6.7%, employing MoO\(_x\) as the anode interlayer.\(^4\) However, the purity of the donor material is limited by the incorporation within the molecular structure of the PT pyridyl nitrogen sites that are sensitive to protonation. This problem was overcome by
substituting a -CF- group as an inert electron-withdrawing functionality in place of PT pyridyl nitrogen.\textsuperscript{[2]} The modified small molecule, p-DTS(FBTTh\textsubscript{2})\textsubscript{2}, yields the PCE value up to 7%. However, the solubility of p-DTS(FBTTh\textsubscript{2})\textsubscript{2} is quite low. In this work, hexylthiophene was introduced to enhance the solubility.

![Figure 6.1 The chemical structure of p-DTS(FBTTh\textsubscript{2})\textsubscript{2}.](image)

High performance polymer bulk heterojunction solar cells made from mixtures of poly(3-hexylthiophene) (P3HT) and PC\textsubscript{61}BM have been reported, with maximum PCE at 4 to 5\%.\textsuperscript{[5]} Also, poly(3-hexylthiophene) and its derivatives showed high charge-carrier mobilities.\textsuperscript{[6]} In the past decade, regioregular poly(3-alkylthiophene-2,5-diyl)s\textsuperscript{[7]} were frequently used in the fabrication of plastic electronics devices,\textsuperscript{[8]} including photovoltaic cells.\textsuperscript{[9]} Therefore, introduction of a regioregular hexylthiophene is an attractive building block.

The incorporation of double bond character between thiophene units as a conjugated spacer in a molecule can reduce the band gap, increase the degree of coplanarity and limit the rotational disorder inherent between thiophene units.\textsuperscript{[10]} Thienylenevinylene based materials can also demonstrate a high charge-carrier
mobility as a result of a high planarity by introduction of vinylene linkages. In addition, incorporation of thienothiophene to polythiophene can increase structural order and crystallinity which then exhibit high hole mobility.\textsuperscript{[11-14]}

Recently, a dithienogermole (DTG)-containing conjugated polymer was reported on inverted BHJ solar cells. The DTG-containing polymer gave a PCE of 7.3\%, compared to 6.6\% for the dithienosilole (DTS)-containing cells under identical conditions. Also, the HOMO level of DTG-containing polymer is higher than that of the DTS-containing polymer.\textsuperscript{[15]}

Based on the above considerations, seven new organic small molecules AT\textsubscript{1}–AT\textsubscript{7} were designed and synthesized with head-to-head coupled hexylthiophene, thienothiophene, thienylenevinylene, dithienosilole and dithienogermole units. These seven small molecules have been applied to the bulk heterojunction solar cells and the corresponding photovoltaic properties, electronic and optical properties are also presented in this contribution.

6.2 Synthesis

The synthesis of the small molecules is shown in Schemes 6.1–6.5. Starting with DTS or DTG, each of the corresponding SnMe\textsubscript{3} derivatives was coupled with FBT under Stille conditions to give Br-FBT-DTS-FBT-Br or Br-FBT-DTG-FBT-Br
Scheme 6.1. 2-Hexylthiophene was stannylated by \( n\)-BuLi to give (5-hexylthiophen-2-yl)trimethylstannane which was then coupled to FBT to afford AT1-Br. On the other hand, the head-to-head-coupled 3-hexyl-2-(3-hexylthiophen-2-yl)thiophene was obtained by Suzuki coupling reaction between 2-bromo-3-hexylthiophene, XPhos, palladium acetate, potassium fluoride and 2-(3-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, in THF and water. The XPhos is one of the Buchwald’s biaryl monophosphine ligand, which was shown to be effective in Suzuki coupling to make hindered carbon-carbon bonds.\(^{16}\) Then, stannylated 3-hexyl-2-(3-hexylthiophen-2-yl)thiophene was coupled to AT1-Br under Stille conditions and then stannylated by 2.2 equivalents of LDA and 1.1 equivalent of trimethyltin chloride at \(-78^\circ C\) to afford AT1-Sn. Finally, AT1 was obtained by Stille coupling between AT1-Sn and Br-FBT-DTS-FBT-Br (Scheme 6.2).

AT2 was obtained by Stille coupling between AT1-Sn and Br-FBT-DTS-FBT-Br and then AT1-Br and (5-(5-hexylthiophen-2-yl)thiophen-2-yl)trimethylstannane. For AT3, the head-to-head-coupled 3-hexyl-2-(3-hexylthiophen-2-yl)thiophene was stannylated first and then coupled with AT1-Br under Stille conditions to yield AT3 (Scheme 6.3).

Stannylated AT5-Sn was prepared by Stille coupling between AT1-Br and
tributyl(thiophen-2-yl)stannane. For the preparation of AT6-Sn, (E)-1,2-bis(trimethylstannyl)ethane was coupled with 2-bromo-3-hexylthiophene under Stille coupling conditions to afford 3-hexyl-2-((E)-2-(3-hexylthiophen-2-yl)vinyl)thiophene. The stannylated 3-hexyl-2-((E)-2-(3-hexylthiophen-2-yl)vinyl)thiophene underwent Stille coupling with AT1-Br followed by stannylation with LDA to give AT6-Sn. For the preparation of AT7-Sn, 2,5-bis(trimethylstannyl)thieno[3,2-b]thiophene was coupled with 2-bromo-3-hexylthiophene under Stille coupling conditions to give 2,5-bis(3-hexylthiophen-2-yl)thieno[3,2-b]thiophene. Afterwards, the stannylated 2,5-bis(3-hexylthiophen-2-yl)thieno[3,2-b]thiophene reacted via Stille coupling with AT1-Br followed by stannylation with LDA to give AT7-Sn (Scheme 6.4). AT4, AT5, AT6 and AT7 were obtained by Stille coupling between Br-FBT-DTG-FBT-Br and AT1-Sn, AT5-Sn, AT6-Sn and AT7-Sn, respectively.

The structures of all the molecules were verified by NMR spectroscopy and field desorption (FD) mass spectrometry. The molecules are purple or blue in color and are readily soluble in common organic solvents such as THF, CH₂Cl₂, and CHCl₃.
Scheme 6.1 Synthetic routes of Br-FBT-DTS-FBT-Br and Br-FBT-DTG-FBT-Br: i) 
n-BuLi, Me₃SnCl; ii) toluene, Pd(PPh₃)₄.

Scheme 6.2 Synthetic routes of AT1: i) n-BuLi, Me₃SnCl; ii) toluene, Pd(PPh₃)₄; iii) 
KF, Pd(OAc)₂, 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos), 
THF/H₂O; iv) n-BuLi, Me₃SnCl; v) toluene, Pd(PPh₃)₄, microwave; vi) LDA, 
Me₃SnCl; vii) toluene, Pd(PPh₃)₄, microwave.
Scheme 6.3 Synthetic routes of AT2 and AT3: i) toluene, Pd(PPh₃)₄, microwave; ii) toluene, Pd(PPh₃)₄, microwave; iii) n-BuLi, Me₃SnCl; iv) toluene, Pd(PPh₃)₄, microwave.
Scheme 6.4 Synthetic routes of AT5-Br to AT7-Br: i) toluene, Pd(PPh₃)₄, microwave; ii) LDA, Me₃SnCl; iii) toluene, Pd(PPh₃)₄, microwave; iv) n-BuLi, Me₃SnCl; v) toluene, Pd(PPh₃)₄, microwave; vi) LDA, Me₃SnCl; vii) toluene, Pd(PPh₃)₄, microwave; viii) n-BuLi, Me₃SnCl; ix) toluene, Pd(PPh₃)₄, microwave; x) LDA, Me₃SnCl.
Scheme 6.5 Synthetic routes of AT4 to AT7: toluene, Pd(PPh₃)₄, microwave.

6.3 Results and Discussion

6.3.1 Computational Studies

The molecules AT1–AT7 were subjected to geometrical optimizations using the DFT/B3LYP suite with a 6-31G** basis set.[17, 18] The minimum energy geometric structures of AT1–AT7 were also calculated. AT1, AT2, AT3, AT4, AT6 and AT7 were found to have a dihedral twist angle of 71°, 71°, 70°, 71°, 2°, and 58°
respectively (Figure 6.2). Only AT5 does not have a dihedral twist angle. It is completely linear.

Density functional theory (DFT) calculations of AT1 and AT5 were carried out in order to gain better insights into the electronic properties. The calculated HOMO of AT1 is −5.12 eV and LUMO is −3.11 eV (Figure 6.3). The calculated HOMO of AT5 is −4.83 eV and LUMO is −2.98 eV (Figure 6.4). For AT1, the HOMO density is mainly delocalized on the FBT-DTS-FBT and the head-to-head coupled hexylthiophene moiety. The LUMO density is located predominantly on the FBT-DTS-FBT. The orbitals are mainly localized on FBT-DTS-FBT due to the dihedral kink angle. These kinks can lead to conjugation breaks that confine the electronic excitations over small subunits.\[19\] For AT5, the HOMO density and LUMO density are entirely delocalized on the whole molecule. From this result, it indicates that the electron densities can be delocalized on the entire molecules only if there is a lack of dihedral twist angle.
Figure 6.2 Optimized geometries for AT1–AT7 using DFT calculations.
Figure 6.3 Contour plots of selected frontier orbitals of AT1.

Figure 6.4 Contour plots of selected frontier orbitals of AT5.
6.3.2 Spectroscopic Characterization

All the newly synthesized small molecules were well characterized by common spectroscopic techniques such as NMR spectroscopy. All the small molecules are air-stable and soluble in common organic solvents. All the compounds displayed characteristic $^1$H NMR spectra. All the NMR data of the intermediates and dyes are summarized in the experimental part of Chapter 8.

All the proton signals of aromatic rings of the small molecules are on the downfield region (above 6.90 ppm) and those of the alkyl chain are on the upfield region (below 3.00 ppm). The $^1$H NMR spectra of AT1, AT2 and AT4 are shown in Figures 6.5, 6.6 and 6.7, respectively. AT5 and AT6 showed well-defined resonance peaks in 1,1,2,2-tetrachloroethane-d$_2$ by increasing the measuring temperature (Figures 6.8 and 6.9).

All the carbon signals of aromatic rings of the small molecules are shown at above 100 ppm. In the upfield region, the signals of butyl group are shown below 40 ppm (Figures 6.10–6.12).

Mass spectra of the small molecules were carried out in a typical FD TOF experiment; molecules are ionized by a high-potential electric field. AT1 showed M$^+$, M$^{2+}$, and M$^{3+}$, and AT5 shows M$^+$ and M$^{2+}$ (Figures 6.13–6.14).
Figure 6.5 $^1$H NMR spectrum of AT1 in THF-d$_8$.

Figure 6.6 $^1$H NMR spectrum of AT2 in THF-d$_8$. 
Figure 6.7 $^1$H NMR spectrum of AT4 in THF-d$_8$. 
Figure 6.8 $^1$H NMR spectrum of AT5 in 1,1,2,2-tetrachloroethane-d$_2$. 

[Image of the NMR spectra at 60 °C, 80 °C, and 100 °C]
Figure 6.9 $^1$H NMR NMR spectrum of AT6 in 1,1,2,2-tetrachloroethane-d$_2$. 
Figure 6.10 $^{13}$C NMR spectrum of AT1 in THF-d$_8$.

Figure 6.11 $^{13}$C NMR spectrum of AT2 in THF-d$_8$. 
Figure 6.12 $^{13}$C NMR spectrum of AT3 in THF-d$_8$.

Figure 6.13 Mass spectrum of AT1.
6.3.3 Thermal Properties

Figures 6.15 and 6.16 illustrate the thermal transitions as determined by differential scanning calorimetry (DSC) at different heating rate to carry out the nonisothermal study of AT1 to AT6 and the data are summarized in Table 6.1. Cold crystallizations (T_{cc}) were observed for AT1 to AT3. AT1 has a cold crystallization at 68.8 °C followed by a melting transition at 85.8 °C; AT2 has a cold crystallization at 56.7 °C followed by a melting transition at 72.6 °C; AT3 has a cold crystallization at 69.3 °C followed by a melting transition at 106.2 and 123.6 °C. The cold
crystallization temperature is defined as the onset of an exothermic peak on heating from a sub-cooled liquid state to a crystalline solid state.\textsuperscript{[14]} This behavior is typical of polymers and other amorphous materials.\textsuperscript{[15, 16]} Distinct melting temperatures ($T_m$) of 259.3 °C and 244.3 °C upon heating and exothermic peaks ($T_c$) at 214.6 °C and 243.2 °C upon cooling were observed for AT5 and AT6, respectively. There are no exothermic peak and endothermic peak observed in AT4.

Table 6.1 Differential scanning calorimetry data of AT1–AT6.

<table>
<thead>
<tr>
<th></th>
<th>$T_{cc}$ (°C)$^a$</th>
<th>$T_c$ (°C)$^b$</th>
<th>$T_m$ (°C)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AT1</td>
<td>68.8</td>
<td>--</td>
<td>85.8</td>
</tr>
<tr>
<td>AT2</td>
<td>56.7</td>
<td>--</td>
<td>72.6</td>
</tr>
<tr>
<td>AT3</td>
<td>69.3</td>
<td>--</td>
<td>106.2, 123.6</td>
</tr>
<tr>
<td>AT4</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>AT5</td>
<td>--</td>
<td>214.6</td>
<td>259.3</td>
</tr>
<tr>
<td>AT6</td>
<td>--</td>
<td>243.2</td>
<td>244.3</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Temperature of cold crystallization

\textsuperscript{b} Exothermic temperature

\textsuperscript{c} Melting temperature
Figure 6.15 Phase transition of AT1 – AT3 as measured by differential scanning calorimetry.

Figure 6.16 Phase transition of AT4 – AT6 as measured by differential scanning calorimetry.
6.3.4 Photophysical Properties

Figure 6.17 provides the optical absorption spectra of AT1–AT7 in CHCl₃ solution and spin-casted films on glass from CHCl₃ (10 mg mL⁻¹), and the data are summarized in Table 6.2. AT1–AT7 exhibited broad low energy transitions with favorable overlap with the solar spectrum at 488 nm to 617 nm in CHCl₃. Upon substitution of the silicon atom (AT1) for germanium (AT4), a red-shifted absorption spectrum was observed with peaks at 569 and 571 nm.

Figure 6.17 shows that transitioning from solution to solid state gives rise to a red shift in wavelength of 30, 18, 90, 40, 36, 36 and 34 nm for compounds AT1–AT7, respectively. Normalized thin film absorption spectra of AT1, AT2, AT4, AT6 and AT7 displayed only red shift from solution to thin film with no additional features being observed, suggesting that as-cast films do not contain a large fraction of highly ordered domains. However, AT3 and AT5 showed distinct additional features in the low energy absorption bands which may be attributed to space interactions such as electron exchange and dipole-dipole in the solid state.[19,20]

Thermal annealing the thin films at 60 °C and 80 °C for 2 minutes led to a growth of blue shift for compounds AT1, AT3, AT4, AT5 and AT6, while AT2 and AT7 are red-shifted upon annealing the films. It suggests that the films of AT1, AT3, AT4, AT5 and AT6 cannot be heated when fabricating the BHJ devices.
Figure 6.17 Normalized absorption spectra of AT1–AT7 measured in solution, spin-casted films at room temperature, 60°C and 80°C.
Table 6.2 Photophysical data of AT1−AT6 in solution and films.

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{abs}$ in CHCl$_3$ (nm)</th>
<th>$\lambda_{abs}$ in film (nm)</th>
<th>$\lambda_{abs}$ in film at 60 °C (nm)</th>
<th>$\lambda_{abs}$ in film at 80 °C (nm)</th>
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<tr>
<td>AT1</td>
<td>569</td>
<td>597</td>
<td>594</td>
<td>590</td>
</tr>
<tr>
<td>AT2</td>
<td>578</td>
<td>596</td>
<td>614</td>
<td>596</td>
</tr>
<tr>
<td>AT3</td>
<td>488</td>
<td>578, 628</td>
<td>577, 627</td>
<td>574, 624</td>
</tr>
<tr>
<td>AT4</td>
<td>571</td>
<td>611</td>
<td>598</td>
<td>598</td>
</tr>
<tr>
<td>AT5</td>
<td>592</td>
<td>628, 683</td>
<td>627, 682</td>
<td>627, 682</td>
</tr>
<tr>
<td>AT6</td>
<td>617</td>
<td>653</td>
<td>647</td>
<td>646</td>
</tr>
<tr>
<td>AT7</td>
<td>575</td>
<td>609</td>
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</tr>
</tbody>
</table>

6.3.5 Electrochemical Properties

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of small molecules AT1−AT7 were calculated using the redox potentials as determined from electrochemical measurements using cyclic voltammetry. Cyclic voltammograms obtained by this technique are shown in Figures 6.18 and 6.19, and the data are summarized in Table 6.3. The cyclic voltammetry (CV) measurements were conducted using a standard three-electrode configuration under an argon atmosphere. A three-electrode cell equipped with a glassy carbon working
electrode, a silver wire reference electrode, and a Pt wire counter electrode was employed. The measurements were performed in absolute acetonitrile with tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte at a scan rate of 50–100 mV s\(^{-1}\). Films for CV test were drop-casted onto the glassy carbon working electrode from a chloroform solution at 2 mg mL\(^{-1}\). The absolute energy level of ferrocene/ferrocenium (Fc/Fc\(^+\)) is 4.8 eV below vacuum.

The highest occupied molecular orbital (HOMO) of AT1–AT7 lies in the range of –4.91 to –5.35 eV, and the lowest unoccupied molecular orbital (LUMO) of AT1–AT7 are in the range of –2.93 to –3.18 eV. These data suggest that the absorption and the frontier molecular orbitals of AT1–AT7 line up favorably with those of common fullerene acceptors to generate useful V\(_{oc}\) in BHJ solar cells.\(^{[17,18]}\)

By comparing dithienosilole (DTS)-containing small molecule (AT1) and dithienogermole (DTG)-containing small molecule (AT4), the onset of oxidation for DTS-containing (0.97 V vs Fc/Fc\(^+\)) is about 60 mV higher than that of DTG-containing (0.82 V vs Fc/Fc\(^+\)), giving the estimated HOMO level at –5.31 eV and –5.16 eV, respectively. These findings are consistent with the previously reported polymers where germole-containing polymers were found to have slightly higher HOMO levels than the silole analogues.\(^{[15]}\)
Table 6.3 Electrochemical properties of AT1–AT7.

<table>
<thead>
<tr>
<th></th>
<th>$E_{ox}$ / eV&lt;sup&gt;a&lt;/sup&gt;</th>
<th>HOMO / eV&lt;sup&gt;b&lt;/sup&gt;</th>
<th>$E_{red}$ / 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>AT1</td>
<td>0.97</td>
<td>−5.31</td>
<td>−1.19</td>
<td>−3.15</td>
<td>2.16</td>
</tr>
<tr>
<td>AT2</td>
<td>1.01</td>
<td>−5.35</td>
<td>−1.17</td>
<td>−3.17</td>
<td>2.18</td>
</tr>
<tr>
<td>AT3</td>
<td>0.96</td>
<td>−5.30</td>
<td>−1.16</td>
<td>−3.18</td>
<td>2.12</td>
</tr>
<tr>
<td>AT4</td>
<td>0.82</td>
<td>−5.16</td>
<td>−1.33</td>
<td>−3.01</td>
<td>2.15</td>
</tr>
<tr>
<td>AT5</td>
<td>0.83</td>
<td>−5.17</td>
<td>−1.30</td>
<td>−3.04</td>
<td>2.13</td>
</tr>
<tr>
<td>AT6</td>
<td>0.57</td>
<td>−4.91</td>
<td>−1.41</td>
<td>−2.93</td>
<td>1.98</td>
</tr>
<tr>
<td>AT7</td>
<td>0.60</td>
<td>−4.94</td>
<td>−1.34</td>
<td>−3.00</td>
<td>1.94</td>
</tr>
</tbody>
</table>

<sup>a</sup> Onset oxidation and reduction potentials

<sup>b</sup> HOMO = −e($E_{ox}$ + 4.34) (eV)

<sup>c</sup> LUMO = −e($E_{red}$ + 4.34) (eV)
Figure 6.18 Cyclic voltammograms of the AT1–AT3 thin films on glassy carbon electrode measured in 0.1 mol L$^{-1}$ Bu$_4$NPF$_6$ acetonitrile solutions at a scan rate of 50 mV s$^{-1}$. 
Figure 6.19 Cyclic voltammograms of the AT4–AT7 thin films on glassy carbon electrode measured in 0.1 mol L\(^{-1}\) Bu\(_4\)NPF\(_6\) acetonitrile solutions at a scan rate of 50 mV s\(^{-1}\).
6.3.6 XRD Studies

The crystallinity of AT1–AT7 was investigated by X-ray diffraction (XRD) as shown in Figures 6.20–6.23 and the data are summarized in Table 6.4. Out-of-plane X-ray scans (Bragg-geometry) reveal a sharp peak of AT1–AT7 with intensity at 2θ ≈ 5.47° (d ≈ 1.61 nm), ≈ 5.60° (d ≈ 1.57 nm), ≈ 6.12° (d ≈ 1.44 nm), ≈ 5.31° (d ≈ 1.66 nm), ≈ 4.28° (d ≈ 2.06 nm), ≈ 5.18° (d ≈ 1.70 nm) and ≈ 6.02° (d ≈ 1.46 nm), respectively. These large d-spacing are most reasonably due to the lattice spacing for the alkyl groups.[21]

In-plane incidence X-ray scans showed fundamental reflections of AT1–AT3 at 2θ ≈ 24.87° (d ≈ 0.35 nm), ≈ 24.85° (d ≈ 0.35 nm), and ≈ 23.82° (d ≈ 0.37 nm), respectively. The d-spacing is in the range of 0.35 to 0.37 nm, indicates of π-π stacking with strong intermolecular interaction along the π-π stacking direction parallel to the surface of the substrate.[21] The similarity in the high angle diffractions of AT1 and AT2 indicates that their intermolecular π-π distances are similar. Smaller diffraction peaks of AT1–AT3 were observed at 5.35°, 5.34° and 5.91°. AT4 to AT7 did not show obvious fundamental reflections.
Figure 6.20 X-ray diffraction patterns of films of AT1–AT3 (Out of plane measurements).

Figure 6.21 X-ray diffraction patterns of films of AT1–AT3 (In plane measurements).
Figure 6.22 X-ray diffraction patterns of films of AT4–AT7 (Out of plane measurements).

Figure 6.23 X-ray diffraction patterns of films of AT4–AT7 (In plane measurements).
Table 6.4 X-ray diffraction data of AT1–AT7.

<table>
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<tr>
<th></th>
<th>Out of plane</th>
<th>In plane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 theta (θ)</td>
<td>d-spacing (nm)</td>
</tr>
<tr>
<td>AT1</td>
<td>5.47</td>
<td>1.61</td>
</tr>
<tr>
<td>AT2</td>
<td>5.60</td>
<td>1.57</td>
</tr>
<tr>
<td>AT3</td>
<td>6.12</td>
<td>1.44</td>
</tr>
<tr>
<td>AT4</td>
<td>5.31</td>
<td>1.66</td>
</tr>
<tr>
<td>AT5</td>
<td>4.28</td>
<td>2.06</td>
</tr>
<tr>
<td>AT6</td>
<td>5.18</td>
<td>1.70</td>
</tr>
<tr>
<td>AT7</td>
<td>6.02</td>
<td>1.46</td>
</tr>
</tbody>
</table>

6.4 Application in BHJ Solar Cells

The SM-BHJ solar cells for AT1–AT7 were prepared on cleaned, UV/ozone and solvent treated ITO-glass substrates. The hole transport layer of PEDOT:PSS (Clevious PH) was spin-cast with the thickness of ~35 nm at 5000 rpm for 40 s. The active layer was spin-cast at ca. ~80 nm thicknesses from the blend of small molecule:PC$_{71}$BM = 50:50 weight ratio in chlorobenzene with 0.4 v/v% DIO, with the overall concentration of 35 mg mL$^{-1}$. Then, the small molecule layer was evaporated with a thickness of 100 nm. The light source was calibrated by using silicon reference cells with an AM 1.5 Global solar simulator with an intensity of 100 mW cm$^{-2}$. The
Characteristics of the solar cells were measured by a Keithley 2400 Sourcemeter unit. The $J$–$V$ curves and PCE parameters of $V_{oc}$, $J_{sc}$, $FF$ were obtained under exposure to AM 1.5 Global solar simulator with an intensity of 100 mW cm$^{-2}$. The cell area was determined by the aperture of 4.50 mm$^2$ during the measurement. The EQE was measured using a QE measurement system (PV measurements, Inc.) after monochromatic power calibration to confirm the $J_{sc}$ value.

The $J$–$V$ curves of the solution processable AT1/PC$_{71}$BM (50:50) solar cells without DIO, with DIO and annealed at 60$^\circ$C prior to AT1 deposition are given in Figure 6.24. The PCE critically depends on DIO and treatment temperature. Without the DIO, the PCE is 0.27% [$V_{oc}$: 0.592 V, $J_{sc}$: 1.777 mA cm$^{-2}$, $FF$: 25.5%]. DIO addition enhanced the PCE to 1.26%. However, the PCE of the annealed film at 60 °C was dropped sharply to 0.5%. The DIO reduced the series resistance and increased the shunt resistance consistent with the improved PCE and $J_{sc}$. The $J$–$V$ curves in the dark are shown in Figure 6.24b. Figure 6.24c shows the IPCE which corresponds to the $J$–$V$ curve in Figure 6.24a. The IPCE value exceeded 25% with the DIO additive as compared to ~13% without DIO over the wavelength range of 400 nm and 700 nm. However, the annealed sample showed degradation which accounted for the reduced PCE of the solar cell, although the dark current was decreased after annealing.
Figure 6.24 (a), (b) $J-V$ curves of the AT1/PC$_{71}$BM BHJ solar cells with and without light and (c) IPCE of the AT1/PC$_{71}$BM SM-BHJ solar cells.
Various PCEs were obtained from solar cells made from the different active layer sof small molecules blended with PC$_71$BM (60:40) which are shown in Figures 6.25–6.26 and the data are summarized in Table 6.5.

The PCE of dithienosilole (DTS)-containing small molecule (AT1) was 0.22% while the PCE of dithienogermole (DTG)-containing small molecule (AT4) was 0.70%. All device parameters ($V_{oc} = 0.88$ V, $J_{sc} = 3.13$ mA cm$^{-2}$ and $FF = 0.25$) of AT4 are higher than those of AT1 ($V_{oc} = 0.78$ V, $J_{sc} = 1.25$ mA cm$^{-2}$ and $FF = 0.23$).

For the DTG-containing small molecules AT4–AT7, the highest PCE of 4.93% was achieved for AT5 with a $V_{oc} = 0.79$ V, $J_{sc} = 1.22$ mA cm$^{-2}$ and $FF = 0.51$ under illumination of an AM 1.5 solar cell simulator. The PCE of 1.76% of thienylenevinylene containing molecule (AT6) was achieved with a $V_{oc} = 0.58$ V, $J_{sc} = 5.63$ mA cm$^{-2}$ and $FF = 0.56$; 1.33% of thienothiophene containing molecule (AT7) was achieved with a $V_{oc} = 0.75$ V, $J_{sc} = 5.62$ mA cm$^{-2}$ and $FF = 0.31$; 0.70 % of head-to-head coupled hexylthiophene containing molecule (AT4) was achieved with a $V_{oc} = 0.78$ V, $J_{sc} = 1.25$ mA cm$^{-2}$ and $FF = 0.23$ under illumination of an AM 1.5 solar cell simulator. It is interesting that the PCE of the small molecules decrease (AT5 > AT6 > AT7 > AT4) when the dihedral twist angle increase (AT5 > AT6 > AT7 > AT4). This is because the larger the dihedral twist angle, the bigger the conjugation breaks over small subunits.\textsuperscript{[19]}
**Figure 6.25** $J$–$V$ curves of solar cells with AT1–AT3/PC$_{71}$BM (60:40, w/w) active layers under simulated AM 1.5 solar irradiation.

**Figure 6.26** $J$–$V$ curves of solar cells with AT4–AT7/PC$_{71}$BM (60:40, w/w) active layers under simulated AM 1.5 solar irradiation.
Table 6.5 Photovoltaic performance of AT1–AT7 under the AM 1.5 sunlight illumination.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$V_{oc} / \text{V}$</th>
<th>$J_{sc} / \text{mA cm}^{-2}$</th>
<th>$FF$</th>
<th>PCE / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>AT1</td>
<td>0.78</td>
<td>1.25</td>
<td>0.23</td>
<td>0.22</td>
</tr>
<tr>
<td>AT2</td>
<td>0.88</td>
<td>0.96</td>
<td>0.25</td>
<td>0.21</td>
</tr>
<tr>
<td>AT3</td>
<td>0.58</td>
<td>0.80</td>
<td>0.28</td>
<td>0.30</td>
</tr>
<tr>
<td>AT4</td>
<td>0.88</td>
<td>3.13</td>
<td>0.25</td>
<td>0.70</td>
</tr>
<tr>
<td>AT5</td>
<td>0.79</td>
<td>1.22</td>
<td>0.51</td>
<td>4.93</td>
</tr>
<tr>
<td>AT6</td>
<td>0.58</td>
<td>5.63</td>
<td>0.56</td>
<td>1.76</td>
</tr>
<tr>
<td>AT7</td>
<td>0.75</td>
<td>5.62</td>
<td>0.31</td>
<td>1.33</td>
</tr>
</tbody>
</table>

6.5 Concluding Remarks

Seven new organic small molecules AT1–AT7 were designed and synthesized comprising head-to-head coupled hexylthiophene, thienothiophene, thienylenevinylene, dithienosilole and dithienogermole units. AT1–AT7 exhibited broad absorption peaks with favorable overlap with the solar spectrum at 488 nm to 617 nm in CHCl₃, and 578 to 653 nm in thin films. The HOMOs of AT1–AT7 are in the range of −4.91 to −5.35 eV, and LUMOs are in the range of −2.93 to −3.18 eV. These data suggest that AT1–AT7 line up favorably with those of common fullerene
acceptors to generate useful $V_{oc}$ in BHJ solar cells. These seven small molecules have
been applied to the bulk heterojunction solar cells. The highest PCE of 4.93% was
achieved for AT5 with a $V_{oc} = 0.79$ V, $J_{sc} = 1.22$ mA cm$^{-2}$ and $FF = 0.51$ under
illumination of an AM 1.5 solar cell simulator.
References:


Chapter 7 Concluding Remarks and Future Work

To begin with, a series of novel donor-acceptor-π-acceptor organic dyes for dye-sensitized solar cells (DSSCs) were successfully synthesized and fully characterized. For the bithiazole-based organic dyes (D1–D5), we found that the performance of the photovoltaic devices depend significantly on the nature and strength of the electron-donating end group along the conjugated main. Among all of the dyes examined, DSSCs based on D4 exhibited the best overall light to electricity conversion efficiency of 4.65% under AM 1.5 irradiation (100 mW cm$^{-2}$). For the fluorenone-based organic dyes (F1–F4), DSSCs based on F4 exhibited the best overall light to electricity conversion efficiency of 4.71% ($V_{oc} = 565$ mV, $J_{sc} = 11.71$ mA cm$^{-2}$, $FF = 0.71$) under AM 1.5 irradiation (100 mW cm$^{-2}$). All the results reveal that these metal-free organic dyes are promising molecular materials in the development of high-performance DSSCs.

Furthermore, ten novel donor-donor-π-acceptor organic dyes have been synthesized and applied for the fabrication of DSSCs, including six dibenzothiophene-based dye photosensitizers (DT1–DT6) and carbazole-based dye photosensitizers (C1–C4). All the dyes have efficient charge injection from the excited photosensitizer molecule to TiO$_2$ conduction band and can provide ample
driving force for efficient dye regeneration and thus the charge separation. Among 
**DT1–DT6**, DSSCs based on **DT4** exhibited the best overall light to electricity 
conversion efficiency of 4.87% ($V_{oc} = 0.70$ V, $J_{sc} = 9.94$ mA cm$^{-2}$, $FF = 0.70$) under 
AM 1.5 irradiation, which reached 68% with respect to that of an **N719**-based device fabricated under similar fabrication conditions. For **C1–C4**, DSSCs based on **C4** exhibited the best overall light to electricity conversion efficiency of 5.28% ($V_{oc} = 0.70$ V, $J_{sc} = 11.06$ mA cm$^{-2}$, $FF = 0.68$) under AM 1.5 irradiation, which reached 73% with respect to that of an **N719**-based device fabricated under similar fabrication conditions.

Besides, nine novel di-anchoring organic sensitizers (**B1–B9**) employing two different electron-donating cores, which are the fluorene (**B1–B4**) and carbazole (**B5–B9**) units, and two symmetrical anchoring cyanoacrylic acid (acceptor) termini groups have been synthesized and studied for their applications in DSSCs. For the fluorine-based dyes, **B2** dye (containing electron-donating 9-butylcarbazole units) showed the highest molar extinction coefficient, as a result, it produced the highest PCE value of 3.73% ($V_{oc} = 0.69$ V, $J_{sc} = 9.43$ mA cm$^{-2}$, $FF = 0.56$) under standard AM 1.5 sunlight with a IPCE plateau of 71%. For the symmetrical carbazole-based dyes, they showed an effective PCE of 4.00%, $J_{sc}$ 8.91 mA cm$^{-2}$,  $V_{oc}$ of 0.71 mV and a $FF$ of 0.63.
In addition, we have also studied four new platinum polyyne polymers prepared via the Sonogashira-type dehydrohalogenation reaction between the ethynyl precursor and trans-Pt(PBu3)2Cl2. All the polymers were carefully purified by column chromatography over silica gel and repeated precipitation, leading to the polymers in good yields and high purity. All of them are air-stable and well characterized by different spectroscopic methods and photophysical measurements. Their photovoltaic behaviors were fully investigated. Their model compounds were also prepared and studied. The highest PCE of 1.95% was achieved from solar cell based on P2 with a $V_{oc} = 0.81$ V, $J_{sc} = 4.24$ mA cm$^{-2}$ and $FF = 0.57$ under illumination of an AM 1.5 solar cell simulator in a 1:3 (P2:PCBM) blend ratio.

Finally, a series of new organic small molecules AT1–AT7 were designed and synthesized comprising head-to-head coupled hexylthiophene, dithienosilole and dithienogermole units. AT1–AT7 exhibited broad absorption peaks with favorable spectral overlap with the solar spectrum. The HOMOs of AT1–AT7 are in the range of $-4.91$ to $-5.35$ eV, and LUMOs are in the range of $-2.93$ to $-3.18$ eV. These data suggest that AT1–AT7 line up favorably with those of common fullerene acceptors to generate useful $V_{oc}$ in BHJ solar cells. These seven small molecules have been applied to the bulk heterojunction solar cells. The highest PCE of 4.93% was achieved for AT5 with a $V_{oc} = 0.79$ V, $J_{sc} = 1.22$ mA cm$^{-2}$ and $FF = 0.51$ under illumination of an AM
1.5 solar cell simulator.

**Figure 7.1** The chemical structures of dyes in this thesis.
Figure 7.2 The chemical structures of polymers and small molecules in this thesis.
In the future, we will concentrate on the full uses of these molecules and polymers in various domains of optoelectronic and material applications. Also, we may develop new type of materials for both dye-sensitized and organic solar cell applications (Figure 7.3–7.4).

**Figure 7.3** Some possible new classes of photosensitizers for DSSCs.
Some possible new classes of small molecules and polymers for organic solar cells.
Chapter 8 Experimental Details

8.1 General

All reactions were carried out under nitrogen atmosphere with the use of standard Schlenk techniques, but no special precautions were taken to exclude oxygen during workup. Glasswares were oven-dried at about 120 °C. Analytical grade solvents were purified by distillation over appropriate drying agents under an inert nitrogen atmosphere prior to use. All reagents and chemicals, unless otherwise stated, were purchased from commercial sources and used without further purification. Separation and purification of products were achieved by column chromatography on silica gel or preparative thin-layer chromatography on glass plates (20 cm × 20 cm), pre-coated with Merck Kieselgel 60 GF254 prepared in our laboratory (0.7 mm). TLC was carried out in air using laboratory grade solvents as eluents. Microwave assisted reactions were performed in a Biotage Initiator TM microwave reactor.

The positive-ion fast atom bombardment (FAB) mass spectra were recorded in m-nitrobenzyl alcohol matrices on a Finngin-MAT SSQ710 mass 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. Infrared spectra were recorded on the Nicolet Magna 550 Series II FTIR
spectrometer, using KBr pellets for solid state spectroscopy. NMR spectra were measured in deuteriated solvents as the lock and reference on a JEOL JNM-EX270 FT NMR system, Varian INOVA 400 instrument or a Bruker AV 400 MHz FT-NMR spectrometer, with $^1$H, and $^{13}$C NMR chemical shifts quoted relative to Me$_4$Si standard and $^{31}$P chemical shifts relative to an 85% H$_3$PO$_4$ external reference. Electronic absorption spectra were obtained with a Hewlett Packard 8453 spectrometer. Solution state photoluminescence measurements were obtained by the LS50B fluorescent spectrometer. The PL spectra were measured in THF with a PTI Fluorescence Master Series QM1 spectrophotometer. Cyclic voltammetry measurements were performed for the dyes in thin films on glassy carbon electrode measured in 0.1 M tetrabutylammonium hexafluorophosphate solution in acetonitrile at a scan rate of 50 mV s$^{-1}$. Under these conditions, the $E_{1/2}$ of ferrocene was 0.07 V vs Ag/AgCl.

Differential scanning calorimetry (DSC) was determined by a TA Instruments DSC (Model Q-20) with about 5 mg polymers samples at a rate of 10 °C min$^{-1}$ in the temperature range of −20 to 300 °C.

The molecular weights of the polymers were determined by GPC (HP 1050 series HPLC with visible wavelength and fluorescent detectors) using polystyrene
standards and thermal analyses were performed with a Perkin-Elmer TGA6 thermal analyzer.

AFM images were obtained with a Nanoscope IIIa instrument (Digital Instruments), in the tapping mode. A crystal silicon tip, with a resonant frequency of 299 300–350 kHz and a spring constant of 20–100 N m$^{-1}$ was used. The scanner was a 10 µm piezo scanner and the scan rate was 1–2 Hz. Off-line image processing and analysis (grain size, roughness) were performed using D1 off-line software (Veeco Corp).

Molecular geometries were optimized at the B3LYP level of the density functional theory (DFT). Time-dependent density functional theory (TDDFT) was performed based on the optimized structures to obtain the excitation energies. The basis set used for C, N, O and H atoms was 6–31G while effective core potentials with a LanL2DZ basis set were employed for Ru and S.$^{[1]}$ All the calculations were carried out using the Gaussian 03 program.$^{[2]}$ Molecular orbitals obtained from the B3LYP calculations were plotted using the Molden 3.7 program written by Schaftenaar.$^{[3]}$

Human HaCaT skin keratinocytes were removed from 75 mL sterile cell culture flasks with trypsin and neutralized with fetal bovine serum. After washing with phosphate buffered saline and centrifugation, skin cells were re-suspended in
complete cell culture medium at a concentration of approximately $1 \times 10^5$ cells mL$^{-1}$ and counted manually using a haematocytometer under an inverted microscope. Human cells seeded in the 96 wells microtitre plates for 24 h were prepared for the screening of the synthesized compounds. The five compounds were dissolved in dimethyl sulfoxide at a stock concentration of 20 mg mL$^{-1}$. Doxorubicin was used as the positive reference compound and it was added at 4 µg mL$^{-1}$. The five compounds were also added at 100 µg mL$^{-1}$ and incubated with cells for a further period of 24 h. Afterwards, the evaluation of possible anti-proliferative potential of our synthesized compounds was performed by the sulforhodamine B protein staining methods. Briefly, cancer cells were fixed with trichloroacetic acid, washed with distilled water and stained with sulforhodamine B. Afterwards, cells were washed again with acetic acid and stained cells were dissolved in 100 µL unbuffered Tris-base. Finally, optical absorptions were measured at 575 nm using a microplate reader (Victor V form Perkin Elmer, Life Sciences).
8.2 Materials

Compounds bromine or $N$-bromosuccinimide (NBS), PtCl$_2$ or K$_2$PtCl$_4$, PBu$_3$ or PEt$_3$, Pd(OAc)$_2$, CuI, PPh$_3$, Pd(PPh$_3$)$_4$, trimethylsilylacetylene, magnesium (Mg), $n$-BuLi, tributylchlorostannane, trimethylborate and other starting materials were purchased from commercial sources and used as received unless otherwise specified. The compounds $trans$-[Pt(PPh$_3$)$_2$PhCl],$^{[4a]}$ $trans$-[Pt(PBu$_3$)$_2$Cl$_2$],$^{[4b]}$ aryl boronic acid,$^{[5]}$ and aryl tributylstannane$^{[6]}$ were prepared according to the literature methods. In each case, only a typical example is given for the reaction.
8.3 Experimental Details for Chapter 2

8.3.1 Experimental Details for Various Boronic Acid Derivatives

**Synthesis of 5-formylthiophen-2-yl-2-boronic acid**

A benzene (50 mL) solution of thiophene-2-carbaldehyde (1.35 g, 12.0 mmol), ethylene glycol (3 mL) and p-toluenesulfonic acid (0.01 g, 0.06 mmol) was heated to vigorous reflux overnight in a flask equipped with a Dean-Stark trap to remove water. Then, the solution was poured into a 10% sodium hydroxide solution and extracted with CH₂Cl₂. The combined organic layer was dried over Na₂SO₄ and filtered. Afterwards, the mixture was concentrated under reduced pressure to give 2-(thiophen-2-yl)-1,3-dioxolane as a brown liquid (1.79 g, 10 mmol, 95%).

**Spectral Data:** ¹H NMR (400 MHz, CDCl₃): δ = 7.30–7.28 (m, 1H, Ar), 7.14 (m, 1H, Ar), 6.97–6.94 (m, 1H, Ar), 6.07 (s, 1H, Ar), 4.08–4.05 (m, 2H, CH₂), 3.96–3.92 (m, 2H, CH₂) ppm. FAB-MS (m/z): 156.0 [M]+.

A THF (30 mL) solution of 2-(thiophen-2-yl)-1,3-dioxolane (1.82 g, 11.66 mmol) was cooled to –78 °C under nitrogen atmosphere and then 2.5 M n-butyllithium (7 mL, 17.50 mmol) was added dropwise over 15 min. The mixture was stirred at –78 °C for 1 h and then at –40 °C for 4 h. After cooling back to –78 °C, trimethylborate (1.39 mL, 12.24 mmol) was added dropwise, and the solution was stirred at room temperature
for 24 h. The reaction was quenched by the addition of 2 M HCl and the mixture was extracted with diethyl ether. The combined organic layer was dried over Na$_2$SO$_4$ and filtered. Afterwards, the mixture was concentrated under reduced pressure. The residue was washed by $n$-hexane to obtain 5-formylthiophen-2-yl-2-boronic acid as a pale brown solid (1.65 g, 0.01 mol, 90%).

*Spectral Data:* $^1$H NMR (400 MHz, $d_6$-DMSO): $\delta = 9.95$ (s, 1H, CHO), 8.65 (s, 2H, B(OH)$_2$), 8.01 (d, $J = 3.7$ Hz, 1H, Ar), 7.77 (d, $J = 3.6$ Hz, 1H, Ar) ppm. FAB-MS ($m/z$): 156.0 [M]$^+$. 

**Synthesis of 3-bromo-9-butylcarbazole boronic acid**

In the absence of light, NBS (1.67 mg, 9.40 mmol) was added in small portions to a solution of 9-butylcarbazole (2.0 g, 8.96 mmol) in a mixture of acetic acid (30 mL) and chloroform (30 mL) and the mixture was stirred overnight. It was then concentrated under reduced pressure and purified by chromatography on a silica gel column using CH$_2$Cl$_2$ as eluent to afford 3-bromo-9-butylcarbazole as a pale yellow oil (2.49 mg, 8.24 mmol, 92%).

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.20$ (m, 1H, Ar), 8.05–8.02 (m, 1H, Ar), 7.54–7.46 (m, 2H, Ar), 7.41–7.38 (m, 1H, Ar), 7.28–7.21 (m, 2H, Ar), 4.28–4.25 (t, $J = 7.1$ Hz, 2H, butyl), 1.86–1.81 (m, 2H, butyl), 1.40–1.34 (m, 2H,
butyl), 0.95–0.91 (t, J = 14.7 Hz, 3H, butyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 140.75, 139.10, 128.24, 126.37, 124.59, 123.09, 121.84, 120.58, 119.23, 111.55, 110.17, 108.99 (Ar), 41.95, 31.09, 20.58, 13.93 (butyl) ppm. FAB-MS (m/z): 301.1 [M]$^+$.

A THF (30 mL) solution of 3-bromo-9-butylcarbazole (2.0 g, 6.42 mmol) was cooled to −78 °C under nitrogen atmosphere, and then 2.5 M n-butyllithium (3.1 mL, 7.70 mmol) was added dropwise over 15 min. The mixture was stirred at −78 °C for 20 min and then trimethylborate (3 mL, 25.7 mmol) was added dropwisely, and the solution was stirred at room temperature for 24 h. The reaction was quenched by the addition of 2 M HCl and extracted with diethyl ether. The combined organic layer was dried over Na$_2$SO$_4$ and filtered. Afterwards, the mixture was concentrated under reduced pressure. The residue was washed by n-hexane to obtain 3-bromo-9-butylcarbazole boronic acid as a white solid (994 mg, 3.72 mmol, 58%). This compound was used directly without further purification and characterization.

**Synthesis of 9,9-dibutylfluoren-2-ylboronic acid**

To a solution of 2-bromofluorene (3.0 g, 7.99 mmol) and 1-bromobutane (5 mL, 31.97 mmol) in DMSO (50 mL) was added 50 wt% aqueous sodium hydroxide (10
mL). The reaction mixture was stirred at room temperature for two days. A dark purple solution was obtained. The solution was poured into brine and extracted with three portions of 30 mL ethyl acetate. The organic layer was combined and dried over Na$_2$SO$_4$. The solvent was then removed by vacuum and purified by chromatography on a silica gel column using CH$_2$Cl$_2$ as eluent to afford 2-bromo-9,9-dibutylfluorene as a white crystal (2.25 g, 6.30 mmol, 79%).

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.66–7.65$ (m, 1H, Ar), 7.54–7.52 (d, $J = 8.0$ Hz, 1H, Ar), 7.46–7.42 (m, 2H, Ar), 7.31–7.30 (m, 3H, Ar), 1.96–1.91 (m, 4H, butyl), 1.26–0.86 (m, 8H, butyl), 0.67–0.54 (m, 6H, butyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 153.07, 150.39, 140.28, 140.46, 130.06, 127.62, 127.08, 126.27, 122.98, 121.18, 121.16, 119.90$ (Ar), 55.42, 40.28, 26.02, 23.17, 13.95 (butyl) ppm. FAB-MS ($m/z$): 356.1 [M]$^+$.  

A THF (30 mL) solution of 2-bromo-9,9-dibutylfluorene (2 g, 5.62 mmol) was cooled to $–78$ °C under nitrogen atmosphere, and then 2.5 M $n$-butyllithium (2.7 mL, 6.74 mmol) was added dropwisely over 15 min. The mixture was stirred at $–78$ °C for 20 min and then trimethylborate (0.96 mL, 11.23 mmol) was added, and the solution was stirred at room temperature for 24 h. The reaction was quenched by the addition of 2 M HCl followed by extraction with diethyl ether. The combined organic layer
was dried over Na$_2$SO$_4$ and filtered. The mixture was concentrated under reduced pressure. The residue was washed by $n$-hexane to obtain 9,9-dibutylfluoren-2-ylboronic acid as a white solid (1.21 g, 3.92 mol, 69%). This compound was used directly without further purification and characterization.

8.3.2 Experimental Details for Halide Precursors

*Synthesis of D1-Br*

Bromine (3.35 mL, 65.1 mmol) was added dropwise to a stirring solution of 2-undecanone (11.1 g, 64.9 mmol) in methanol (100 mL) at –10 °C. The mixture was stirred at 0 °C for 1 h and then another 1 h at room temperature. Water (20 mL) and then concentrated sulfuric acid (35 mL) were added to the mixture in an ice bath. After the mixture was stirred overnight at room temperature, a white solid was precipitated from the reaction mixture. The precipitate was filtered, washed with water, and then dried to acquire 1-bromo-undecan-2-one (13.5 g, 54.5 mmol, 84%).

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): δ = 3.88 (s, 2H, CH$_2$Br), 2.66–2.62 (t, $J = 7.4$ Hz, 2H, nonyl), 1.63–1.59 (m, 2H, nonyl), 1.31–1.26 (m, 12H, nonyl), 0.89–0.86 (t, $J = 7.0$ Hz, 3H, CH$_3$) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 202.29 (CO), 39.84, 34.30, 31.82, 29.36, 29.30, 29.22, 29.01, 23.84, 22.64, 14.08 (nonyl) ppm. FAB-MS ($m/z$): 248.1 [M]$^+$.
1-Bromo-undecan-2-one (5.23 g, 21.0 mmol), dithiooxamide (1.20 g, 10.0 mmol) and ethanol (50 mL) were placed in a 100 mL round-bottom flask equipped with a reflux condenser. The solution was heated to reflux for 6 h. After cooling, it was poured into the crushed ice. The mixture was extracted with CH₂Cl₂ and then dried over anhydrous Na₂SO₄. After evaporation of the solvent, the residue was purified by silica gel column using CH₂Cl₂/n-hexane (1:5, v/v) as eluent to get 4,4'-dinonyl-2,2'-bithiazole as a pale yellow solid (3.57 mg, 8.50 mmol, 85%).

*Spectral Data:* ¹H NMR (400 MHz, CDCl₃): δ = 6.94 (s, 2H, Ar), 2.82–2.78 (t, J = 7.4 Hz, 4H, nonyl), 1.75–1.71 (m, 4H, nonyl), 1.35–1.26 (m, 24H, nonyl), 0.89–0.86 (t, J = 7.0 Hz, 6H, nonyl) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 160.84, 159.16, 114.54 (Ar), 31.87, 31.53, 29.52, 29.42, 29.30, 29.25, 29.18, 22.67, 14.11 (nonyl) ppm. FAB-MS (m/z): 420.2 [M⁺].

In the absence of light, NBS (432 mg, 2.38 mmol) was added in small portions at −20 °C to a solution of 4,4'-dinonyl-2,2'-bithiazole (1 g, 2.38 mmol) in DMF (30 mL) and the mixture was stirred overnight. Then it was poured into ice and extracted several times with CH₂Cl₂. The combined organic layer was washed with water and dried over anhydrous Na₂SO₄. The mixture was then concentrated under reduced pressure. The residue was purified by chromatography using CH₂Cl₂/n-hexane (1:4,
v/v) as eluent to obtain 5-bromo-4-nonyl-2-(4-nonylthiazol-2-yl)thiazole as a white solid (689 mg, 1.38 mmol, 58%).

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 6.95 (s, 1H, Ar), 2.80–2.73 (t, $J$ = 7.4 Hz, 4H, nonyl), 1.73–1.70 (m, 4H, nonyl), 1.33–1.26 (m, 24H, nonyl), 0.89–0.85 (m, 6H, nonyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ =160.64, 160.15, 159.31, 157.17, 114.85, 106.31 (Ar), 31.94, 31.51, 29.59, 29.48, 29.44, 29.37, 29.29, 29.23, 29.20, 28.82, 22.74, 14.19 (nonyl) ppm. FAB-MS ($m/z$): 499.1 [M]$^+$. 

**Synthesis of D2-Br**

In the absence of light, NBS (108 mg, 0.067 mmol) was added dropwise to a solution of 5-(4,4′-dinyonyl-2,2′-thiazol-5-yl)thiophene-2-carbaldehyde (307 g, 0.58 mmol) in a mixture of acetic acid (30 mL) and chloroform (30 mL) and the entire mixture was stirred overnight. Then, it was concentrated under reduced pressure and purified by silica gel column using CH$_2$Cl$_2$/n-hexane (2:1, v/v) as eluent to afford 5-(5′-bromo-4,4′-dinyonyl-2,2′-thiazol-5-yl)thiophene-2-carbaldehyde as a yellow solid (195 mg, 0.32 mmol, 55%).

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 9.91 (s, 1H, CHO), 7.74–7.73 (d, $J$ = 4.0 Hz, 1H, Ar), 7.27 (s, 1H, Ar), 2.98–2.95 (t, $J$ = 7.7 Hz, 2H, nonyl), 2.79–2.75 (t, $J$ = 7.6 Hz, 2H, nonyl), 1.80–1.70 (m, 4H, nonyl), 1.43–1.31 (m, 24H,
nonyl), 0.89–0.86 (m, 6H, nonyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 182.64 (CHO), 159.75, 158.94, 157.74, 156.73, 143.46, 142.73, 136.76, 127.93, 126.45 (Ar), 31.92, 31.62, 31.47, 30.71, 30.20, 29.55, 29.45, 29.40, 29.34, 29.20, 28.80, 22.74, 14.18 (nonyl) ppm. FAB-MS ($m/z$): 608.1 [M]$^+$. C$_{29}$H$_{41}$N$_2$BrOS$_3$ (609.74): calcd. C 57.13, H 6.78, N 4.59; found C 57.05, H 6.92, N 4.68.

**Synthesis of F1-Br**

In a 50 mL round bottom flask, 2-bromo-9H-fluoren-9-one (2 g, 7.72 mmol) in tetrahydrofuran (40 mL) was added to a mixture of thiophenyl-2-boronic acid (1.04 g, 8.11 mmol), Pd(PPh$_3$)$_4$ (892 mg, 0.77 mmol) and 2 M Na$_2$CO$_3$ (15.44 mL, 30.88 mmol). The mixture was heated at 80 °C for two days. Afterwards, water was added and the solution mixture was extracted with ethyl acetate. The combined organic layer was dried by Na$_2$SO$_4$ and filtered. The mixture was then concentrated under reduced pressure. The residue was purified by column chromatography using CH$_2$Cl$_2$/n-hexane (1:4, v/v) as eluent to give 2-(thiophenyl)fluoren-9-one as a yellow solid (1.84 g, 7.02 mmol, 91%).

**Spectral Data:** $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.91–7.90 (m, 1H, Ar), 7.74–7.71 (m, 1H, Ar), 7.68–7.66 (m, 1H, Ar), 7.54–7.48 (m, 3H, Ar), 7.39–7.38 (m, 1H, Ar), 7.33–7.28 (m, 2H, Ar), 7.12–7.09 (m, 1H, Ar) ppm. $^{13}$C NMR (100 MHz,
In the absence of light, NBS (712 mg, 4.00 mmol) was added dropwise to a solution of 2-(thiophenyl)fluoren-9-one (1 g, 3.81 mmol) in a mixture of acetic acid (20 mL) and chloroform (20 mL) and the entire mixture was stirred overnight. Then, it was concentrated under reduced pressure and purified by silica gel column chromatography using CH₂Cl₂/n-hexane (1:4, v/v) as eluent to afford compound 2-(5-bromothiophenyl)fluoren-9-one as a yellow solid (1.23 g, 3.62 mmol, 95%).

**Spectral Data:** ¹H NMR (400 MHz, CDCl₃): δ = 7.81 (m, 1H, Ar), 7.69–7.66 (m, 1H, Ar), 7.62–7.60 (m, 1H, Ar), 7.54–7.50 (m, 3H, Ar), 7.33–7.29 (m, 1H, Ar), 7.13–7.05 (m, 2H, Ar) ppm. ¹³C NMR (100 MHz, CDCl₃): 192.30, 143.49, 143.04, 142.31, 133.93, 133.90, 133.54, 133.26, 130.21, 130.03, 128.13, 123.45, 122.81, 120.04, 119.83, 119.39, 111.16 (Ar) ppm. MALDI-TOF (m/z): 341.22 [M]⁺.

**Synthesis of F2-Br**

In a 50 mL round bottom flask, 2,7-dibromo-9H-fluoren-9-one (2 g, 5.93 mmol) in tetrahydrofuran (40 mL) was added to a mixture of
9,9-dibutyl-9H-fluoren-2-yl-2-boronic acid (2.86 g, 8.90 mmol), Pd(PPh$_3$)$_4$ (681 mg, 0.59 mmol) and 2 M Na$_2$CO$_3$ (11.86 mL, 23.72 mmol). The mixture was heated at 80 ºC for two days. Afterwards, water was added and the solution mixture was extracted with ethyl acetate. The combined organic layer was dried by Na$_2$SO$_4$ and filtered. The mixture was then concentrated under reduced pressure. The residue was purified by column chromatography using CH$_2$Cl$_2$/n-hexane (1:4, v/v) as eluent to give 2-bromo-7-(9,9-dibutylfluorenyl)fluoren-9-one as an orange solid (1.71 g, 3.20 mmol, 54%).

**Spectral Data:** $^1$H NMR (400 MHz, CDCl$_3$): δ = 8.04–8.03 (m, 1H, Ar), 7.85–7.73 (m, 4H, Ar), 7.66–7.57 (m, 3H, Ar), 7.45–7.33 (m, 4H, Ar), 2.02–2.00 (m, 4H, butyl), 1.12–1.09 (m, 4H, butyl), 0.71–0.62 (m, 10H, butyl) ppm. $^{13}$C NMR (400 MHz, CDCl$_3$): δ 192.55, 190.91, 151.62, 150.97, 143.08, 142.93, 142.90, 142.58, 142.20, 142.13, 141.12, 140.51, 138.26, 137.43, 136.02, 135.20, 135.17, 133.51, 133.37, 127.64, 127.28, 126.85, 125.61, 123.18, 122.92, 122.78, 121.74, 120.82, 120.75, 120.08 (Ar), 55.16 (quat.), 40.27, 25.97, 23.07, 13.86 (butyl) ppm. MALDI-TOF (m/z): 534.16 [M]$^+$.

**Synthesis of F3-Br**

In a 50 mL round bottom flask, 2,7-dibromo-9H-fluoren-9-one (2 g, 5.93 mmol)
in tetrahydrofuran (40 mL) was added to a mixture of thiophen-2-yl-2-boronic acid (1.13 g, 8.90 mmol), Pd(PPh$_3$)$_4$ (681 mg, 0.59 mmol) and 2 M Na$_2$CO$_3$ (11.86 mL, 23.72 mmol). The mixture was heated at 80 °C for two days. Afterwards, water was added and the solution mixture was extracted with ethyl acetate. The combined organic layer was dried by Na$_2$SO$_4$ and filtered. The mixture was then concentrated under reduced pressure. The residue was purified by column chromatography using CH$_2$Cl$_2$/n-hexane (1:4, v/v) as eluent to give 2-bromo-7-(thiophenyl)fluoren-9-one as a pink solid (970 mg, 2.84 mmol, 48%).

**Spectral Data:**

$^1$H NMR (400 MHz, CDCl$_3$): δ = 7.88 (m, 1H, Ar), 7.76−7.70 (m, 2H, Ar), 7.61−7.59 (m, 1H, Ar), 7.49−7.47 (m, 1H, Ar), 7.38−7.31 (m, 3H, Ar), 7.11−7.09 (m, 1H, Ar) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 192.08, 142.87, 142.83, 142.17, 137.28, 135.94, 135.85, 134.49, 131.85, 128.29, 127.67, 125.68, 123.91, 122.88, 121.73, 121.70, 120.91 (Ar) ppm. MALDI-TOF (m/z): 339.96 [M]$^+$.

In a 50 mL round bottom flask, 2-bromo-7-(thiophenyl)fluoren-9-one (2 g, 5.86 mmol) in tetrahydrofuran (40 mL) was added to a mixture of 9,9-dibutyl-9H-fluoren-2-yl-2-boronic acid (2.83 g, 8.79 mmol), Pd(PPh$_3$)$_4$ (681 mg, 0.59 mmol) and 2 M Na$_2$CO$_3$ (11.72 mL, 23.44 mmol). The mixture was heated at 80 °C for two days. Afterwards, water was added and the solution mixture was extracted
with ethyl acetate. The combined organic layer was dried by Na$_2$SO$_4$ and filtered. The mixture was then concentrated under reduced pressure. The residue was purified by column chromatography using CH$_2$Cl$_2$/n-hexane (1:4, v/v) as eluent to give 2-(9,9-dibutylfluorenyl)-7-(thiophenyl)fluoren-9-one as an orange solid (2.84 g, 5.21 mmol, 89%).

Spectral Data: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.88$–7.80 (m, 2H, Ar), 7.68–7.58 (m, 4H, Ar), 7.50–7.37 (m, 4H, Ar), 7.26–7.19 (m, 5H, Ar), 7.00–6.99 (m, 1H, Ar), 1.96–1.92 (m, 4H, butyl), 1.04–0.98 (m, 4H, butyl), 0.60–0.55 (m, 10H, butyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 193.73$ (C=O), 151.63, 151.02, 143.13, 142.92, 142.78, 142.62, 141.17, 140.54, 138.48, 135.33, 135.22, 135.07, 133.37, 131.70, 128.26, 127.32, 126.88, 125.65, 125.44, 123.71, 123.01, 122.96, 121.58, 120.97, 120.83, 120.72, 120.12, 119.89 (Ar), 55.22, 40.31, 31.65, 26.06, 23.13, 22.72, 14.19, 13.91 (butyl) ppm. MALDI-TOF (m/z): 538.23 [M$^+$].

In the absence of light, NBS (354 mg, 1.98 mmol) was added dropwise to a solution of 2-(9,9-dibutylfluorenyl)-7-(thiophenyl)fluoren-9-one (1 g, 1.80 mmol) in a mixture of acetic acid (20 mL) and chloroform (20 mL) and the entire mixture was stirred overnight. Then, it was concentrated under reduced pressure and purified by silica gel column chromatography using CH$_2$Cl$_2$/n-hexane (1:4, v/v) as eluent to
afford compound 2-(5-bromothiophenyl)-7-(9,9-dibutylfluorenyl)fluoren-9-one as an
orange solid (1.02 g, 1.65 mmol, 92%).

Spectral Data: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.83$ (m, H, Ar), 7.63–7.61 (m, 4H, Ar), 7.49–7.35 (m, 4H, Ar), 7.30–7.23 (m, 4H, Ar), 6.93–6.87 (m, 2H, Ar), 1.96–1.91 (m, 4H, butyl), 1.03–0.97 (m, 4H, butyl), 0.59–0.52 (m, 10H, butyl) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 193.43$ (C=O), 151.67, 151.04, 144.48, 143.20, 142.74, 142.55, 141.23, 140.53, 138.38, 135.23, 134.99, 134.34, 133.37, 131.24, 131.09, 127.37, 126.91, 125.67, 123.79, 122.99, 121.00, 120.95, 120.87, 120.79, 120.15, 119.93, 112.23 (Ar), 55.22, 40.29, 31.64, 26.07, 23.13, 22.71, 14.20, 13.91 (butyl) ppm. MALDI-TOF (m/z): 616.14 [M$^+$].

Synthesis of F4-Br

In a 50 mL round bottom flask, 2-bromo-7-(thiophenyl)fluoren-9-one (2 g, 5.86 mmol) in tetrahydrofuran (40 mL) was added to a mixture of 4-(di-$p$-tolylamino)phenylboronic acid (2.78 g, 8.79 mmol), Pd(PPh$_3$)$_4$ (681 mg, 0.59 mmol) and 2 M Na$_2$CO$_3$ (11.72 mL, 23.44 mmol). The mixture was heated at 80 °C for two days. Afterwards, water was added and the solution mixture was extracted with ethyl acetate. The combined organic layer was dried by Na$_2$SO$_4$ and filtered. The mixture was then concentrated under reduced pressure. The residue was purified by
column chromatography using CH$_2$Cl$_2$/n-hexane (1:4, v/v) as eluent to give 2-(4-(di-p-tolylamino)phenyl)-7-(thiophenyl)fluoren-9-one as an orange solid (2.91 g, 5.21 mmol, 89%).

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.91-7.88$ (m, 2H, Ar), 7.74-7.68 (m, 2H, Ar), 7.55-7.45 (m, 4H, Ar), 7.38-7.31 (m, 2H, Ar), 7.12-7.02 (m, 11H, Ar), 2.33 (s, 6H, CH$_3$) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 193.64$ (C=O), 148.21, 144.97, 143.18, 142.99, 142.16, 141.68, 135.16, 135.08, 135.02, 132.95, 132.43, 132.18, 131.59, 130.00, 128.22, 127.23, 125.34, 124.96, 123.61, 122.27, 122.14, 121.43, 120.66, 120.65 (Ar), 20.88 (CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 193.64$ (C=O), 148.21, 144.97, 143.18, 142.99, 142.16, 141.68, 135.16, 135.08, 135.02, 132.95, 132.43, 132.18, 131.59, 130.00, 128.22, 127.23, 125.34, 124.96, 123.61, 122.27, 122.14, 121.43, 120.66, 120.65 (Ar), 20.88 (CH$_3$) ppm. MALDI-TOF (m/z): 533.18 [M$^+$].

In the absence of light, NBS (333 mg, 1.98 mmol) was added dropwise to a solution of 2-(4-(di-p-tolylamino)phenyl)-7-(thiophenyl)fluoren-9-one (1 g, 1.87 mmol) in a mixture of acetic acid (20 mL) and chloroform (20 mL) and the entire mixture was stirred overnight. Then, it was concentrated under reduced pressure and purified by silica gel column chromatography using CH$_2$Cl$_2$/n-hexane (1:4, v/v) as
eluent to afford 2-(4-(di-p-tolylamino)phenyl)-7-(5-bromothiophenyl)fluoren-9-one as a red solid (1.08 g, 1.66 mmol, 89%).

Spectral Data: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.84–7.83 (m, 1H, Ar), 7.72–7.71 (m, 1H, Ar), 7.64–7.61 (m, 1H, Ar), 7.53–7.38 (m, 8H, Ar), 7.14–7.00 (m, 7H, Ar), 6.70–6.68 (m, 2H, Ar), 2.34 (s, 6H, CH$_3$) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 193.44 (C=O), 147.46, 144.59, 143.40, 142.27, 141.95, 141.88, 137.14, 135.24, 134.96, 134.92, 134.16, 132.48, 131.46, 131.24, 131.07, 129.66, 129.50, 129.44, 129.21, 129.03, 128.86, 127.14, 123.88, 123.72, 122.34, 122.15, 121.43, 120.97, 120.73, 119.44, 112.10 (Ar), 20.71 (CH$_3$) ppm. MALDI-TOF (m/z): 612.58 [M]$^+$.

8.3.3 Experimental Details for Aldehyde Precursors

Synthesis of D1-CHO

In a 50 mL round bottom flask, 5-bromo-4,4′-dinonyl-2,2′-bithiazole (858 mg, 1.71 mmol) in tetrahydrofuran (40 mL) was added to a mixture of 5-formylthiophen-2-yl-2-boronic acid (401 g, 2.58 mmol), Pd(PPh)$_3$)$_4$ (136 mg, 0.17 mmol) and 2 M Na$_2$CO$_3$ (3.4 mL, 6.89 mmol). The mixture was heated at 80 °C for two days. Afterwards, water was added and the solution mixture was extracted with ethyl acetate. The combined organic layer was dried by Na$_2$SO$_4$ and filtered. The mixture was then concentrated under reduced pressure. The residue was purified by
column chromatography using CH$_2$Cl$_2$ as eluent to get 5-(4,4'-dinonyl-2,2'-bithiazol-5-yl)thiophene-2-carbaldehyde as a yellow solid (445 mg, 0.84 mmol, 49%).

**Spectral Data**: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.91$ (s, 1H, CHO), 7.74–7.73 (d, $J = 4.0$ Hz, 1H, Ar), 7.27–7.26 (d, $J = 2.8$ Hz, 1H, Ar), 7.01 (s, 1H, Ar), 3.00–2.96 (t, $J = 7.7$ Hz, 2H, nonyl), 2.83–2.79 (t, $J = 7.6$ Hz, 2H, nonyl), 1.81–1.72 (m, 4H, nonyl), 1.42–1.31 (m, 24H, nonyl), 0.89–0.85 (m, 6H, nonyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 182.65$ (CHO), 159.99, 159.70, 159.67, 156.65, 143.29, 142.99, 136.80, 127.82, 126.18, 115.57 (Ar), 37.12, 31.92, 31.56, 30.81, 29.74, 29.57, 29.52, 29.46, 29.35, 29.34, 29.28, 29.25, 27.13, 22.72, 19.77, 14.18 (nonyl) ppm. FAB-MS (m/z): 531.3 [M$^+$]. C$_{29}$H$_{42}$N$_2$OS$_3$ (530.85): calcd. C 65.62, H 7.97, N 5.28; found C 65.34, H 8.10, N 5.35.

**Synthesis of D2-CHO**: Yield: 81%; deep yellow solid.

**Spectral Data**: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.79$ (s, 1H, CHO), 7.61–7.60 (d, $J = 3.9$ Hz, 1H, Ar), 7.29–7.27 (m, 1H, Ar), 7.15–7.14 (d, $J = 4.0$ Hz, 1H, Ar), 7.10–7.08 (m, 1H, Ar), 7.00–6.98 (m, 1H, Ar), 2.89–2.81 (m, 4H, nonyl), 1.77–1.64 (m, 4H, nonyl), 1.35–1.20 (m, 24H, nonyl), 0.83–0.73 (m, 6H, nonyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 182.49$ (CHO), 159.36, 156.97, 156.71, 154.75, 143.24,
142.93, 136.71, 132.74, 128.42, 127.80, 127.72, 127.55, 126.68, 126.34 (Ar), 31.92, 30.83, 30.34, 29.57, 29.56, 29.52, 29.50, 29.45, 29.33, 29.21 (nonyl) ppm. FAB-MS (m/z): 612.2 [M]+. C₃₃H₄₄N₂OS₄ (612.97): calcd. C 64.66, H 7.24, N 4.57; found C 64.80, H 7.43, N 4.55.

**Synthesis of D₃-MCHO:** Yield: 81%; orange solid.

*Spectral Data:* ¹H NMR (400 MHz, CDCl₃): δ = 9.90 (s, 1H, CHO), 7.73–7.72 (d, J = 4.0 Hz, 1H, Ar), 7.29–7.25 (m, 5H, Ar), 7.15–7.11 (m, 4H, Ar), 7.07–7.05 (m, 5H, Ar), 3.00–2.97 (t, J = 7.7 Hz, 2H, nonyl), 2.84–2.80 (t, J = 7.6 Hz, 2H, nonyl), 2.34 (s, 3H, Ar-CH₃), 1.80–1.76 (m, 4H, nonyl), 1.42–1.22 (m, 24H, nonyl), 0.88–0.84 (m, 6H, nonyl) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 182.58 (CHO), 160.01, 156.74, 156.68, 153.85, 148.21, 147.32, 144.57, 143.19, 143.17, 136.76, 135.47, 133.73, 130.16, 129.92, 129.36, 127.69, 125.90, 125.67, 124.64, 124.07, 123.28, 121.83 (Ar) 53.43 (Ar-CH₃) 31.91, 31.89, 30.94, 30.81, 29.84, 29.78, 29.70, 29.56, 29.53, 29.48, 29.44, 29.33, 29.31, 29.25, 29.90 (nonyl) ppm. FAB-MS (m/z): 787.3 [M]+. C₄₈H₅₇N₃OS₃ (788.18): calcd. C 73.15, H 7.29, N 5.33; found C 73.34, H 7.10, N 5.41.
**Synthesis of D4-CHO:** Yield: 80%; orange solid.

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): δ = 9.90 (s, 1H, CHO), 8.17 (d, $J = 1.5$ Hz, 1H, Ar), 8.10–8.08 (d, $J = 7.7$ Hz, 1H, Ar), 7.72–7.71 (d, $J = 4.0$ Hz, 1H, Ar), 7.56–7.42 (m, 4H, Ar), 7.27–7.25 (m, 2H, Ar), 4.34–4.31 (t, $J = 7.2$ Hz, 2H, butyl), 3.02–2.98 (t, $J = 7.7$ Hz, 2H, nonyl), 2.92–2.88 (t, $J = 7.6$ Hz, 2H, nonyl), 1.90–1.80 (m, 6H, nonyl and butyl), 1.46–1.21 (m, 24H, nonyl), 0.99–0.95 (t, $J = 14.7$ Hz, 3H, butyl), 0.89–0.82 (m, 8H, nonyl and butyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 182.59 (CHO), 160.13, 156.98, 156.68, 153.86, 143.26, 143.13, 140.91, 140.20, 136.78, 136.66, 127.66, 127.03, 126.24, 125.83, 123.16, 122.50, 121.80, 121.36, 120.47, 119.31, 109.01, 108.95 (Ar) 43.04, 31.90, 31.60, 31.16, 30.85, 29.94, 29.67, 29.58, 29.55, 29.52, 29.46, 29.43, 29.32, 29.27, 20.60, 14.12, 13.90 (nonyl and butyl) ppm. FAB-MS (m/z): 751.3 [M]$^+$.

C$_{45}$H$_{57}$N$_3$OS$_3$ (752.15): calcd. C 71.86, H 7.64, N 5.59; found C 71.78, H 7.88, N 5.70.

**Synthesis of D5-CHO:** Yield: 83%; orange solid.

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): δ = 9.92 (s, 1H, CHO), 7.77–7.73 (m, 3H, Ar), 7.45–7.43 (m, 2H, Ar), 7.37–7.35 (m, 3H, Ar), 7.29–7.26 (m, 1H, Ar), 3.03–2.99 (m, 2H, nonyl), 2.90–2.86 (m, 2H, nonyl), 2.02–1.98 (m, 4H, butyl), 1.82–1.80 (m, 4H, butyl), 1.27–1.24 (m, 30H, nonyl and butyl), 1.11–1.09 (m, 4H,
butyl), 0.69–0.67 (m, 10H, nonyl and butyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 182.61$ (CHO), 159.92, 157.33, 156.76, 154.39, 151.34, 150.96, 143.26, 143.14, 141.50, 140.29, 136.78, 136.04, 130.03, 128.21, 127.76, 127.61, 126.98, 126.07, 123.69, 122.97, 122.01, 119.98 (Ar) 55.14, 40.18, 31.91, 30.86, 29.96, 29.58, 29.55, 29.53, 29.52, 29.47, 29.32, 26.03, 23.08, 13.86 (nonyl and butyl) ppm. FAB-MS ($m/z$): 806.4 [M$^+$]. $C_{50}H_{66}N_2O_S_3$ (807.27): calcd. C 74.39, H 8.24, N 3.47; found C 74.55, H 8.39, N 3.62.

**Synthesis of F1-CHO:** Yield: 46%; yellow solid.

In a 50 mL round bottom flask, 2-(5-bromothiophenyl)fluoren-9-one (500 mg, 1.46 mmol) in toluene/ethanol (3:1, 40 mL) was added to a mixture of 5-formylnithiophenyl-2-boronic acid (274 g, 1.76 mmol), Pd(PPh$_3$)$_4$ (168 mg, 0.14 mmol) and 2 M Na$_2$CO$_3$ (2.92 mL, 5.84 mmol). The mixture was heated at 80 °C for two days. Afterwards, water was added and the solution mixture was extracted with ethyl acetate. The combined organic layer was dried by Na$_2$SO$_4$ and filtered. The mixture was then concentrated under reduced pressure. The residue was purified by column chromatography using CH$_2$Cl$_2$/n-hexane (1:1, v/v) as eluent to yield compound 4 as a yellow solid (250 mg, 0.67 mmol, 46%).

**Spectral Data:** $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.87$ (s, 1H, CHO), 7.90 (m, 1H,
Ar), 7.73–7.68 (m, 3H, Ar), 7.56–7.51 (m, 3H, Ar), 7.36–7.28 (m, 4H, Ar) ppm. 13C
NMR (100 MHz, CDCl3): δ 193.35 (C=O), 182.48 (CHO), 146.72, 144.68, 144.06,
143.71, 141.85, 137.36, 135.69, 135.05, 135.02, 134.48, 134.35, 131.51, 129.31,
127.21, 124.81, 124.58, 124.31, 121.37, 120.95, 120.53 (Ar) ppm. MALDI-TOF (m/z):
372.03 [M]+.

**Synthesis of F2-CHO:** Yield: 45%; orange solid.

*Spectral Data:* 1H NMR (400 MHz, CDCl3): δ = 9.91 (s, 1H, CHO), 8.02–7.98
(m, 1H, Ar), 7.85–7.73 (m, 6H, Ar), 7.65–7.59 (m, 4H, Ar), 7.48–7.47 (m, 1H, Ar),
7.36–7.26 (m, 3H, Ar), 2.05–2.01 (m, 4H, butyl), 1.11–1.07 (m, 4H, butyl), 0.68–0.64
(m, 10H, butyl) ppm. 13C NMR (100 MHz, CDCl3): δ 193.13 (C=O), 182.63 (CHO),
152.65, 151.73, 151.06, 144.87, 143.40, 142.87, 142.30, 141.40, 140.49, 138.42,
138.32, 137.25, 135.44, 135.16, 133.93, 133.58, 132.57, 128.30, 127.40, 126.91,
125.70, 124.59, 123.24, 122.99, 122.02, 121.13, 121.09, 121.05, 120.15, 119.92 (Ar),
55.23, 40.24, 31.60, 26.04, 23.07, 22.66, 14.11, 13.82 (butyl) ppm. MALDI-TOF
(m/z): 566.23 [M]+.

**Synthesis of F3-CHO:** Yield: 48%; deep orange solid.

*Spectral Data:* 1H NMR (400 MHz, CDCl3): δ = 9.86 (s, 1H, CHO), 8.00–7.90
(m, 2H, Ar), 7.81–7.66 (m, 5H, Ar), 7.60–7.54 (m, 4H, Ar), 7.37–7.32 (m, 5H, Ar),
7.27–7.25 (m, 1H, Ar), 2.05–2.01 (m, 4H, butyl), 1.13–1.07 (m, 4H, butyl),
0.72–0.62 (m, 10H, butyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 193.45 (C=O),
182.42 (CHO), 151.67, 151.02, 146.70, 144.68, 143.64, 142.98, 142.56, 141.86,
141.29, 140.49, 138.371, 137.32, 135.69, 135.36, 135.09, 134.32, 133.48, 131.60,
127.35, 127.21, 126.88, 125.64, 124.77, 124.29, 123.13, 122.95, 121.42, 120.98,
120.89, 120.11, 119.88 (Ar), 55.20, 40.26, 31.60, 26.01, 23.07, 22.66, 14.11, 13.83
(butyl) ppm. MALDI-TOF (m/z): 649.29 [M]$^+$. 

**Synthesis of F4-CHO:** Yield: 42%; red solid.

$^1$H NMR (400 MHz, CDCl$_3$): δ 9.84 (s, 1H, CHO), 7.84–7.82 (m, 2H, Ar),
7.65–7.64 (m, 2H, Ar), 7.50–7.41 (m, 4H, Ar), 7.30–7.22 (m, 3H, Ar), 7.10–7.02 (m,
11H, Ar), 2.33 (s, 6H, CH$_3$) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 193.40 (C=O),
182.42 (CHO), 148.31, 146.72, 144.92, 144.72, 143.71, 142.02, 141.93, 141.75,
137.37, 135.54, 135.28, 135.04, 134.05, 133.03, 132.53, 131.99, 131.48, 131.24,
130.00, 129.82, 127.22, 124.99, 124.65, 124.23, 123.35, 122.38, 122.06, 121.24,
120.85, 120.78, 120.06 (Ar), 20.88 (CH$_3$) ppm. MALDI-TOF (m/z): 643.97 [M]$^+$. 

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8.3.4 Experimental Details for Dyes

*Synthesis of D1*

5-(4,4'-Dinonyl-2,2'-bithiazol-5-yl)thiophene-2-carbaldehyde (100 mg, 0.19 mmol) in 4 mL of dry chloroform, cyanoacetic acid (32.1 mg, 0.38 mmol) and piperidine (0.1 mL) were added. The mixture was heated at reflux temperature overnight. Afterwards, the mixture was concentrated under reduced pressure. The residue was purified by chromatography on a silica gel column using CH₂Cl₂/MeOH (1:1, v/v) as eluent. The mixture was then washed with methanol to give D1 as a red solid (82 mg, 0.14 mmol, 72%).

*Spectral Data*: ¹H NMR (400 MHz, CDCl₃): δ = 8.81 (s, 1H, COOH), 8.26 (s, 1H, C=CH), 7.52 (s, 1H, Ar), 6.99 (s, 1H, Ar), 6.86 (s, 1H, Ar), 3.34 (s, 2H, nonyl), 2.74 (m, 2H, nonyl), 1.68–1.67 (m, 4H, nonyl), 1.33–1.20 (m, 24H, nonyl), 0.88–0.81 (m, 6H, nonyl) ppm. MALDI-TOF (m/z): 598.1 [M]+. C₃₂H₄₃N₃O₂S₃ (597.89): calcd. C 64.28, H 7.25, N 7.03; found C 64.40, H 7.32, N 7.20.

*Synthesis of D2*: Yield: 68%; deep red solid.

*Spectral Data*: ¹H NMR (400 MHz, d₆-DMSO): δ = 8.03 (s, 1H, C=CH), 7.75–7.73 (m, 2H, Ar), 7.70–7.69 (d, J = 4.0 Hz, 1H, Ar), 7.46–7.45 (d, J = 3.9 Hz, 1H, Ar), 7.40–7.39 (m, 1H, Ar), 2.97–2.88 (m, 4H, nonyl), 1.71–1.70 (m, 4H, nonyl),
1.34−1.21 (m, 24H, nonyl), 0.83−0.80 (m, 6H, nonyl) ppm. MALDI-TOF (m/z): 680.4 [M]^+. C_{36}H_{45}N_{3}O_{2}S_{4} (680.01): calcd. C 63.59, H 6.67, N 6.18; found C 63.69, H 6.78, N 6.22.

**Synthesis of D3**: Yield: 65%; dark red solid.

*Spectral Data*: ¹H NMR (400 MHz, d₆-DMSO): δ = 8.05 (s, 1H, C=CH), 7.71−7.69 (d, J = 4.0 Hz, 1H, Ar), 7.45−7.30 (m, 5H, Ar), 7.18−7.16 (d, J = 8.2 Hz, 2H, Ar), 7.10−6.99 (m, 5H, Ar), 6.95–6.93 (m, 2H, Ar), 2.96−2.91 (m, 2H, nonyl), 2.78−2.75 (m, 2H, nonyl), 2.28 (s, 3H, Ar-CH₃), 1.72–1.60 (m, 4H, nonyl), 1.36−1.19 (m, 24H, nonyl), 0.85−0.79 (m, 6H, nonyl) ppm. MALDI-TOF (m/z): 854.5 [M]^+. C_{51}H_{58}N_{4}O_{2}S_{3} (855.23): calcd. C 71.63, H 6.84, N 6.55; found C 71.76, H 6.91, N 6.63.

**Synthesis of D4**: Yield: 73%; deep red solid.

*Spectral Data*: ¹H NMR (400 MHz, d₆-DMSO): δ = 8.32 (s, 1H, C=CH), 8.22−8.20 (d, J = 7.7 Hz, 1H, Ar), 8.04 (s, 1H, Ar), 7.72−7.45 (m, 6H, Ar), 7.24−7.20 (t, J = 7.4 Hz, 1H, Ar), 4.44−4.40 (m, 2H, butyl), 2.97−2.84 (t, 4H, nonyl), 1.76−1.70 (m, 6H, nonyl and butyl), 1.34−1.09 (m, 24H, nonyl), 0.90−0.72 (m, 11H, nonyl and butyl) ppm. MALDI-TOF (m/z): 819.5 [M]^+. C_{48}H_{58}N_{4}O_{2}S_{3} (819.19): calcd. C 70.38,
Synthesis of D5: Yield: 70%; deep orange solid.

Spectral Data: $^1$H NMR (400 MHz, $d_6$-DMSO): $\delta$ = 8.06 (s, 1H, C=CH), 7.93–7.86 (m, 2H, Ar), 7.73–7.72 (m, 1H, Ar), 7.69 (s, 1H, Ar), 7.51–7.48 (m, 3H, Ar), 7.37–7.36 (m, 2H, Ar), 3.03–2.97 (m, 10H, nonyl and butyl), 2.06–2.02 (m, 4H, nonyl and butyl), 1.63–1.54 (m, 10H, nonyl and butyl), 1.15–1.01 (m, 20H, nonyl and butyl), 0.64–0.50 (m, 12H, nonyl and butyl) ppm. MALDI-TOF (m/z): 874.6 [M]$^+$. C$_{53}$H$_{67}$N$_3$O$_2$S$_3$ (874.31): calcd. C 72.81, H 7.72, N 4.81; found C 72.90, H 7.97, N 4.90.

Synthesis of F1: Yield: 69%; orange solid.

Spectral Data: $^1$H NMR (400 MHz, $d_6$-DMSO): $\delta$ 7.73 (s, 1H, Ar), 7.58–7.45 (m, 5H, Ar), 7.37–7.30 (m, 4H, Ar), 7.18–7.15 (m, 1H, Ar), 7.08–7.05 (m, 1H, Ar) ppm. MALDI-TOF (m/z): 440.7 [M]$^+$. C$_{25}$H$_{13}$NO$_3$S$_2$ (439.50): calcd. C 68.32, H 2.98, N 3.19; found C 68.45, H 3.12, N 3.33.


Spectral Data: $^1$H NMR (400 MHz, $d_6$-DMSO): $\delta$ 8.10–7.75 (m, 13H, Ar), 7.46–7.45 (m, 1H, Ar), 7.36–7.34 (m, 2H, Ar), 2.11–2.03 (m, 4H, butyl), 1.07–1.02
(m, 4H, butyl), 0.68–0.62 (m, 10H, butyl) ppm. MALDI-TOF (m/z): 634.1 [M]+.

C₄₂H₃₅NO₃S (633.80): calcd. C 79.59, H 5.57, N 2.21; found C 79.49, H 5.68, N 2.43.

**Synthesis of F3:** Yield: 61%; deep orange solid.

*Spectral Data:* ¹H NMR (400 MHz, d₆-DMSO): δ 8.06 (s, 1H, Ar), 7.98–7.84 (m, 9H, Ar), 7.72–7.66 (m, 3H, Ar), 7.51–7.44 (m, 3H, Ar), 7.36–7.34 (m, 2H, Ar), 2.11–2.01 (m, 4H, butyl), 1.05–1.00 (m, 4H, butyl), 0.62–0.49 (m, 10H, butyl) ppm. MALDI-TOF (m/z): 716.2 [M]+. C₄₆H₃₇NO₃S₂ (715.92): calcd. C 77.17, H 5.21, N 1.96; found C 77.30, H 5.23, N 2.13.

**Synthesis of F4:** Yield: 67%; red solid.

*Spectral Data:* ¹H NMR (400 MHz, d₆-DMSO): δ 7.99 (s, 1H, Ar), 7.80–7.69 (m, 7H, Ar), 7.61–7.58 (m, 2H, Ar), 7.54–7.50 (m, 2H, Ar), 7.42–7.39 (m, 2H, Ar), 7.14–7.08 (m, 4H, Ar), 7.90–7.85 (m, 5H, Ar), 2.23 (s, 6H, CH₃) ppm. MALDI-TOF (m/z): 711.0 [M]+. C₄₅H₃₀N₂O₃S₂ (710.86): calcd. C 76.03, H 4.25, N 3.94; found C 76.24, H 4.35, N 4.09.
8.4 Experimental Details for Chapter 3

8.4.1 Experimental Details for Various Boronic Acid Derivatives

Synthesis of dibenzothiophen-2-ylboronic acid

A THF (30 mL) solution of 2-bromodibenzothiophene (2 g, 7.60 mmol) was cooled to −78 °C under nitrogen atmosphere, and then 2.5 M n-butyllithium (3.6 mL, 9.10 mmol) was added dropwise over 15 minutes. The mixture was stirred at −78 °C for 20 minutes and then trimethylborate (1.3 mL, 11.40 mmol) was added dropwise, and the solution was stirred at room temperature for 24 hours. The reaction was quenched by the addition of 2 M HCl and the mixture was extracted with diethyl ether. The combined organic layer was dried by Na₂SO₄ and was filtered. Afterwards, the mixture was concentrated under reduced pressure. The residue was washed by n-hexane to obtain dibenzothiophen-2-ylboronic acid as a white solid (1.18 g, 5.18 mol, 68%).

Synthesis of 9-phenylcarbazol-3-ylboronic acid

In the absence of light, NBS (1.46 mg, 8.20 mmol) was added dropwise to a solution of 9-phenylcarbazole (2 g, 8.20 mmol) in chloroform (30 mL) and was stirred overnight. The mixture was then concentrated under reduced pressure and filtered by chromatography on a silica gel column using CH₂Cl₂ as eluent to afford
3-bromo-9-phenylcarbazole as a pale yellow oil (2.51 g, 7.79 mmol, 95%).

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.24$ (m, 1H, Ar), 8.09–8.07 (m, 1H, Ar), 7.62–7.57 (m, 2H, Ar), 7.53–7.37 (m, 7H, Ar), 7.31–7.28 (m, 1H, Ar) ppm.

A THF (30 mL) solution of 3-bromo-9-phenylcarbazole (2 g, 9.55 mmol) was cooled to $-78$ °C under nitrogen atmosphere, and then 2.5 M $n$-butyllithium (4.6 mL, 11.5 mmol) was added dropwise over 15 minutes. The mixture was stirred at $-78$ °C for 20 minutes and then trimethylborate (1.6 mL, 14.3 mmol) was added dropwise, and the solution was stirred at room temperature for 24 hours. The reaction was quenched by the addition of 2 M HCl and the mixture was extracted with diethyl ether. The combined organic layer was dried by Na$_2$SO$_4$ and was filtered. Afterwards, the mixture was concentrated under reduced pressure. The residue was washed by $n$-hexane to obtain 9-phenylcarbazol-3-ylboronic acid as a white solid (1.51 g, 5.25 mol, 55%).

### 8.4.2 Experimental Details for Halide Precursors

**Synthesis of DT1-Br**

In a 50 mL round bottom flask placed in an ice-water bath was charged with dibenzothiophene (4.00 g, 21.71 mmol) in chloroform (15 mL) and then bromine
(3.46 g, 21.71 mmol) was added dropwisely. After 30 minutes, the ice-water bath was removed and the mixture was stirred at room temperature for three days. Afterwards, the mixture was filtered and washed with methanol. The product 2-bromodibenzothiophene was obtained as a white solid in 59% yield.

**Spectral Data:** $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.28−8.27 (d, $J$ = 2.0 Hz, 1H, Ar), 8.12−8.10 (m, 1H, Ar), 7.86−7.84 (m, 1H, Ar), 7.72−7.70 (d, $J$ = 8.6 Hz, 1H, Ar), 7.56−7.54 (m, 1H, Ar), 7.49−7.47 (m, 2H, Ar) ppm. MALDI-TOF ($m/z$): 261.95 [M]$^+$.

To a solution of 2-bromodibenzothiophene (3.30 g, 12.60 mmol) in 40 mL of tetrahydrofuran was added thiophen-2-yl-2-boronic acid (2.42 g, 18.90 mmol), Pd(PPh$_3$)$_4$ (300 mg, 1.26 mmol) and 2 M Na$_2$CO$_3$ (15 mL, 30 mmol). The mixture was heated at reflux temperature for two days. After being cooled to room temperature, water was added and the solution mixture was extracted with ethyl acetate. The combined organic layer was dried by Na$_2$SO$_4$ and was filtered. Afterwards, the mixture was concentrated under reduced pressure. The residue was purified by chromatography on a silica gel column using $n$-hexane as eluent. The product 2-(thiophen-2-yl)dibenzothiophene was obtained as a white solid (2.58 g, 9.68 mmol, 77%).

**Spectral Data:** $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.35 (d, $J$ = 1.6 Hz, 1H, Ar),
8.22–8.19 (m, 1H, Ar), 7.86–7.83 (m, 2H, Ar), 7.72–7.70 (m, 1H, Ar), 7.48–7.46 (m, 2H, Ar), 7.42–7.41 (m, 1H, Ar), 7.32–7.31 (m, 1H, Ar), 7.14–7.12 (m, 1H, Ar) ppm.

MALDI-TOF (m/z): 266.02 [M]⁺.

In a 50 mL bottom flask, 2-(thiophen-2-yl)dibenzothiophene (1.00 g, 3.76 mmol) was placed in chloroform (30 mL). N-Bromosuccinimide (635 mg, 3.57 mmol) was then added and the mixture was stirred at room temperature overnight. Afterwards, the mixture was filtered by a silica gel column using CH₂Cl₂ and concentrated under reduced pressure. The final product 2-(5-bromothiophen-2-yl)dibenzothiophene was obtained as a pale green solid in 83% yield.

Spectral Data: ¹H NMR (400 MHz, CDCl₃): δ = 8.25–8.24 (d, J = 1.6 Hz, 1H, Ar), 8.20–8.17 (m, 1H, Ar), 7.87–7.83 (m, 2H, Ar), 7.62–7.60 (m, 1H, Ar), 7.49–7.47 (m, 2H, Ar), 7.16–7.15 (d, J = 3.8 Hz, 1H, Ar), 7.08–7.07 (d, J = 3.8 Hz, 1H, Ar) ppm.

MALDI-TOF (m/z): 343.93 [M]⁺.

**Synthesis of DT2-Br**

To a solution of 2-(5-bromothiophen-2-yl)dibenzothiophene (1.05 g, 3.04 mmol) in 40 mL of tetrahydrofuran was added thiophen-2-yl-2-boronic acid (710 g, 4.55 mmol), Pd(PPh₃)₄ (350 mg, 0.30 mmol) and 2 M Na₂CO₃ (6 mL, 12 mmol). The
mixture was heated at reflux temperature for two days. After being cooled to room temperature, water was added and the solution mixture was extracted with ethyl acetate. The combined organic layer was dried by \( \text{Na}_2\text{SO}_4 \) and was filtered. Afterwards, the mixture was concentrated under reduced pressure. The residue was purified by chromatography on a silica gel column using \( \text{CH}_2\text{Cl}_2/n\text{-hexane} \) (1:5, v/v) as eluent to provide 2-(2,2'-bithiophen-5-yl)dibenzothiophene as a pale green solid (0.93 g, 2.67 mmol, 88%).

**Spectral Data:** \(^1\text{H} \text{NMR} \ (400 \text{ MHz}, \text{CDCl}_3)\): \(\delta = 8.35 (\text{d, } J = 1.6 \text{ Hz, } 1\text{H, Ar}), 8.23 \text{ (m, } 1\text{H, Ar})\), \(7.85 \text{ (m, } 2\text{H, AR}), 7.72 \text{ (m, } 1\text{H, Ar}), 7.49 \text{ (m, } 2\text{H, Ar}), 7.33 \text{ (d, } J = 3.8 \text{ Hz, } 1\text{H, Ar}), 7.23 \text{ (m, } 2\text{H, Ar}), 7.19 \text{ (d, } J = 3.8 \text{ Hz, } 1\text{H, Ar}), 7.05 \text{ (m, } 1\text{H, Ar}) \text{ ppm.}
\)

MALDI-TOF \((m/z)\): 348.01 \([\text{M}]^+\).

In a 50 mL bottom flask, 2-(2,2'-bithiophen-5-yl)dibenzothiophene (500 g, 1.43 mmol) was placed in 30 mL chloroform. \(N\)-Bromosuccinimide (242 mg, 1.36 mmol) was added and the mixture was stirred at room temperature overnight. Afterwards, the mixture was filtered by a silica gel column using \(\text{CH}_2\text{Cl}_2\) and concentrated under reduced pressure to obtain 2-(5'-bromo-2,2'-bithiophen-5-yl)dibenzothiophene as a bright yellow solid (575 g, 1.35 mmol, 94%).

**Spectral Data:** \(^1\text{H} \text{NMR} \ (400 \text{ MHz, CDCl}_3)\): \(\delta = \) \(^1\text{H} \text{NMR} \ (400 \text{ MHz, CDCl}_3)\): \(\delta = \)
8.33 (d, $J = 1.6$ Hz, 1H, Ar), 8.23–8.21 (m, 1H, Ar), 7.88–7.84 (m, 2H, Ar), 7.71–7.68 (m, 1H, Ar), 7.50–7.48 (m, 2H, Ar), 7.33–7.32 (d, $J = 3.8$ Hz, 1H, Ar), 7.13 (d, $J = 3.8$ Hz, 1H, Ar), 7.01–6.97 (m, 2H, Ar) ppm. MALDI-TOF (m/z): 425.92 [M$^+$].

**Synthesis of DT4-Br**

In a 50 mL round bottom flask, in an ice-water bath, was placed dibenzothiophene (6.00 g, 32.60 mmol) in chloroform (15 mL). To this mixture, bromine (3.7 mL, 71.60 mmol) was added dropwise. After 30 minutes, the ice-water bath was removed and the mixture was stirred at room temperature for three days. Afterwards the mixture was filtered and the solid was washed with methanol to obtain 2,8-dibromodibenzothiophene as a white solid (10.28 g, 30.08 mmol, 92%).

**Spectral Data**: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.23$ (d, $J = 1.9$ Hz, 2H, Ar), 7.71–7.69 (m, $J = 8.5$ Hz, 2H, Ar), 7.59–7.56 (m, 2H, Ar) ppm. MALDI-TOF (m/z): 339.86 [M$^+$].

To a solution of 2,8-dibromodibenzothiophene (1 g, 2.92 mmol) in 40 mL of tetrahydrofuran was added thiophen-2-yl-2-boronic acid (393 mg, 3.07 mmol), Pd(PPh$_3$)$_4$ (338 mg, 0.29 mmol) and 2 M Na$_2$CO$_3$ (5.8 mL, 12 mmol). The mixture was heated at reflux temperature for two days. After being cooled to room
temperature, water was added and the solution mixture was extracted with ethyl acetate. The combined organic layer was dried by Na$_2$SO$_4$ and was filtered. Afterwards, the mixture was concentrated under reduced pressure. The residue was purified by chromatography on a silica gel column using CH$_2$Cl$_2$/n-hexane (1:4, v/v) as eluent to acquire 2-bromo-8-(thiophen-2-yl)dibenzothiophene as a white solid (396 mg, 1.15 mmol, 39%).

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.39-8.38$ (d, $J = 1.6$ Hz, 1H, Ar), 7.85–7.83 (m, 1H, Ar), 7.74–7.72 (m, 1H, Ar), 7.45–7.44 (m, 1H, Ar), 7.34–7.32 (m, 3H, Ar) 7.15–7.13 (m, 1H, Ar) ppm. MALDI-TOF ($m/z$): 343.93 [M]$^+$.

To a solution of 2-bromo-8-(thiophen-2-yl)dibenzothiophene (854 mg, 2.47 mmol) in 40 mL of tetrahydrofuran was added 9,9-dibutylfluoren-2-ylboronic acid (1.20 g, 3.70 mmol), Pd(PPh$_3$)$_4$ (286 mg, 0.24 mmol) and 2 M Na$_2$CO$_3$ (5 mL, 9.89 mmol). The mixture was heated at reflux temperature for two days. After being cooled to room temperature, water was added and the solution mixture was extracted with ethyl acetate. The organic layer was dried by Na$_2$SO$_4$ and was filtered. Then, the mixture was concentrated under reduced pressure. The residue was purified by chromatography on a silica gel column using CH$_2$Cl$_2$/n-hexane (1:4, v/v) as eluent to get 2-(9,9-dibutylfluoren-2-yl)-8-(thiophen-2-yl)dibenzothiophene as a white solid.
(924 mg, 1.70 mmol, 69%).

Spectral Data: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.58-8.55$ (m, 2H, Ar), 8.02–7.76 (m, 8H, Ar), 7.62–7.51 (m, 4H, Ar), 7.46–7.43 (m, 1H, Ar), 7.28–7.25 (m, 1H, Ar), 2.39–2.28 (m, 4H, butyl), 1.42–1.37 (m, 4H, butyl), 1.06–0.96 (m, 10H, butyl) ppm. MALDI-TOF (m/z): 542.21 [M]$^+$.  

2-(9,9-Dibutylfluoren-2-yl)-8-(thiophen-2-yl)dibenzothiophene (924 mg, 1.70 mmol) was placed in chloroform (30 mL) in a 50 mL round bottom flask. To this mixture, $n$-bromosuccinimide (360 mg, 2.64 mmol) was added and the mixture was stirred at room temperature overnight. Afterwards, the mixture was filtered by a silica gel column using CH$_2$Cl$_2$ and concentrated under reduced pressure to acquire 2-(5-bromothiophen-2-yl)-8-(9,9-dibutylfluoren-2-yl)dibenzothiophene as a pale green solid (937 mg, 1.51 mmol, 89%).

Spectral Data: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.39$ (m, 1H, Ar), 8.27–8.26 (m, 1H, Ar), 7.90–7.71 (m, 8H, Ar), 7.56–7.54 (m, 1H, Ar), 7.48–7.41 (m, 3H, Ar), 7.13–7.07 (m, 2H, Ar), 2.20–2.13 (m, 4H, butyl), 1.25–1.17 (m, 4H, butyl), 0.88–0.78 (m, 10H, butyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 151.68$, 151.09, 145.90, 140.83, 140.66, 139.92, 139.48, 138.86, 138.59, 136.16, 135.74, 131.01, 130.26, 127.25, 126.98, 126.71, 126.37, 124.52, 123.33, 123.28, 123.08, 123.03,
308

121.75, 120.23, 120.06, 119.94, 118.35, 111.33 (Ar) 55.26, 40.36, 31.74, 26.23, 23.25, 22.82, 14.29, 14.09 (butyl) ppm. MALDI-TOF (m/z): 620.12 [M]⁺.

Synthesis of DT5-Br

To a solution of 2-bromo-8-(thiophen-2-yl)dibenzothiophene (796 mg, 2.30 mmol) in 40 mL of tetrahydrofuran was added di-upported boronic acid (1.10 g, 3.45 mmol), Pd(PPh₃)₄ (338 mg, 0.23 mmol) and 2 M Na₂CO₃ (4.6 mL, 18.4 mmol). The mixture was heated at reflux temperature for two days. After being cooled to room temperature, water was added and the solution mixture was extracted with ethyl acetate. The organic layer was dried by Na₂SO₄ and was filtered. Then, the mixture was concentrated under reduced pressure. The residue was purified by chromatography on a silica gel column using CH₂Cl₂/n-hexane (1:4, v/v) as eluent to give 4-methyl-\(N\)-(4-(8-(thiophen-2-yl)dibenzothiophen-2-yl)phenyl)-\(N\)-p-tolylaniline as a white solid (989 mg, 1.84 mmol, 80%).

Spectral Data: \(^1\)H NMR (400 MHz, CDCl₃): \(\delta = 8.37–8.36 \text{ (d, } J = 1.6 \text{ Hz, } 1\text{H, Ar)}, 7.81–7.79 \text{ (m, } 1\text{H, Ar)}, 7.72–7.69 \text{ (m, } 1\text{H, Ar)}, 7.55–7.53 \text{ (m, } 3\text{H, Ar)}, 7.43–7.36 \text{ (m, } 8\text{H, Ar)} 7.03–7.00 \text{ (m, } 7\text{H, Ar)}, 2.23 \text{ (s, } 6\text{H, CH₃}) \text{ ppm. MALDI-TOF (m/z): 537.16 [M]⁺.}
4-Methyl-N-(4-(8-(thiophen-2-yl)dibenzothiophen-2-yl)phenyl)-N-p-tolylaniline (1.15 g, 2.14 mmol) was placed in chloroform (30 mL) in a 50 mL round bottom flask. To this mixture, n-bromosuccinimide (457 mg, 2.57 mmol) was added and the mixture was stirred at room temperature overnight. Afterwards, the mixture was filtered by a silica gel column using CH$_2$Cl$_2$ and the filtrate was concentrated under reduced pressure to acquire 4-(8-(5-bromothiophen-2-yl)dibenzothiophen-2-yl)-N,N-di-p-tolylaniline as a pale yellow solid (1.21 g, 2.01 mmol, 94%).

**Spectral Data:** $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.36−8.35$ (d, $J = 1.6$ Hz, 1H, Ar), 7.82−7.80 (m, 1H, Ar), 7.72−7.69 (m, 1H, Ar), 7.55−7.53 (m, 2H, Ar), 7.47−7.38 (m, 6H, Ar), 7.32−7.24 (m, 2H, Ar), 7.15−7.11 (m, 2H, Ar), 7.07−7.04 (m, 2H, Ar), 6.97−6.93 (m, 3H, Ar), 2.73 (s, 6H, CH$_3$) ppm. MALDI-TOF ($m/z$): 615.07 [M]$^+$.

**Synthesis of DT6-Br**

To a solution of 2-bromo-8-(thiophen-2-yl)dibenzo[18]cyclophane (833 mg, 2.41 mmol) in 40 mL of tetrahydrofuran was added dibenzo[18]cyclophane-2-ylboronic acid (825 g, 3.62 mmol), Pd(PPh$_3$)$_4$ (278 mg, 0.24 mmol) and 2 M Na$_2$CO$_3$ (4.8 mL, 8.84 mmol). The mixture was heated at reflux temperature for two days. After being cooled to room temperature, water was added and the solution mixture was extracted with ethyl acetate. The organic layer was dried by Na$_2$SO$_4$ and was filtered. Then, the mixture
was concentrated under reduced pressure. The residue was purified by chromatography on a silica gel column using CH₂Cl₂/n-hexane (1:4, v/v) as eluent to give 8-(thiophen-2-yl)-2,2′-bis-dibenzothiophene as a white solid (897 mg, 2.20 mmol, 83%).

**Spectral Data:**

\[ ^1H \text{ NMR (400 MHz, CDCl}_3\]: \( \delta = 8.37 \text{ (s, 3H, Ar), 8.24–8.21 (m, 1H, Ar), 7.91–7.66 (m, 7H, Ar), 7.46–7.39 (m, 3H, Ar), 7.30–7.28 (m, 1H, Ar), 7.11–7.09 (m, 1H, Ar) ppm.} \]

\[ ^13C \text{ NMR (100 MHz, CDCl}_3\]: \( \delta = 144.38, 139.99, 139.05, 139.01, 138.59, 137.93, 137.68, 136.24, 136.07, 135.96, 135.53, 131.16, 128.17, 126.93, 126.61, 126.35, 125.16, 124.80, 124.46, 123.31, 123.20, 123.14, 122.94, 121.76, 120.26, 120.19, 118.77 \text{ (Ar) ppm.} \]

MALDI-TOF (m/z): 448.04 [M]+.

8-(Thiophen-2-yl)-2,2′-bis-dibenzothiophene (330 mg, 0.74 mmol) was placed in chloroform (30 mL) in a 50 mL round bottom flask. To this mixture, \( n \)-bromosuccinimide (157 mg, 0.88 mmol) was added and the mixture was stirred at room temperature overnight. Afterwards, the mixture was filtered by a silica gel column using CH₂Cl₂ and the filtrate was concentrated under reduced pressure to acquire 8-(5-bromothiophen-2-yl)-2,2′-bis-dibenzothiophene as a white solid (351 mg, 0.67 mmol, 90%).

**Spectral Data:**

\[ ^1H \text{ NMR (400 MHz, CDCl}_3\]: \( \delta = 8.44 \text{ (m, 2H, Ar), 8.34–8.28 (m, 1H, Ar), 8.01–7.98 (m, 3H, Ar), 7.89–7.78 (m, 7H, Ar), 7.46–7.39 (m, 3H, Ar), 7.30–7.28 (m, 1H, Ar), 7.11–7.09 (m, 1H, Ar) ppm.} \]
2H, Ar), 7.98–7.79 (m, 6H, Ar), 7.64–7.62 (m, 1H, Ar), 7.51–7.49 (m, 2H, Ar), 7.19–7.18 (d, \( J = 3.8 \) Hz, 1H, Ar), 7.18–7.07 (d, \( J = 3.8 \) Hz, 1H, Ar) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 145.80, 139.99, 139.51, 139.03, 138.66, 138.12, 137.65, 136.27, 136.14, 135.83, 135.51, 130.98, 130.42, 126.99, 126.84, 126.38, 124.74, 124.51, 123.47, 123.43, 123.31, 122.99, 120.32, 120.25, 118.55, 111.35 \) (Ar) ppm. MALDI-TOF (m/z): 525.95 [M]\(^+\).

**Synthesis of C1-Br**

To a solution of 5-bromothiophene-2-carbaldehyde (608 mg, 3.18 mmol) in tetrahydrofuran (40 mL) was added 9-butylcarbazol-3-yl-3-boronic acid (1.15 g, 3.82 mmol), Pd(PPh\(_3\))\(_4\) (368 mg, 0.32 mmol) and 2 M Na\(_2\)CO\(_3\) (6 mL, 12 mmol). The mixture was heated at reflux temperature for two days. After being cooled to room temperature, water was added and the solution mixture was extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na\(_2\)SO\(_4\) and was filtered. Afterwards, the mixture was concentrated under reduced pressure. The residue was purified by chromatography on a silica gel column using CH\(_2\)Cl\(_2\)/n-hexane (1:1, v/v) as eluent to provide compound 5-(9-butylcarbazol-6-yl)thiophene-2-carbaldehyde as a yellow solid (942 mg, 2.83 mmol, 89%).
Spectral Data: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.88$ (s, 1H, CHO), 8.39 (m, 1H, Ar), 8.14–8.12 (m, 1H, Ar), 7.78–7.75 (m, 2H, Ar), 7.52–7.41 (m, 4H, Ar), 7.30–7.25 (m, 1H, Ar), 4.33–4.30 (t, $J = 7.1$ Hz, 2H, butyl), 1.88–1.85 (m, 2H, butyl), 1.57–1.37 (m, 2H, butyl), 0.97–0.93 (t, $J = 14.7$ Hz, 3H, butyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 182.64$ (CHO), 156.39, 141.21, 141.09, 141.03, 137.91, 126.42, 124.40, 124.05, 123.42, 122.86, 122.63, 120.61, 119.55, 118.55, 109.29, 109.15 (Ar), 43.06, 31.12, 20.56, 13.88 (butyl) ppm.

In the absence of light, NBS (567 mg, 3.19 mmol) was added in small portions to a solution of 5-(9-butylcarbazol-6-yl)thiophene-2-carbaldehyde (886 g, 2.65 mmol) in a mixture of acetic acid (30 mL) and chloroform (30 mL) and was stirred overnight. The mixture was then concentrated under reduced pressure and filtered by chromatography on a silica gel column using CH$_2$Cl$_2$ as eluent to afford 5-(3-bromo-9-butylcarbazol-6-yl)thiophene-2-carbaldehyde as a yellow solid (982 mg, 2.38 mmol, 90%).

Spectral Data: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.88$ (s, 1H, CHO), 8.31 (m, 1H, Ar), 8.23–8.22 (m, 1H, Ar), 7.79–7.75 (m, 2H, Ar), 7.58–7.55 (m, 1H, Ar), 7.43–7.40 (m, 2H, Ar), 7.30–7.25 (m, 1H, Ar), 4.29–4.26 (t, $J = 7.1$ Hz, 2H, butyl), 1.86–1.82 (m, 2H, butyl), 1.40–1.34 (m, 2H, butyl), 0.96–0.92 (t, $J = 14.7$ Hz, 3H, butyl) ppm.
\[^{13}\text{C}\] NMR (100 MHz, CDCl\(_3\)): \(\delta = 182.63\) (CHO), 155.81, 141.45, 141.24, 139.64, 137.85, 129.08, 125.09, 124.53, 124.31, 123.36, 123.03, 122.37, 118.62, 112.36, 110.57, 109.58 (Ar), 43.19, 31.05, 20.51, 13.83 (butyl) ppm.

**Synthesis of C3-Br**

To a solution of 5-bromothiophene-2-carbaldehyde (981 mg, 5.13 mmol) in tetrahydrofuran (50 mL) was added thiophen-2-yl-2-boronic acid (788 mg, 6.16 mmol), Pd(PPh\(_3\))\(_4\) (593 mg, 0.51 mmol) and 2 M Na\(_2\)CO\(_3\) (10.3 mL, 20 mmol). The mixture was heated at reflux temperature for two days. After being cooled to room temperature, water was added and the solution mixture was extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na\(_2\)SO\(_4\) and was filtered. Afterwards, the mixture was concentrated under reduced pressure. The residue was purified by chromatography on a silica gel column using CH\(_2\)Cl\(_2\)/n-hexane (1:1, v/v) as eluent to obtain 5-(thiophen-2-yl)thiophene-2-carbaldehyde (967 mg, 4.98 mmol, 97%).

**Spectral Data:** \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\)): \(\delta = 9.86\) (s, 1H, CHO), 7.67–7.66 (m, 1H, Ar), 7.37–7.35 (m, 2H, Ar), 7.26–7.24 (m, 1H, Ar), 7.08–7.06 (m, 1H, Ar) ppm.

\[^{13}\text{C}\] NMR (100 MHz, CDCl\(_3\)): \(\delta = 182.63\) (CHO), 147.21, 141.68, 137.41, 136.04, 128.40, 127.14, 126.19, 124.27 (Ar) ppm.
In the absence of light, NBS (930 mg, 5.97 mmol) was added in small portions to a solution of 5-(thiophen-2-yl)thiophene-2-carbaldehyde (967 mg, 5.97 mmol) in chloroform (30 mL) and the mixture was stirred overnight. The mixture was then concentrated under reduced pressure and filtered by chromatography on a silica gel column using CH$_2$Cl$_2$ as eluent to give 5-(5-bromothiophen-2-yl)thiophene-2-carbaldehyde as a greenish yellow solid (1.02 g, 5.61 mmol, 94%).

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.85$ (s, 1H, CHO), 7.66–7.65 (m, 1H, Ar), 7.18–7.17 (m, 1H, Ar), 7.10–7.09 (m, 1H, Ar), 7.03–7.02 (m, 1H, Ar) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 182.56$ (CHO), 145.67, 141.96, 137.42, 137.32, 131.24, 126.22, 124.43, 114.09 (Ar) ppm.

To a solution of 5-(5-bromothiophen-2-yl)thiophene-2-carbaldehyde (830 mg, 3.04 mmol) in tetrahydrofuran (40 mL) was added 9-butylcarbazol-3-yl-3-boronic acid (1.1 g, 3.65 mmol), Pd(PPh$_3$)$_4$ (351 mg, 0.30 mmol) and 2 M Na$_2$CO$_3$ (6 mL, 12 mmol) in 50 mL round bottom flask. The mixture was heated at reflux temperature for two days. After being cooled to room temperature, water was added and the solution mixture was extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na$_2$SO$_4$ and was filtered. Afterwards, the mixture was concentrated under reduced pressure. The residue was purified by chromatography on a silica gel column.
using CH$_2$Cl$_2$/n-hexane (3:2, v/v) as eluent to provide 5-(5-(9-buty Carlo zol-6-yl)thiophen-2-yl)thiophene-2-carbaldehyde as an orange solid (1.08 g, 2.61 mmol, 86%).

Spectral Data: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 9.83 (s, 1H, CHO), 8.32 (m, 1H, Ar), 8.15–8.13 (m, 1H, Ar), 7.73–7.69 (m, 2H, Ar), 7.50–7.48 (m, 1H, Ar), 7.44–7.37 (m, 3H, Ar), 7.37–7.27 (m, 3H, Ar), 4.33–4.30 (t, $J$ = 7.1 Hz, 2H, butyl), 1.88–1.85 (m, 2H, butyl), 1.41–1.38 (m, 2H, butyl), 0.97–0.93 (t, $J$ = 14.7 Hz, 3H, butyl) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 182.82 (CHO), 148.03, 140.92, 140.77, 140.49, 138.02, 133.59, 127.42, 126.18, 124.47, 123.92, 123.62, 123.00, 122.58, 120.51, 119.23, 117.77, 109.17, 109.03 (Ar), 42.96, 31.10, 20.52, 13.84 (butyl) ppm.

In the absence of light, NBS (440 mg, 2.47 mmol) was added dropwise to a solution of 5-(9-buty Carlo zol-6-yl)thiophene-2-carbaldehyde (978 mg, 2.35 mmol) in a mixture of acetic acid (30 mL) and chloroform (30 mL) and the mixture was stirred overnight. The mixture was then concentrated under reduced pressure and filtered by chromatography on a silica gel column using CH$_2$Cl$_2$ as eluent to give 5-(5-(3-bromo-9-buty Carlo zol-6-yl)thiophen-2-yl)thiophene-2-carbaldehyde as a golden yellow solid (940 mg, 1.90 mmol, 81%).

Spectral Data: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 9.72 (s, 1H, CHO), 8.04–7.97 (m,
2H, Ar), 7.52–7.42 (m, 3H, Ar), 7.17–7.02 (m, 5H, Ar), 4.04–4.01 (t, $J = 7.1$ Hz, 2H, butyl), 1.70–1.66 (m, 2H, butyl), 1.29–1.23 (m, 2H, butyl), 0.88–0.84 (m, 3H, butyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 182.36 (CHO), 147.44, 147.30, 140.91, 140.42, 139.42, 137.61, 133.69, 128.70, 124.83, 124.39, 124.26, 123.51, 123.17, 122.94, 122.14, 117.56, 112.03, 110.42, 109.33 (AR), 42.98, 31.05, 20.53, 13.92 (butyl) ppm.

8.4.3 Experimental Details for Aldehyde Precursors

_Synthesis of DT1-CHO_

$n$-Butyllithium (0.64 mL, 1.60 mmol) was added dropwise to a solution of 2-(5-bromothiophen-2-yl)dibenzothiophene (500 mg, 1.45 mmol) in anhydrous THF (20 mL) at $-78^\circ$C and the resultant mixture was stirred for 20 minutes. A solution of DMF (0.17 mL, 2.18 mmol) was slowly added into the flask. The mixture was then warmed to room temperature and stirred overnight. The reaction was quenched by the addition of 2 M HCl and the mixture was extracted with diethyl ether. The combined organic layer was dried by Na$_2$SO$_4$ and was filtered. Afterwards, the mixture was concentrated under reduced pressure. The residue was purified by chromatography on a silica gel column using CH$_2$Cl$_2$/n-hexane (1:1, v/v) as eluent. The product 5-(dibenzothiophen-2-yl)thiophene-2-carbaldehyde was isolated as a bright yellow
solid (316 mg, 1.07 mmol, 74%).

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.92$ (s, 1H, CHO), 8.42 (d, $J = 1.6$ Hz, 1H, Ar), 8.23–8.21 (m, 1H, Ar), 7.91–7.86 (m, 2H, Ar), 7.70–7.75 (m, 2H, Ar), 7.52–7.50 (m, 3H, Ar) ppm. MALDI-TOF ($m/z$): 294.02 [M$^+$].

**Synthesis of D2-CHO:** Yield: 88%; bright yellow solid.

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.88$ (s, 1H, CHO), 8.36 (d, $J = 1.6$ Hz, 1H, Ar), 8.24–8.22 (m, 1H, Ar), 7.89–7.87 (m, 2H, Ar), 7.73–7.70 (m, 2H, Ar), 7.52–7.49 (m, 2H, Ar), 7.39 (s, 2H, Ar), 7.31–7.30 (d, $J = 3.9$ Hz, 1H, Ar) ppm. MALDI-TOF ($m/z$): 376.01 [M$^+$].

**Synthesis of DT3-CHO**

To a solution of 2-(5'-bromo-2,2'-bithiophen-5-yl)dibenzothiophene (500 mg, 1.17 mmol) in 40 mL of tetrahydrofuran was added 5-formylthiophen-2-yl-2-boronic acid (274 g, 1.76 mmol), Pd(PPh$_3$)$_4$ (135 mg, 0.17 mmol) and 2 M Na$_2$CO$_3$ (2.5 mL, 4.68 mmol). The mixture was heated at reflux temperature for two days. After being cooled to room temperature, water was added and the solution mixture was extracted with ethyl acetate. The combined organic layer was dried by Na$_2$SO$_4$ and was filtered. Afterwards, the mixture was concentrated under reduced pressure. The residue was
purified by chromatography on a silica gel column using CH₂Cl₂/n-hexane (2:1, v/v) as eluent to provide 5"-(dibenzothiophen-2-yl)-2,2',2''-trithiophene-5-carbaldehyde as a bright orange solid (245 mg, 0.53 mmol, 46%).

*Spectral Data:* $^1$H NMR (400 MHz, CDCl₃): δ = 9.86 (s, 1H, Ar), 8.35–8.34 (d, $J$ = 1.6 Hz, 1H, Ar), 8.24–8.21 (m, 1H, Ar), 7.88–7.85 (m, 2H, Ar), 7.72–7.68 (m, 2H, Ar), 7.51–7.48 (m, 2H, Ar), 7.37–7.36 (d, $J$ = 3.7 Hz, 1H, Ar), 7.31–7.30 (d, $J$ = 3.8 Hz, 1H, Ar), 7.26–7.24 (m, 2H, Ar), 7.19–7.18 (d, $J$ = 3.8 Hz, 1H, Ar) ppm. MALDI-TOF (m/z): 457.99 [M]+.

**Synthesis of DT4-MCHO:** Yield: 67%; yellow solid.

*Spectral Data:* $^1$H NMR (400 MHz, CDCl₃): δ = 9.85 (m, 1H, CHO), 8.41–8.39 (m, 2H, Ar), 7.89–7.62 (m, 10H, Ar), 7.36–7.34 (m, 5H, Ar), 2.14–2.104 (m, 4H, butyl), 1.15–1.10 (m, 10H, butyl) ppm. $^{13}$C NMR (100 MHz, CDCl₃): δ = 182.19 (CHO), 151.57, 150.95, 147.08, 146.15, 141.66, 140.71, 140.66, 139.96, 139.86, 138.86, 138.80, 137.15, 136.26, 135.69, 135.06, 130.14, 127.12, 126.83, 126.25, 124.66, 124.19, 123.83, 123.35, 123.05, 122.86, 121.71, 120.12, 120.04, 119.77, 118.57 (Ar) 55.14, 53.22, 40.28, 34.65, 26.91, 26.06, 25.24, 20.56 (butyl) ppm. MALDI-TOF (m/z): 652.19 [M]+.
**Synthesis of DT5-CHO:** Yield: 56%; yellow solid.

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.88$ (s, 1H, CHO), 8.41–8.36 (m, 2H, Ar), 7.97–7.86 (m, 3H, Ar), 7.75–7.68 (m, 4H, Ar), 7.58–7.39 (m, 7H, Ar), 7.31–7.29 (m, 2H, Ar), 7.15–6.92 (m, 3H, Ar), 6.78–6.61 (m, 1H, Ar), 2.35–2.33 (m, 6H, CH$_3$) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 182.40$ (CHO), 147.06, 146.15, 145.94, 145.32, 142.49, 141.48, 139.78, 138.55, 137.86, 136.97, 134.99, 134.89, 133.16, 129.38, 128.79, 127.71, 127.19, 124.62, 124.42, 124.25, 124.15, 123.97, 123.35, 122.99, 122.08, 121.25, 119.86, 119.50, 118.48 (Ar) 20.65 (CH$_3$) ppm. MALDI-TOF (m/z): 647.14 [M]$^+$. 

**Synthesis of DT6-CHO:** Yield: 65%; yellow solid.

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.87$ (s, 1H, Ar), 8.49–8.45 (m, 3H, Ar), 8.31–8.29 (m, 1H, Ar), 7.99–7.96 (m, 2H, Ar), 7.91–7.89 (m, 2H, Ar), 7.85–7.82 (m, 2H, Ar), 7.75–7.73 (m, 1H, Ar), 7.69–7.68 (m, 1H, Ar), 7.52–7.50 (m, 2H, Ar), 7.42–7.38 (m, 2H, Ar), 7.30–7.29 (m, 1H, Ar) ppm. MALDI-TOF (m/z): 558.02 [M]$^+$. 

**Synthesis of C1-CHO:** Yield: 86%; bright yellow solid.

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.86$ (s, 1H, CHO), 8.45–8.41
(m, 2H, Ar), 8.28–8.25 (m, 1H, Ar), 7.94–7.72 (m, 6H, Ar), 7.50–7.39 (m, 6H, Ar),
4.33–4.30 (t, $J = 7.1$ Hz, 2H, butyl), 1.90–1.85 (m, 2H, butyl), 1.44–1.35 (m, 2H,
butyl), 0.98–0.94 (t, $J = 14.7$ Hz, 3H, butyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ =
182.66 (CHO), 156.27, 141.51, 141.21, 140.48, 139.99, 138.43, 137.97, 137.86,
136.24, 135.64, 132.96, 126.84, 126.41, 126.12, 124.59, 124.43, 124.23, 123.53,
123.27, 123.06, 122.95, 122.89, 121.71, 121.64, 120.03, 119.24, 118.62, 109.50 (Ar),
43.18, 31.19, 20.59, 13.90 (butyl) ppm.

**Synthesis of C2-CHO:** Yield: 88%; yellow solid.

* Spectral Data: $^1$H NMR (400 MHz, CDCl$_3$): δ = 9.89 (s, 1H, CHO), 8.50–8.46
(m, 3H, Ar), 8.26–8.24 (m, 1H, Ar), 7.89–7.87 (m, 1H, Ar), 7.82–7.77 (m, 3H, Ar),
7.64–7.62 (m, 4H, Ar), 7.54–7.44 (m, 8H, Ar), 4.39–4.35 (t, $J = 7.1$ Hz, 2H, butyl),
1.94–1.90 (m, 2H, butyl), 1.47–1.41 (m, 2H, butyl), 1.00–0.94 (t, $J = 14.7$ Hz, 3H,
butyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): 182.62, 156.40, 141.54, 141.39, 141.21,
140.18, 140.09, 137.92, 137.78, 134.11, 134.01, 129.95, 129.84, 127.49, 127.09,
126.94, 126.31, 126.12, 125.76, 124.51, 124.12, 124.04, 123.65, 123.57, 123.27,
122.89, 120.44, 120.05, 119.52, 119.14, 118.87, 118.65, 110.10, 109.94, 109.42 (Ar),
43.20, 31.21, 20.59, 13.91 (butyl) ppm.
**Synthesis of C3-CHO:** Yield: 76%; bright orange solid.

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.80$ (s, 1H, Ar), 8.42–8.33 (m, 3H, Ar), 8.25–8.23 (m, 1H, Ar), 7.91–7.77 (m, 4H, Ar), 7.68–7.66 (m, 1H, Ar), 7.59–7.58 (m, 1H, Ar), 7.47–7.44 (m, 3H, Ar), 7.35–7.33 (m, 1H, Ar), 7.29–7.28 (m, 1H, Ar), 7.25–7.23 (m, 1H, Ar), 7.18–7.17 (m, 1H, Ar), 4.28–4.24 (t, $J = 7.1$ Hz, 2H, butyl), 1.87–1.82 (m, 2H, butyl), 1.42–1.38 (m, 2H, butyl), 0.97–0.93 (m, 3H, butyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 182.37$ (CHO), 147.79, 147.66, 141.04, 140.82, 140.42, 140.00, 138.54, 137.78, 137.51, 136.22, 135.67, 133.74, 132.67, 127.28, 126.81, 126.42, 125.89, 124.74, 124.40, 123.49, 123.47, 123.31, 123.01, 122.98, 122.94, 121.69, 120.00, 119.19, 117.85, 109.35, 109.31 (Ar), 43.09, 31.21, 20.60, 13.91 (butyl) ppm.

**Synthesis of C4-CHO:** Yield: 78%; orange solid.

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.73$ (s, 1H, CHO), 8.42–8.30 (m, 3H, Ar), 8.22–8.20 (m, 1H, Ar), 7.80–7.71 (m, 2H, Ar), 7.61–7.39 (m, 12H, Ar), 7.30–7.26 (m, 1H, Ar), 7.23–7.18 (m, 2H, Ar), 7.11–7.10 (m, 1H, Ar), 4.20–4.17 (t, $J = 7.1$ Hz, 2H, butyl), 1.82–1.78 (m, 2H, butyl), 1.36–1.30 (m, 2H, butyl), 0.93–0.89 (m, 3H, butyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 182.48$ (CHO), 171.34, 147.93, 147.78, 141.34, 140.84, 140.80, 140.07, 139.99, 137.76, 137.69, 134.19, 133.59,
133.57, 129.93, 127.44, 127.33, 127.00, 126.90, 126.10, 126.01, 125.74, 124.54, 124.04, 123.93, 123.60, 123.52, 123.49, 123.27, 122.92, 120.44, 120.04, 118.99, 118.76, 117.78, 110.05, 109.93, 109.28, 109.24 (Ar), 43.09, 31.23, 20.62, 13.97 (butyl) ppm.

8.4.4 Experimental Details for Dyes

Synthesis of DT1

To a solution of 5-(dibenzothiophen-2-yl)thiophene-2-carbaldehyde (100 mg, 0.34 mmol) in 5 mL of dry chloroform, cyanoacetic acid (57.78 mg, 0.68 mmol) and piperidine (0.1 mL) was added. The mixture was heated at reflux temperature overnight. Afterwards, the mixture was concentrated under reduced pressure. The residue was purified by chromatography on a silica gel column using CHCl₃/MeOH (1:1, v/v) as eluent. The mixture was then washed with methanol to give DT1 as a yellow solid (80 mg, 0.22 mmol, 65%).

Spectral Data: ¹H NMR (400 MHz, CDCl₃): δ = 9.51 (s, 1H, COOH), 8.41 (d, J = 1.6 Hz, 1H, C=CH), 8.25–8.22 (m, 2H, Ar), 7.89–7.86 (m, 2H, Ar), 7.78–7.75 (m, 1H, Ar), 7.65–7.64 (d, J = 3.9 Hz, 1H, Ar), 7.51–7.46 (m, 3H, Ar) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 168.09 (COOH), 151.28, 143.05, 140.11, 139.89, 136.53, 136.24, 136.02, 135.03, 129.80, 127.29, 124.85, 124.69, 123.93, 123.37, 122.95,
121.89 (Ar), 119.05 (C≡N), 117.53 (-C=) ppm. MALDI-TOF (m/z): 361.9 [M]+.

**Synthesis of DT2:** Yield: 48%; red solid.

*Spectral Data:* $^1$H NMR (400 MHz, $d_6$-DMSO): $\delta = 8.74$ (d, $J = 1.6$ Hz, 1H, C=CH), 8.58–8.56 (m, 1H, Ar), 8.10–8.08 (d, $J = 8.4$ Hz, 1H, Ar), 8.06–8.03 (m, 2H, Ar), 7.88–7.86 (m, 1H, Ar), 7.78–7.77 (d, $J = 3.9$ Hz, 1H, Ar), 7.67–7.66 (d, $J = 4.0$ Hz, 1H, Ar), 7.58–7.57 (d, $J = 3.8$ Hz, 1H, Ar), 7.56–7.54 (m, 2H, Ar), 7.50–7.49 (d, $J = 3.9$ Hz, 1H, Ar) ppm. MALDI-TOF (m/z): 443.9 [M]+.

**Synthesis of DT3:** Yield: 52%; deep red solid.

*Spectral Data:* $^1$H NMR (400 MHz, $d_6$-DMSO): $\delta = 8.72–8.71$ (d, $J = 1.6$ Hz, 1H, C=CH), 8.56–8.54 (m, 1H, Ar), 8.10–8.04 (m, 3H, Ar), 7.86–7.83 (m, 1H, Ar), 7.75–7.74 (d, $J = 3.7$ Hz, 1H, Ar), 7.68–7.67 (d, $J = 3.8$ Hz, 1H, Ar), 7.58–7.55 (m, 2H, Ar), 7.52–7.48 (m, 3H, Ar), 7.43–7.42 (d, $J = 3.8$ Hz, 1H, Ar) ppm. MALDI-TOF (m/z): 526.3 [M]+.

**Synthesis of DT4:** Yield: 67%; red solid.

*Spectral Data:* $^1$H NMR (400 MHz, $d_6$-DMSO): $\delta = 8.97–8.94$ (m, 2H, C=CH and Ar), 8.17–8.11 (m, 2H, Ar), 8.03 (s, 1H, Ar), 7.99–7.88 (m, 4H, Ar), 7.81–7.60
(m, 3H, Ar), 7.51–7.47 (m, 2H, Ar), 7.38–7.35 (m, 2H Ar), 2.14–1.99 (m, 4H, Ar), 1.09–1.02 (m, 4H, Ar), 0.67–0.54 (m, 10H, Ar) ppm. MALDI-TOF (m/z): 720.8 [M]^+.

**Synthesis of DT5**: Yield: 61%; deep red solid.

*Spectral Data*: $^1$H NMR (400 MHz, $d_6$-DMSO): $\delta = 8.93–8.84$ (m, 2H, C=CH and Ar), 8.15–8.05 (m, 5H, Ar), 7.90–7.50 (m, 14H, Ar), 7.25–6.62 (m, 8H, Ar), 2.33–2.30 (m, 6H, CH$_3$) ppm. MALDI-TOF (m/z): 715.8 [M]^+.

**Synthesis of DT6**: Yield: 67%; red solid.

*Spectral Data*: $^1$H NMR (400 MHz, $d_6$-DMSO): $\delta = 9.10–8.92$ (m, 2H, C=CH and Ar), 8.60 (s, 1H, Ar), 8.19–8.07 (m, 6H, Ar), 7.92–7.53 (m, 6H, Ar), 6.86–6.83 (m, 2H, Ar), 6.67 (s, 1H, Ar) ppm. MALDI-TOF (m/z): 626.4 [M]^+.

**Synthesis of C1**: Yield: 67%; red solid.

*Spectral Data*: $^1$H NMR (400 MHz, $d_6$-DMSO): $\delta = 8.83$ (m, 2H, Ar), 8.72–8.71 (m, 1H, Ar), 8.60–8.58 (m, 1H, Ar), 8.14–8.00 (m, 5H, Ar), 7.88–7.85 (m, 1H, Ar), 7.79–7.72 (m, 3H, Ar), 7.68–7.67 (m, 1H, Ar), 7.58–7.55 (m, 2H, Ar), 4.50–4.47 (t, $J = 7.1$ Hz, 2H, butyl), 1.90–1.80 (m, 2H, butyl), 1.36–1.28 (m, 2H, butyl), 0.92–0.88 (t, $J = 14.7$ Hz, 3H, butyl) ppm. MALDI-TOF (m/z): 582.92 [M]^+. 
Synthesis of **C2**: Yield: 70%; red solid.

*Spectral Data*: $^1$H NMR (400 MHz, $d_6$-DMSO): $\delta = 8.75−8.70$ (m, 3H, Ar), 8.40−8.38 (m, 1H, Ar), 8.12−8.08 (m, 1H, Ar), 7.93−7.32 (m, 16H, Ar), 4.74−4.46 (m, 2H, butyl), 1.81−1.77 (m, 2H, butyl), 1.34−1.28 (m, 2H, butyl), 0.91−0.86 (m, 3H, butyl) ppm. MALDI-TOF ($m/z$): 641.02 [M]$^+$. 

Synthesis of **C3**: Yield: 64%; deep red solid.

*Spectral Data*: $^1$H NMR (400 MHz, $d_6$-DMSO): $\delta = 8.92−8.89$ (m, 2H, Ar), 8.77−8.76 (m, 1H, Ar), 8.67−8.65 (m, 1H, Ar), 8.21−8.19 (m, 1H, Ar), 8.14−8.06 (m, 4H, Ar), 7.94−7.92 (m, 1H, Ar), 7.84−7.74 (m, 3H, Ar), 7.68−7.54 (m, 5H, Ar), 4.56−4.48 (t, $J = 7.1$ Hz, 2H, butyl), 1.90−1.86 (m, 2H, butyl), 1.43−1.37 (m, 2H, butyl), 0.99−0.92 (m, 3H, butyl) ppm. MALDI-TOF ($m/z$): 664.03 [M]$^+$. 

Synthesis of **C4**: Yield: 69%; deep red solid.

*Spectral Data*: $^1$H NMR (400 MHz, $d_6$-DMSO): $\delta = 8.77−8.71$ (m, 3H, Ar), 8.42−8.40 (m, 1H, Ar), 8.09 (m, 1H, Ar), 7.95−7.91 (m, 2H, Ar), 7.87−7.85 (m, 1H, Ar), 7.77−7.69 (m, 7H, Ar), 7.62−7.56 (m, 3H, Ar), 7.52−7.42 (m, 4H, Ar), 7.37−7.33 (m, 1H, Ar), 4.47 (m, 2H, butyl), 1.82−1.80 (m, 2H, butyl), 1.35−1.33 (m, 2H, butyl), 0.93−0.89 (m, 3H, butyl) ppm. MALDI-TOF ($m/z$): 723.04 [M]$^+$. 

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8.5 Experimental Details for Chapter 4

8.5.1 Experimental Details for Various Boronic Acid Derivatives

*Synthesis of 9,9-dihexyl-9H-fluoren-2,7-diyl-2,7-diboronic acid*

To a solution of 2-bromofluorene (3.0 g, 9.25 mmol) and 1-bromohexane (5.2 mL, 37.03 mmol) in DMSO (50 mL) was added 50 wt% aqueous sodium hydroxide (10 mL). The reaction mixture was stirred at room temperature for two days. A dark purple solution was obtained. The solution was poured into brine and extracted with three portions of 30 mL ethyl acetate. The organic layer was combined and dried over Na$_2$SO$_4$. The solvent was then removed by vacuum and purified by chromatography on a silica gel column using CH$_2$Cl$_2$ as eluent to afford 2,7-dibromo-9,9-dihexyl-9H-fluorene as a white crystal (3.62 g, 7.40 mmol, 80%).

*Spectral Data: *$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.52–7.50$ (m, 2H, Ar), $7.46–7.43$ (m, 4H, Ar), $1.92–1.88$ (m, 4H, alkyl), $1.13–1.02$ (m, 12H, alkyl), $0.79–0.76$ (m, 6H, alkyl), $0.59–0.55$ (m, 4H, alkyl) ppm.

A THF (100 mL) solution of 2,7-dibromo-9,9-dihexyl-9H-fluorene (2 g, 4.06 mmol) was cooled to $-78$ °C under nitrogen atmosphere, and then 2.5 M $n$-butyllithium (3.2 mL, 8.13 mmol) was added dropwise over 15 min. The mixture was stirred at $-78$ °C for 4 h and then trimethylborate (1 mL, 8.13 mmol) was added.
dropwise, and the solution was stirred at room temperature for 24 h. The reaction was quenched by the addition of 2 M HCl and extracted with diethyl ether. The combined organic layer was dried over Na$_2$SO$_4$ and filtered. Afterwards, the mixture was concentrated under reduced pressure. The residue was washed by $n$-hexane to obtain 9,9-dihexyl-9H-fluoren-2,7-diyl-2,7-diboronic acid as a white solid (960 mg, 2.27 mol, 56%). This compound was used directly without further purification and characterization.

**Synthesis of 9-octyl-9H-carbazol-2,7-diyl-2,7-diboronic acid**

A mixture of 2,5-dibromonitrobenzene (2 g, 7.17 mmol) and activated copper powder (1.43 g, 25 mmol) was dissolved in 20 mL of dimethylformamide and the mixture was stirred for 3 h at 120 °C. Then the mixture was allowed to cool to room temperature, and 50 mL of toluene was added. The mixture was stirred for a few minutes, then the brown residue was filtered off. The organic layer was washed with water and brine, the solution dried over Na$_2$SO$_4$, and the solvent evaporated to dryness. Then recrystallization from the solvent mixture of ethanol/toluene (4:1) gave 4,4'-dibromo-2,2'-dinitrobiphenyl as a light brown solid (1.22 g, 3.03 mmol, 85%).

**Spectral Data:** $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.38$ (d, $J = 3.7$ Hz, 2H, Ar), 7.82 ($J_1 = 1.0$ Hz, $J_2 = 3.7$ Hz, 2H, Ar), 7.15 (d, $J = 3.7$ Hz, 2H, Ar) ppm. FAB-MS: $m/z$:
While a mixture of 4,4′-dibromo-2,2′-dinitrobiphenyl (1.0 g, 2.45 mmol), 10 mL of concd. HCl, and 20 mL of ethanol was stirred, small portions of tin powder (1.2 g, 10.1 mmol) were added into the mixture. The reaction mixture was heated to reflux for 3 h. Then the mixture was poured into 200 mL of cold water, and added 2 M NaOH solution into the mixed solution, until pH 8 was reached. The solution was extracted with diethyl ether for several times. The organic layer was washed with water and dried by Na₂SO₄ and removed the solvent under reduced pressure. The residue was purified by column chromatography on silica gel using methylene chloride/n-hexane (30:1) as the eluent to yield 4,4′-dibromo-2,2′-diaminobiphenyl as a colorless solid (1.2 g, 3.51 mmol, 72%).

*Spectral Data:* $^1$H NMR (400 MHz, $d_6$-DMSO): $\delta = 7.01$ (d, $J = 0.8$ Hz, 2H, Ar), 6.88 (d, $J_1 = 3.7$ Hz, $J_2 = 3.8$ Hz, 2H, Ar), 6.80 (dd, $J_1 = 3.7$ Hz, $J_2 = 1.8$ Hz, 2H, Ar), 4.99 (s, 4H, N-H) ppm. FAB-MS: $m/z$: 342 [M]$^+$. 

4,4′-Dibromo-2,2′-diaminobiphenyl (350 mg, 1.05 mmol) was added into 15 mL of conc. H₃PO₄, and then the reaction mixture was refluxed at 190 °C for a whole day. Afterwards, the crude product was filtered and washed with water thoroughly. Then
the residue was diluted with toluene and filtered over silica gel. Subsequently, the product was recrystallized from toluene/n-hexane (10:1) as a white solid to afford (200 mg, 0.62 mmol, 60%) of 2,7-dibromocarbazole.

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.09$ (s, H, N-H), 7.88 (d, $J = 3.5$, 2H, Ar), 7.58 (d, $J = 1.8$ Hz, 2H, Ar), 7.37 (dd, $J_1 = 0.7$ Hz, $J_2 = 3.7$ Hz, 2H, Ar) ppm.

FAB-MS: $m/z$: 325 [M]$^+$.

2,7-Dibromocarbazole (1.44 g, 5.82 mmol) was dissolved in 20 mL of toluene. With the presence of the phase-transfer catalyst benzyltrimethylammonium chloride (66 mg, 0.29 mmol), 1-bromooctane (3 mL, 17.48 mmol), and 50 wt% NaOH (10 mL) were added into the reaction solution, which was refluxed for 4 h. Afterwards, the solvent was removed and the residue suspended in diethyl ether. The precipitate was filtered off and the organic phase washed with water several times. Then the residue was purified by column chromatography on silica gel using $n$-hexane/ethyl acetate (8:1, v/v) as the eluent to give 2,7-dibromo-9-octyl-$9H$-carbazole (1.44 g, 3.29 mmol, 57%) as a white solid.

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.61–7.59$ (d, $J = 4.2$ Hz, 2H, Ar), 7.30 (m, 2H, Ar), 7.15–7.12 (m, 2H, Ar), 3.89–3.85 (m, 2H, alkyl), 1.59–1.58 (m, 2H, alkyl), 1.13–1.09 (m, 10H, alkyl), 0.76–0.72 (m, 3H, alkyl) ppm. $^{13}$C NMR (100 MHz,
A THF (100 mL) solution of 2,7-dibromo-9-octyl-9H-carbazole (1.81 g, 4.16 mmol) was cooled to −78 °C under nitrogen atmosphere, and then 2.5 M \( n \)-butyllithium (3.33 mL, 8.32 mmol) was added dropwise over 15 min. The mixture was stirred at −78 °C for 4 h and then trimethylborate (1.41 mL, 12.48 mmol) was added dropwise, and the solution was stirred at room temperature for 24 h. The reaction was quenched by the addition of 2 M HCl and the mixture was extracted with diethyl ether. The combined organic layer was dried over \( \text{Na}_2\text{SO}_4 \) and filtered. Afterwards, the mixture was concentrated under reduced pressure. The residue was washed by \( n \)-hexane to obtain 9-octyl-9H-carbazol-2,7-diyl-2,7-diboronic acid as a white solid (885 mg, 2.32 mmol, 58%). This compound was used directly without further purification and characterization.

8.4.2 Experimental Details for Halide Precursors

**Synthesis of B1-Br**

To an ice-cooled POCl\(_3\) (8.9 mL, 92 mmol) in a two necked flask, DMF (7.1 mL, 92 mmol) solution was added and the mixture was stirred for 30 min at 0 °C. Then,
the reaction mixture was warmed to room temperature. 2-Bromothiophene (5.9 mL, 61.33 mmol) was then added and the mixture was heated to 90 °C overnight. The solution was then cooled to room temperature and the solvent mixture was evaporated in vacuo. The crude product was purified by column chromatography on silica gel with a solvent combination of *n*-hexane/CH$_2$Cl$_2$ (1:2, v/v) as eluent to provide B1-Br as a pale brown solid (9.3 g, 48.69 mmol, 80%)

_Spectral Data:_ $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.67$ (s, 1H, CHO), 7.46–7.45 (m, 1H, Ar), 7.10–7.09 (m, 1H, Ar) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 181.91$ (CHO), 145.05, 136.84, 124.95 (Ar) ppm.

_Synthesis of B2-Br_

To a solution of B1-Br (532 mg, 2.78 mmol) in 40 mL of tetrahydrofuran was added 9-phenyl-9H-carbazol-3-yl-3-boronic acid (1.6 g, 5.57 mmol), Pd(PPh$_3$)$_4$ (320 mg, 0.27 mmol) and 2 M Na$_2$CO$_3$ (5.57 mL, 11.15 mmol). The mixture was heated at reflux temperature for two days. After being cooled to room temperature, water was added and the solution mixture was extracted with ethyl acetate. The organic layer was dried by Na$_2$SO$_4$ and was filtered. Then, the mixture was concentrated under reduced pressure. The residue was purified by chromatography on a silica gel column using CH$_2$Cl$_2$/*n*-hexane (1:1, v/v) as eluent to afford 5-(9-phenyl-9H-carbazol-3-yl)
thiophene-2-carbaldehyde as a yellow solid (667 mg, 1.89 mmol, 68%).

Spectral Data: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.60$ (s, 1H, CHO), 8.13 (m, 2H, Ar), 7.93–7.91 (m, 1H, Ar), 7.42–7.41 (m, 1H, Ar), 7.39–7.35 (m, 3H, Ar), 7.28–7.24 (m, 3H, Ar), 7.21–7.18 (m, 2H, Ar), 7.12–7.08 (m, 3H, Ar) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 182.51$ (CHO), 155.76, 141.45, 141.30, 137.85, 137.07, 130.01, 127.83, 126.89, 126.73, 125.09, 124.54, 123.94, 123.05, 123.02, 120.63, 120.56, 118.33, 110.32, 110.16 (Ar) ppm.

5-(9-Phenyl-9H-carbazol-3-yl)thiophene-2-carbaldehyde (1.09 g, 3.09 mmol) was placed in DMF/acetic acid (30 mL) in a 50 mL round bottom flask. To this mixture n-bromosuccinimide (660 mg, 3.71 mmol) was added and the mixture was stirred at room temperature overnight. Afterwards, the mixture was filtered by a silica gel column using CH$_2$Cl$_2$ and concentrated under reduced pressure to acquire B2-Br as a yellow solid (983 mg, 2.28 mmol, 74%).

Spectral Data: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.79$ (s, 1H, CHO), 8.35 (m, 2H, Ar), 8.22–8.21 (m, 2H, Ar), 7.69–7.64 (m, 4H, Ar), 7.59–7.54 (m, 4H, Ar), 7.47–7.44 (m, 10H, Ar), 7.38–7.36 (m, 3H, Ar), 7.22–7.19 (m, 2H, Ar) ppm.
Synthesis of B3-Br

To an ice-cooled POCl₃ (0.58 mL, 6.01 mmol) in a two necked flask and DMF (0.46 mL, 6.01 mmol) solution was added and stirred for 30 min at 0 °C. Then, the reaction mixture was warmed to room temperature. 3-Bromo-9-butyl-9H-carbazole (1.21 g, 4.00 mmol) was then added and the mixture was heated to 90 °C overnight. The solution was then cooled to room temperature and the solvent mixture was evaporated in vacuo. The crude product was purified by column chromatography on silica gel with a solvent combination of n-hexane/CH₂Cl₂ (1:2, v/v) as eluent to provide B3-Br as a pale yellow solid (1.08 g, 3.27 mmol, 77%)

Spectral Data: ¹H NMR (400 MHz, CDCl₃): δ = 9.92 (s, 1H, CHO), 8.30 (s, 1H, Ar), 8.03 (m, 1H, Ar), 7.87–7.85 (m, 1H, Ar), 7.45–7.42 (m, 1H, Ar), 7.29–7.27 (m, 1H, Ar), 7.13–7.11 (m, 1H, Ar), 4.12–4.08 (m, 2H, alkyl), 1.71–1.67 (m, 2H, alkyl), 1.27–1.22 (m, 2H, alkyl), 0.84–0.81 (m, 3H, alkyl) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 191.47 (CHO), 144.08, 139.69, 129.32, 128.76, 127.41, 124.56, 124.21, 123.37, 121.84, 113.08, 110.81, 109.22 (Ar), 43.26, 30.96, 20.46, 13.81 (alkyl) ppm.

Synthesis of B4-Br

n-Butyllithium (1.06 mL, 2.64 mmol) was added dropwise to a solution of 2,7-dibromo-9,9-dibutyl-9H-fluorene (1.15 g, 2.64 mmol) in anhydrous THF (20 mL)
at −78 °C and the resultant mixture was stirred for 20 minutes. A solution of DMF (0.31 mL, 3.97 mmol) was slowly added into the flask. The mixture was then warmed to room temperature and stirred overnight. The reaction was quenched by the addition of 2 M HCl and extracted with diethyl ether. The combined organic layer was dried by Na₂SO₄ and was filtered. Afterwards, the mixture was concentrated under reduced pressure. The residue was purified by chromatography over a silica gel column using CH₂Cl₂/n-hexane (1:1, v/v) as eluent. The product 7-bromo-9,9-dibutyl-9H-fluorene-2-carbaldehyde was isolated as a pale yellow solid (547 mg, 1.42 mmol, 54%).

*Spectral Data:* ¹H NMR (400 MHz, CDCl₃): δ = 9.95 (s, 1H, CHO), 7.78–7.67 (m, 3H, Ar), 7.52–7.37 (m, 3H, Ar), 1.94–1.86 (m, 4H, alkyl), 0.98–0.93 (m, 4H, alkyl), 0.55–0.45 (m, 10H, alkyl) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 191.94 (CHO), 154.25, 151.13, 146.30, 138.60, 135.75, 130.52, 130.47, 126.48, 123.15, 123.12, 122.23, 120.09 (Ar), 55.53, 39.93, 31.59, 25.90, 22.92, 22.66, 14.11, 13.72 (alkyl) ppm.

8.4.3 Experimental Details for Aldehyde Precursors

*Synthesis of B1-CHO*

To a solution of B3-Br (135 mg, 0.41 mmol) in 40 mL of tetrahydrofuran was
added 9,9-dihexyl-9H-fluoren-2,7-diy1-2,7-diboronic acid (58 g, 0.13 mmol),
Pd(PPh3)4 (15 mg, 0.04 mmol) and 2 M Na2CO3 (0.71 mL, 0.54 mmol). The mixture
was heated at reflux temperature for two days. After being cooled to room
temperature, water was added and the solution mixture was extracted with ethyl
acetate. The combined organic layer was dried by Na2SO4 and was filtered.
Afterwards, the mixture was concentrated under reduced pressure. The residue was
purified by chromatography over a silica gel column using CH2Cl2/n-hexane (2:1, v/v)
as eluent to provide B1-CHO as a yellow solid (146 mg, 0.17 mmol, 43%).

Spectral Data: 1H NMR (400 MHz, CDCl3): δ = 10.13 (s, 2H, CHO), 8.71 (m, 2H, Ar), 8.48–8.47 (m, 2H, Ar), 8.04–8.02 (m, 2H, Ar), 7.91–7.85 (m, 4H, Ar), 7.76–7.73 (m, 4H, Ar), 7.56–7.47 (m, 4H, Ar), 4.37–4.33 (m, 4H, alkyl), 2.22–2.18 (m, 4H, alkyl), 1.93–1.89 (m, 4H, alkyl), 1.46–1.41 (m, 4H, alkyl), 1.20–1.15 (m, 15H, alkyl), 1.00–0.97 (m, 7H, alkyl), 0.82–0.78 (m, 6H, alkyl) ppm. 13C NMR (100 MHz, CDCl3): δ = 191.75 (CHO), 151.88, 144.51, 140.59, 140.36, 139.77, 134.37, 128.60, 127.37, 126.37, 126.23, 124.01, 123.60, 123.25, 121.65, 120.15, 119.14, 109.72, 109.15 (Ar), 55.46, 53.51, 43.34, 40.67, 31.63, 31.16, 29.87, 29.78, 24.03, 22.70, 20.59, 14.14, 13.93 (alkyl) ppm.

Spectral Data: $^1$H NMR (400 MHz, CDCl$_3$): δ = 9.89 (s, 2H, CHO), 8.50 (m, 2H, Ar), 8.44–8.43 (m, 2H, Ar), 7.86–7.72 (m, 12H, Ar), 7.54–7.45 (m, 6H, Ar), 4.37–4.35 (m, 4H, alkyl), 2.18–2.14 (m, 4H, alkyl), 1.94–1.90 (m, 4H, alkyl), 1.43 (m, 4H, alkyl), 1.16–1.12 (m, 13H, alkyl), 0.98–0.90 (m, 6H, alkyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 182.65 (CHO), 156.32, 151.81, 141.55, 141.25, 140.53, 140.47, 139.68, 137.94, 133.68, 126.20, 126.14, 124.59, 124.22, 123.62, 123.24, 122.93, 121.62, 120.05, 119.00, 118.65, 109.49, 109.44 (Ar), 55.42, 43.20, 40.61, 31.58, 31.21, 29.80, 29.74, 23.94, 22.65, 20.60, 14.13, 13.92 (alkyl) ppm.

Synthesis of B3-CHO: Yield: 49%; yellow solid.

Spectral Data: $^1$H NMR (400 MHz, CDCl$_3$): δ = 9.87 (s, 2H, CHO), 8.04–8.00 (m, 4H, Ar), 7.80 (s, 2H, Ar), 7.55–7.48 (m, 8H, Ar), 7.39–7.37 (m, 8H, Ar), 7.27–7.24 (m, 2H, Ar), 7.23–7.20 (m, 2H, Ar), 7.16–7.11 (m, 6H, Ar), 1.56–1.52 (m, 4H, alkyl), 0.82–0.78 (m, 9H, alkyl), 0.62–0.59 (m, 6H, alkyl), 0.54–0.51 (m, 7H, alkyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 182.76 (CHO), 151.36, 149.60, 141.11, 140.87, 140.02, 139.99, 139.47, 139.43, 136.70, 134.31, 130.09, 129.25, 128.11, 127.92, 127.84, 126.87, 125.47, 124.72, 123.47, 123.13, 122.59, 121.37, 120.15, 113.30, 111.56, 110.14 (Ar), 55.07, 54.99, 40.31, 39.91, 31.62, 31.41, 31.26, 29.73,
Synthesis of B4-CHO: Yield: 58%; yellow oil.

Spectral Data: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 10.09$ (s, 2H, CHO), 7.92–7.84 (m, 10H, Ar), 7.74–7.67 (m, 8H, Ar), 2.13–2.09 (m, 12H, alkyl), 1.15–1.10 (m, 22H, alkyl), 0.77–0.68 (m, 28H, alkyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 192.15$ (CHO), 152.99, 151.93, 151.78, 147.291, 142.34, 140.34, 140.17, 138.80, 135.38, 130.67, 126.55, 126.36, 123.10, 121.56, 121.28, 120.19, 120.01 (Ar), 55.39, 31.67, 31.49, 29.80, 29.69, 26.09, 23.88, 23.07, 22.73, 22.58, 14.15, 14.03, 13.81 (alkyl) ppm.

Synthesis of B5-CHO: Yield: 51%; yellow solid.

Spectral Data: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.89$ (s, 2H, CHO), 8.09–8.07 (m, 2H, Ar), 7.77–7.76 (m, 2H, Ar), 7.64 (m, 2H, Ar), 7.56–7.54 (m, 2H, Ar), 7.51–7.50 (m, 2H, Ar), 2.13–2.09 (m, 2H, alkyl), 1.91–1.87 (m, 2H, alkyl), 1.41–1.32 (m, 7H, alkyl), 0.88–0.81 (m, 6H, alkyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 182.73$ (CHO), 155.26, 142.26, 141.52, 137.56, 131.15, 124.20, 123.37, 121.25, 118.13, 106.74 (Ar), 43.23, 31.80, 31.60, 29.34, 29.18, 27.27, 22.67, 22.63 (alkyl) ppm.
**Synthesis of B6-CHO:** Yield: 52%; orange solid.

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.90$ (s, 2H, CHO), 8.11–8.09 (m, 2H, Ar), 7.73–7.72 (s, 2H, Ar), 7.61–7.53 (m, 4H, Ar), 7.43–7.41 (m, 4H, Ar), 7.33–7.32 (m, 2H, Ar), 4.41–4.37 (m, 2H, alkyl), 1.98–1.95 (m, 2H, alkyl), 1.48–1.42 (m, 6H, alkyl), 0.93–0.87 (m, 7H, alkyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 182.46 (CHO), 147.32, 147.27, 141.53, 141.47, 137.47, 134.92, 131.40, 127.25, 124.26, 123.92, 122.70, 120.99, 117.74, 105.93 (Ar), 43.13, 31.88, 31.61, 29.38, 29.23, 28.98, 27.28, 22.68 (alkyl) ppm.

**Synthesis of B7-CHO:** Yield: 56%; yellow solid.

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 10.09$ (s, 2H, CHO), 8.19–8.17 (m, 2H, Ar), 8.01–8.00 (m, 4H, Ar), 7.90–7.88 (m, 4H, Ar), 7.65 (m, 2H, Ar), 7.55–7.53 (m, 2H, Ar), 4.41–4.37 (m, 4H, alkyl), 1.97–1.93 (m, 9H, alkyl), 1.48–1.36 (m, 6H, alkyl), 0.94–0.86 (m, 7H, alkyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 191.90 (CHO), 148.03, 141.62, 137.83, 135.08, 130.29, 128.04, 122.65, 121.08, 118.94, 107.62 (Ar), 43.11, 31.83, 31.62, 29.36, 29.21, 29.01, 27.31, 22.64 (alkyl) ppm.
**Synthesis of B8-CHO:** Yield: 59%; yellow solid.

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 10.09$ (s, 2H, CHO), 8.24–8.21 (m, 2H, Ar), 7.93–7.90 (m, 3H, Ar), 7.79–7.67 (m, 9H, Ar), 7.60–7.58 (m, 2H, Ar), 7.35–7.31 (m, 2H, Ar), 4.49–4.45 (m, 2H, alkyl), 2.14–1.95 (m, 12H, alkyl), 1.17–1.05 (m, 12H, alkyl), 0.69–0.65 (m, 9H, alkyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 192.38$ (CHO), 152.96, 151.78, 142.92, 141.65, 139.25, 138.68, 135.27, 130.71, 128.81, 126.89, 123.09, 122.15, 121.52, 121.29, 120.79, 119.67, 118.91, 107.39 (Ar), 55.37, 40.21, 40.10, 31.83, 31.63, 29.74, 29.41, 29.29, 27.46, 26.07, 25.97, 23.09, 23.04, 14.17, 14.10, 13.85 (alkyl) ppm.

**Synthesis of B9-CHO:** Yield: 48%; orange solid.

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 9.88$ (s, 2H, CHO), 8.49–8.47 (m, 4H, Ar), 8.21–8.19 (m, 2H, Ar), 7.92–7.89 (m, 2H, Ar), 7.81–7.75 (m, 4H, Ar), 7.71–7.70 (m, 2H, Ar), 7.64–7.61 (m, 2H, Ar), 7.54–7.52 (m, 2H, Ar), 7.48–7.44 (m, 4H, Ar), 4.49–4.45 (m, 2H, alkyl), 2.14–1.95 (m, 12H, alkyl), 1.17–1.05 (m, 12H, alkyl), 0.69–0.65 (m, 9H, alkyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 182.64$ (CHO), 156.28, 141.68, 141.54, 141.20, 140.42, 139.62, 137.97, 134.21, 126.50, 124.55, 124.17, 123.60, 123.21, 122.92, 121.55, 120.59, 119.42, 118.98, 118.63, 109.49, 109.43, 107.30 (Ar), 43.22, 31.85, 31.62, 31.21, 30.94, 29.73, 29.47, 29.27,
8.4.4 Experimental Details for Dyes

Synthesis of B1

To a solution of B1-CHO (100 mg, 0.30 mmol) in 5 mL of dry chloroform, cyanoacetic acid (103 mg, 1.21 mmol) and piperidine (0.1 mL) was added. The mixture was heated at reflux temperature overnight. Afterwards, the mixture was concentrated under reduced pressure. The residue was purified by reprecipitation in water. The mixture was then washed with methanol to give B1 as an orange solid (134 mg, 0.16 mmol, 54%).

Spectral Data: $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 8.71 (s, 2H, Ar), 8.53 (m, 2H, Ar), 8.19–8.16 (m, 4H, Ar), 7.88–7.83 (m, 6H, Ar), 7.76–7.73 (m, 6H, Ar), 4.44 (m, 4H, alkyl), 2.13 (m, 4H, alkyl), 1.79–1.76 (m, 4H, alkyl), 1.66–1.52 (m, 14H, alkyl), 0.87–0.83 (m, 9H, alkyl) ppm. MALDI-TOF: Calculated for C$_{65}$H$_{66}$N$_4$O$_4$: 966.5084. Found: 966.6 ($m/z$).


Spectral Data: $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 8.70–8.68 (m, 2H, Ar), 8.05 (m, 2H, Ar), 7.93–7.88 (m, 6H, Ar), 7.83–7.81 (m, 4H, Ar), 7.74–7.69 (m, 6H, Ar),
7.65–7.64 (m, 2H, Ar), 4.46 (m, 4H, alkyl), 2.20–2.18 (m, 4H, alkyl), 1.62–1.52 (m, 18H, alkyl), 0.90–0.86 (m, 9H, alkyl). MALDI-TOF: Calculated for C_{73}H_{70}N_{4}O_{4}S_{2}: 1130.4838. Found: 1130.8 (m/z).

**Synthesis of B3:** Yield: 61%; red solid.

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.48–8.47$ (m, 2H, Ar), 8.40–8.39 (m, 2H, Ar), 8.18–8.17 (m, 2H, Ar), 7.94–7.93 (m, 2H, Ar), 7.86–7.84 (m, 2H, Ar), 7.73–7.58 (m, 15H, Ar), 7.46–7.27 (m, 8H, Ar), 7.18 (m, 1H, Ar), 3.07–3.04 (m, 12H, alkyl), 1.73–1.61 (m, 18H, alkyl), 0.59–0.50 (m, 14H, alkyl) ppm. MALDI-TOF: Calculated for C$_{77}$H$_{62}$N$_4$O$_4$S$_2$: 1170.4212. Found: 1171.4 (m/z).

**Synthesis of B4:** Yield: 64%; orange solid.

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.14$ (s, 2H, Ar), 8.02–7.67 (m, 18H, Ar), 3.03–3.00 (m, 10H, alkyl), 1.65–1.55 (m, 16H, alkyl) ppm. MALDI-TOF: Calculated for C$_{83}$H$_{100}$N$_2$O$_4$: 1188.7683. Found: 1189.4 (m/z).

**Synthesis of B5:** Yield: 58%; orange solid.

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.49$ (s, 2H, Ar), 8.21–8.19 (m, 2H, Ar), 8.08 (m, 2H, Ar), 7.95–7.94 (m, 2H, Ar), 7.74–7.70 (m, 4H, Ar), 7.58–7.57
(m, 2H, Ar), 7.52–7.51 (m, 2H, Ar), 4.54 (m, 2H, alkyl), 1.81–1.80 (m, 2H, alkyl),
1.13–1.12 (m, 10H, alkyl), 0.75–0.72 (m, 3H, alkyl) ppm. MALDI-TOF: Calculated
for C\textsubscript{36}H\textsubscript{31}N\textsubscript{3}O\textsubscript{4}S\textsubscript{2}: 633.1756. Found: 633.2 (m/z).

**Synthesis of B\textsubscript{6}:** Yield: 64%; red solid.

*Spectral Data:* \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 8.31\) (s, 2H, Ar), 8.27–8.25 (m, 2H, Ar), 8.05–8.03 (m, 4H, Ar), 7.93–7.92 (m, 2H, Ar), 7.61–7.59 (m, 2H, Ar), 4.52 (m, 2H, alkyl), 1.80–1.79 (m, 2H, alkyl), 1.12–1.19 (m, 10H, alkyl), 0.74–0.72 (m, 3H, alkyl) ppm. MALDI-TOF: Calculated for C\textsubscript{44}H\textsubscript{35}N\textsubscript{3}O\textsubscript{4}S\textsubscript{4}: 797.151. Found: 797.3 (m/z).

**Synthesis of B\textsubscript{7}:** Yield: 65%; yellow solid.

*Spectral Data:* \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 8.51\) (s, 2H, Ar), 8.22–8.20 (m, 2H, Ar), 8.08–7.82 (m, 6H, Ar), 7.53–7.51 (m, 4H, Ar), 4.54 (m, 2H, alkyl), 1.80–1.79 (m, 2H, alkyl), 1.33–1.14 (m, 10H, alkyl), 0.75–0.74 (m, 3H, alkyl) ppm. MALDI-TOF: Calculated for C\textsubscript{40}H\textsubscript{35}N\textsubscript{3}O\textsubscript{4}: 621.2628. Found: 622.2 (m/z).

**Synthesis of B\textsubscript{8}:** Yield: 69%; red solid.

*Spectral Data:* \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 8.39\) (s, 2H, Ar), 8.26–8.24 (m,
2H, Ar), 8.18 (m, 2H, Ar), 8.06–8.02 (m, 4H, Ar), 7.96–7.87 (m, 6H, Ar), 7.70–7.61 (m, 4H, Ar), 4.61 (m, 2H, alkyl), 2.14–1.86 (m, 14H, alkyl), 0.84–0.71 (m, 19H, alkyl) ppm. MALDI-TOF: Calculated for C_{70}H_{75}N_{3}O_{4}: 1021.5758. Found: 1021.7 (m/z).

**Synthesis of B9:** Yield: 62%; red solid.

*Spectral Data:* \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.75\) (s, 2H, Ar), 8.69 (m, 2H, Ar), 8.25–8.23 (m, 2H, Ar), 8.07 (m, 2H, Ar), 7.98 (m, 2H, Ar), 7.84–7.82 (m, 2H, Ar), 7.75–7.65 (m, 12H, Ar), 4.46 (m, 4H, alkyl), 1.82–1.78 (m, 8H, alkyl), 0.90–0.81 (m, 14H, alkyl) ppm. MALDI-TOF: Calculated for C_{68}H_{61}N_{5}O_{4}S_{2}: 1075.4165. Found: 1076.5 (m/z).
8.6 Experimental Details for Chapter 5

8.6.1 Experimental Details for Halide Precursors

*Synthesis of L1-Br*

1, 2, 3-Benzotriazole (6.00 g, 50 mmol), potassium hydroxide (6.78 g, 120 mmol) and 1-bromohexane (8.5 mL, 60 mmol) were dissolved in methanol (50 mL). The reaction mixture was refluxed for 24 h. After removal of the solvent by evaporation, the residue was dissolved in 200 mL of CHCl$_3$ and washed with water twice. The organic extraction was dried over anhydrous MgSO$_4$ and the solvent was evaporated under reduced pressure. Column chromatography on silica gel was performed to obtain 2-hexylbenzotriazole as a colorless oil with a 30% yield.

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.77$–$7.75$ (m, 2H, Ar), $7.27$–$7.24$ (m, 2H, Ar), $4.63$–$4.61$ (m, 2H, alkyl), $2.02$–$2.01$ (m, 2H, alkyl), $1.23$–$1.21$ (m, 6H, alkyl), $0.77$–$0.76$ (m, 3H, alkyl) ppm.

In a 50 mL round bottom flask with an ice-water bath, was placed 2-hexyl-2$H$-benzo[d][1,2,3]triazole (1.00 g, 4.92 mmol) in chloroform (15 mL). To this mixture, bromine (776.9 mg, 4.92 mmol) was added dropwise. After 30 min, the ice-water bath was removed and the mixture was stirred at room temperature for one day. After then, the mixture was filtered and washed with methanol. The product
4,7-dibromo-2-hexyl-2H-benzo[d][1,2,3]triazole was obtained as a colorless oil (1.1 g, 3.04 mmol, 62%).

**Spectral Data:** $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.43$ (s, 2H, Ar), 4.78–4.76 (m, 2H, alkyl), 2.16–2.12 (m, 2H, alkyl), 1.33–1.32 (m, 6H, alkyl), 0.87–0.86 (m, 3H, alkyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 144.27$, 132.79, 128.75 (Ar), 40.33, 30.08, 29.05, 23.59, 23.19, 14.19 (alkyl) ppm.

To a solution of 4,7-dibromo-2-hexyl-2H-benzo[d][1,2,3]triazole (2 g, 5.43 mmol) in 30 mL of tetrahydrofuran was added thiophen-2-yl-2-boronic acid (1.7 g, 13.58 mmol), Pd(PPh$_3$)$_4$ (627 mg, 1.26 mmol, 10 mol%) and 2 M Na$_2$CO$_3$ (11 mL, 21.7 mmol). The mixture was heated at reflux temperature for two days. After being cooled to room temperature, water was added and the solution mixture was extracted with ethyl acetate. The combined organic layer was dried by Na$_2$SO$_4$ and was filtered. Afterwards, the mixture was concentrated under reduced pressure. The residue was purified by chromatography on a silica gel column using $n$-hexane/CH$_2$Cl$_2$ (4:1, v/v) as eluent. 4,7-Dibromo-2-hexyl-2H-benzo[d][1,2,3]triazole was obtained as a light yellow solid (1.43 g, 3.89 mmol, 75%).

**Spectral Data:** $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.06$ (d, $J = 4.1$ Hz, 2H, Ar), 7.53 (s, 2H, Ar), 7.32 (d, $J = 8.0$ Hz, 2H, Ar), 7.14–7.12 (m, 2H, Ar), 4.74–4.71 (m, 2H,
alkyl), 2.14−2.10 (m, 2H, alkyl), 1.37−1.26 (m, 6H, alkyl), 0.86−0.83 (t, 3H, \( J = 6.2 \) Hz, CH₃) ppm.

To a solution of 4,7-dibromo-2-hexyl-2\( H \)-benzo[d][1,2,3]triazole (268 mg, 0.70 mmol) in 20 mL of tetrahydrofuran. The mixture was shielded from light and cooled in an ice-water bath and NBS (285 mg, 1.60 mmol) was added stepwise. Then the mixture was stirred overnight at room temperature and was filtered. The residue was washed several times with \( n \)-hexane, and then dried in vacuo to give \( \mathbf{L1-MBr} \) as a yellow solid (300 mg, 0.57 mmol, 82%).

**Spectral Data:** \(^1\)H NMR (400 MHz, CDCl₃): \( \delta = 7.73 \) (d, \( J = 5.6 \) Hz, 2H, Ar), 7.44 (s, 2H, Ar), 7.04 (d, \( J = 6.0 \) Hz, 2H, Ar), 4.72 (t, \( J = 7.0 \) Hz, 2H, Ar), 2.10 (m, 2H, alkyl), 1.30−1.18 (m, 6H, alkyl), 0.82 (m, 3H, alkyl) ppm. \(^{13}\)C NMR (100 MHz, CDCl₃): \( \delta = 144.42, 142.21, 140.43, 127.35, 125.81, 123.92, 123.01 \) (Ar), 59.12, 31.52, 26.43, 25.74, 22.71, 14.12 (alkyl) ppm.

**Synthesis of L2-Br**

To a solution of \( \mathbf{L1-Br} \) (735 mg, 1.39 mmol) in 30 mL of tetrahydrofuran was added thiophen-2-yl-2-boronic acid (448 mg, 3.49 mmol), Pd(PPh₃)₄ (161 mg, 0.13 mmol, 10 mol%) and 2 M Na₂CO₃ (2.8 mL, 5.56 mmol). The mixture was heated at
reflux temperature for two days. After being cooled to room temperature, water was added and the solution mixture was extracted with ethyl acetate. The combined organic layer was dried by Na$_2$SO$_4$ and was filtered. Afterwards, the mixture was concentrated under reduced pressure. The residue was purified by chromatography on a silica gel column using $n$-hexane/CH$_2$Cl$_2$ (2:1, v/v) as eluent. 2-Hexyl-4,7-bis(5-(thiophen-2-yl)thiophen-2-yl)-2H-benzo[d][1,2,3]triazole was obtained as an orange solid (531 mg, 0.76 mmol, 72%).

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): δ = 8.02−8.01 (m, 2H, Ar), 7.59 (s, 2H, Ar), 7.27 (m, 2H, Ar), 7.26−7.24 (m, 4H, Ar), 7.06−7.04 (m, 2H, Ar), 4.85−4.81 (m, 2H, alkyl), 2.22−2.19 (m, 2H, alkyl), 1.28−1.26 (m, 6H, alkyl), 0.89−0.86 (t, 3H, $J$ = 6.2 Hz, CH$_3$) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 144.95, 138.76, 137.49, 137.45, 127.92, 127.86, 124.75, 124.56, 123.85, 123.26, 122.41 (Ar), 56.87, 53.41, 31.23, 30.06, 26.30, 22.50 (alkyl) ppm.

To a solution of 2-hexyl-4,7-bis(5-(thiophen-2-yl)thiophen-2-yl)-2H-benzo[d][1,2,3]triazole (741 mg, 1.39 mmol) in 20 mL of tetrahydrofuran. The mixture was shielded from light and cooled in an ice-water bath and NBS (546 mg, 3.06 mmol) was added stepwise. Then the mixture was stirred overnight at room temperature and filtered. The residue was washed several times with $n$-hexane, and then dried in vacuo
to give L3-Br as a deep orange solid (848 mg, 0.99 mmol, 89%).

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.99–7.98$ (m, 2H, Ar), 7.58 (s, 2H, Ar), 7.18–7.17 (m, 2H, Ar), 7.00 (s, 2H, Ar), 4.84–4.81 (t, $J = 7.0$ Hz, 2H, Ar), 2.17 (m, 2H, alkyl), 1.39–1.33 (m, 6H, alkyl), 0.88 (m, 3H, alkyl) ppm.

*Synthesis of L3-Br*

After adding 38.42 g (0.31 mol) thiophene-3-carboxylic acid and 60 mL of methylene chloride into a 250 mL flask. The mixture was cooled by ice-water bath, and then oxalyl chloride (76.21 g, 0.62 mol) was added into the reaction mixture. The reactant was stirred overnight at room temperature, then a clear solution was obtained. After removing the solvent and unreacted oxalyl chloride by rotary evaporation, the product was obtained as a colorless solid.

After adding 6.25 mL of diethylamine (4.38 g, 6 mmol) into 15 mL methylene chloride, the solution was cooled by ice-water bath, and then the solution of thiophene-3-carbonyl chloride was added into the flask slowly. After all of the solution was added, the ice bath was removed, and the reactant was stirred at room temperature for half an hour. Afterwards, the reactant was washed by water several times, and the organic layer was dried by anhydrous MgSO$_4$. After removing the
solvent, the crude product was purified by distillation under vacuum, then the product

\( N,N \)-diethylthiophene-3-carboxamide was obtained as a pale yellow oil (4.9 g, 26.77
mmol, 90\%).

*Spectral Data:* \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.48 \) (s, 1H, Ar), 7.32 (d, \( J = 2.1 \) Hz, 1H, Ar), 7.20 (d, \( J = 3.7 \) Hz, 1H, Ar), 3.41 (m, 4H, alkyl), 1.19 (t, \( J = 5.6 \) Hz, 6H, alkyl) ppm.

\( N,N \)-Diethylthiophene-3-carboxamide (2.0 mmol, 366 mg) was put into a well-dried
flask with 30 mL of tetrahydrofuran under an inert atmosphere. The solution was
cooled down by an ice-water bath, and 0.8 mL \( n \)-butyllithium (2.0 mmol, 2.5 M) was
added into the flask dropwise about half an hour. Then, the reactant was stirred at
room temperature for 30 min. Afterwards, the reactant was poured into 200 mL ice
water and stirred for several hours. The mixture was filtrated, and the yellow
precipitate was washed by 60 mL of water, 20 mL of methanol, and 20 mL of
\( n \)-hexane successively. The product 4,8-dihydrobenzo[1,2-b:4,5-b’]dithiophen-4,8-
dione was obtained as a yellow powder (343 mg, 1.6 mmol, 78\%).

*Spectral Data:* \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.95 \) (d, \( J = 3.7 \) Hz, 2 H, Ar),
7.75 (d, \( J = 3.8 \) Hz, 2 H, Ar) ppm.
4,8-Dihydrobenzo[1,2-b:4,5-b']dithiophen-4,8-dione (440 mg, 2.0 mmol), zinc powder (286 mg, 4.4 mmol), and 15 mL of water were put into a 100 mL flask; then 1.2 g NaOH was added into the mixture. The mixture was vigorously stirred and refluxed for 1h. The color of the mixture changed from yellow to red and then to orange during the reaction. After that, 2-ethylhexyl bromide (1.2 g, 6 mmol) and a catalytic amount of tetrabutylammonium bromide were added into the flask. Then the mixture was refluxed for 2 h, and the color of the reactant turned to yellow or orange: if the color of the reactant was red or deep red, an excess amount of zinc powder (130 mg, 2 mmol) should be added, and the reactant was refluxed for 6 h. Afterwards, the reactant was poured into ice-water and extracted with diethyl ether several times. The organic layer was dried by anhydrous MgSO₄. After removing the solvent, the crude product was purified by recrystallization from ethyl alcohol. Then the product 4,8-didodeceoxybenzo[1,2-b;3,4-b]dithiophene was obtained as a colorless crystal (926 mg, 2.07 mmol, 83%).

Spectral Data: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.85$ (d, $J = 3.8$ Hz, 2 H, Ar), 7.68 (d, $J = 4.2$ Hz, 2 H, Ar), 4.22–4.13 (m, 4H, alkyl), 1.76–1.68 (m, 2H, alkyl), 1.58–1.54 (m, 8H, alkyl), 1.40–1.35 (m, 8H, alkyl), 0.99–0.92 (m, 12H, alkyl) ppm.

4,8-Didodecyleoxybenzo[1,2-b;3,4-b]dithiophene (461 mg, 1.0 mmol) was dissolved
in 30 mL of methylene chloride in a 250 mL flask. Bromine (320 mg, 2.0 mmol) was dissolved in 20 mL of methylene chloride in a funnel and added drop by drop into the flask under an ice-bath, and then the reactant was stirred for 6 h at room temperature. When the color of bromine was diminished, all volatile substances were removed under vacuum. The residue was recrystallized by **n-hexane** to give the product as a white solid (637.2 mg, 1.05 mmol, 89%).

**Spectral Data:** $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.43$ (s, 2H, Ar), 4.17–4.15 (m, 4H, alkyl), 1.82–1.78 (m, 2H, alkyl), 1.53–1.51 (m, 8H, alkyl), 1.36–1.27 (m, 8H, alkyl), 0.92–0.89 (m, 12H, alkyl) ppm.

**Synthesis of L4-MBr**

To a solution of **L3-MBr** (650 mg, 1.07 mmol) in 30 mL of tetrahydrofuran was added thiophen-2-yl-2-boronic acid (344 mg, 2.68 mmol), Pd(PPh$_3$)$_4$ (124 mg, 0.17 mmol, 10 mol%) and 2 M Na$_2$CO$_3$ (2.2 mL, 4.28 mmol). The mixture was heated at reflux temperature for two days. After being cooled to room temperature, water was added and the solution mixture was extracted with ethyl acetate. The combined organic layer was dried by Na$_2$SO$_4$ and was filtered. Afterwards, the mixture was concentrated under reduced pressure. The residue was purified by chromatography over a silica gel column using **n-hexane/CH$_2$Cl$_2$$^v/v$$^v/v$$^v$$^v$ as eluent. The product was
obtained as a yellow solid (522 mg, 0.85 mmol, 80%).

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.52$ (s, 2H, Ar), 7.35–7.31 (m, 4H, Ar), 7.10–7.08 (m, 2H, Ar), 4.23–4.21 (m, 4H, alkyl), 1.88–1.84 (m, 2H, alkyl), 1.77–1.66 (m, 8H, alkyl), 1.48–1.30 (m, 8H, alkyl), 1.12–1.01 (m, 12H, alkyl) ppm.

To a solution of the previous product (477.5 mg, 0.78 mmol) in 20 mL of tetrahydrofuran, the mixture was shielded from light and cooled in an ice-water bath and NBS (281 mg, 1.57 mmol) was added stepwise. Then the mixture was stirred overnight at room temperature. Then the reaction mixture was filtered. The residue was washed several times with $n$-hexane, and then dried in vacuo to give L$_4$MBr as a yellow solid (406 mg, 0.52 mmol, 68%).

*Spectral Data:* $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.32–7.31$ (m, 2H, Ar), 7.25 (s, 2H, Ar), 7.10–7.09 (m, 2H, Ar), 4.04–4.03 (m, 4H, alkyl), 2.05–2.02 (m, 2H, alkyl), 1.56–1.38 (m, 8H, alkyl), 1.26–1.03 (m, 8H, alkyl), 1.01–0.74 (m, 12H, alkyl) ppm.

8.6.2 Experimental Details of Sonogashira Coupling (Synthesis of L$_1$-TMS to L$_4$-TMS)

*Synthesis of L$_1$-TMS*

To an ice-cooled mixture of L$_1$-Br (146.5 mg, 0.28 mmol) in dichloromethane (15
mL) and Et₃N (15 mL) solution mixture was added CuI (5.3 mg, 0.03 mmol), Pd(OAc)₂ (6.3 mg, 0.02 mmol) and PPh₃ (7.4 mg, 0.02 mmol). After the solution was stirred for 30 min at 0 °C, trimethylsilylacetylene (0.20 mL, 1.39 mmol) was then added and the suspension was stirred for 30 min in an ice-water bath before being warmed to room temperature. After reacting for 30 min at room temperature, the mixture was heated to 55 °C overnight. Then the solution was cooled to room temperature and the solvent mixture was evaporated in vacuo. The crude product was purified by column chromatography on silica gel with a solvent combination of n-hexane/CH₂Cl₂ (3:1, v/v) as eluent to provide L₁-TMS as a yellow solid (117 mg, 0.21 mmol, 75 %).

*Spectral Data:* ¹H NMR (400 MHz, CDCl₃): δ = 7.93 (d, J = 3.9 Hz, 2H, Ar), 7.59 (s, 2H, Ar), 7.29 (d, J = 3.9 Hz, 2H, Ar), 4.82–4.74 (m, 2H, alkyl), 1.43–1.26 (m, 6H, alkyl), 0.91–0.88 (t, J = 6.9 Hz, 3H, Me), 0.28 (s, 18H, TMS) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 144.46, 136.01, 133.17, 132.50, 130.65, 128.48, 125.32 (Ar), 100.94, 97.29 (C≡C), 57.02, 31.70, 30.18, 26.38, 22.61, 14.12 (alkyl), 0.003 (TMS) ppm.

**Synthesis of L₂-TMS:** Red solid, yield: 75%.

*Spectral Data:* ¹H NMR (400 MHz, CDCl₃): δ = 8.00–7.99 (m, 2H, Ar), 7.59 (s,
2H, Ar), 7.24–7.23 (m, 2H, Ar), 7.16–7.09 (m, 2H, Ar), 4.84–4.80 (t, \( J \) = 7.0 Hz, 2H, Ar), 2.22–2.15 (m, 2H, alkyl), 1.54–1.36 (m, 6H, alkyl), 0.90–0.88 (m, 3H, alkyl), 0.26 (s, 18H, TMS) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 141.94, 139.49, 139.02, 136.78, 133.70, 128.01, 125.33, 123.45, 123.26, 122.53, 122.01 \) (Ar), 100.41, 97.60 (C≡C), 56.98, 31.35, 30.15, 26.42, 22.63, 14.15 (alkyl), 0.003 (TMS) ppm.

**Synthesis of L3-TMS:** Yellow solid, yield: 78%.

*Spectral Data:* \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.55 \) (s, 2H, Ar), 4.12–4.10 (m, 4H, alkyl), 1.79–1.76 (m, 2H, alkyl), 1.56–1.64 (m, 8H, alkyl), 1.39–1.35 (m, 10H, alkyl), 1.01–0.92 (m, 12H, alkyl), 0.28 (s, 18H, TMS) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 144.21, 131.80, 130.12, 126.17, 122.98 \) (Ar), 101.81, 98.02(C≡C), 40.82, 30.52, 29.36, 23.96, 29.56, 22.32, 14.36, 11.51, 0.003 (TMS) ppm.

**Synthesis of L4-TMS:** Yellow solid, yield: 68%.

*Spectral Data:* \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.52 \) (s, 2H, Ar), 7.24–7.19 (m, 4H, Ar), 4.21–4.20 (m, 4H, alkyl), 2.05–2.02 (m, 2H, alkyl), 1.89–1.66 (m, 8H, alkyl), 1.48–1.32 (m, 8H, alkyl), 1.12–0.94 (m, 12H, alkyl), 0.33 (s, 18H, TMS) ppm.
8.6.3 Experimental Details of the Deprotection of Trimethylsilyl Group

(Synthesis of L1−L4)

Synthesis of L1

To a solution of L1-TMS (85 mg, 0.15 mmol) in a MeOH/CH₂Cl₂ mixture (v/v = 1:1) was added K₂CO₃ (53 mg, 0.37 mmol). The reaction mixture was stirred at room temperature overnight under N₂ atmosphere. After removal of the solvent, the crude product was purified by column chromatography on silica gel using n-hexane/CH₂Cl₂ (3:1, v/v) as eluent to afford the desired diethynyl ligand L1 (57 mg, 0.13 mmol, 92%) as a yellow solid.

Spectral Data: 

\(^1\)H NMR (400 MHz, CDCl₃): \(\delta = 7.76−7.75\) (d, \(J = 3.9\) Hz, 2H, Ar), 7.40 (s, 2H, Ar), 7.15−7.14 (d, \(J = 3.8\) Hz, 2H, Ar), 4.64−4.60 (m, 2H, alkyl), 3.27 (s, 2H, C≡CH), 2.02−1.98 (m, 2H, alkyl), 1.30−1.22 (m, 6H, alkyl), 0.71−0.69 (m, 3H, alkyl) ppm. 

\(^13\)C NMR (100 MHz, CDCl₃): \(\delta = 142.44, 141.94, 134.68, 127.23, 123.84, 123.37, 122.57\) (Ar), 83.12, 85.67 (C≡C), 57.50, 32.13, 30.57, 30.24, 23.19, 14.65 (alkyl) ppm. IR (KBr) (cm\(^{-1}\)): \(\nu = 3294\) (w, \(\nu(C≡C−H))\), 2090 (w, \(\nu(C≡C))\).

Synthesis of L2: Red solid, yield: 75%.

Spectral Data: 

\(^1\)H NMR (400 MHz, CDCl₃): \(\delta = 8.00−7.99\) (m, 2H, Ar), 7.58 (s, 2H, Ar), 7.25−7.20 (m, 4H, Ar), 7.11−7.10 (m, 2H, Ar), 4.84−4.80 (t, \(J = 7.0\) Hz, 2H, alkyl), 3.53 (s, 2H, C≡CH), 2.04 (m, 2H, alkyl), 1.32−1.22 (m, 6H, alkyl), 0.70−0.68 (m, 3H, alkyl) ppm. IR (KBr) (cm\(^{-1}\)): \(\nu = 3300\) (w, \(\nu(C≡C−H))\), 2080 (w, \(\nu(C≡C))\).
Ar), 3.43 (s, 2H, C≡CH), 2.22–2.17 (m, 2H, alkyl), 1.56–1.25 (m, 6H, alkyl), 0.92–0.87 (m, 3H, alkyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 141.90, 139.53, 139.21, 136.51, 134.04, 127.93, 125.41, 123.32, 123.24, 122.52, 120.71 (Ar), 82.43 (C≡C), 56.92, 31.22, 30.05, 26.29, 22.50, 14.01 (alkyl) ppm.

**Synthesis of L3**: Yellow crystal, yield: 85%.

*Spectral Data*: $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.61 (s, 2H, Ar), 3.48 (s, 2H, C≡CH), 4.13–4.12 (m, 4H, alkyl), 1.80–1.74 (m, 2H, alkyl), 1.65–1.53 (m, 8H, alkyl), 1.38–1.36 (m, 10H, alkyl), 1.09–0.92 (m, 12H, alkyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 144.12, 131.54, 129.96, 126.56, 121.84 (Ar), 83.45, 81.26 (C≡C), 40.61, 30.36, 29.17, 23.78, 23.10, 22.51, 14.15, 11.31 (alkyl) ppm. IR (KBr) (cm$^{-1}$): $\nu =$ 3280 (w, $\nu$(C≡C–H)), 2094 (w, $\nu$(C≡C)).

**Synthesis of L4**: Brown solid, yield: 87%.

*Spectral Data*: $^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.30 (s, 2H, Ar), 7.05–6.95 (m, 4H, Ar), 3.98–3.97 (m, 4H, alkyl), 3.22 (s, 2H, C≡CH), 1.65–1.63 (m, 2H, alkyl), 1.54–1.24 (m, 8H, alkyl), 1.08 (m, 8H, alkyl), 0.84–0.52 (m, 12H, alkyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 144.94, 139.67, 136.44, 134.52, 129.96, 125.35, 122.65, 117.42 (Ar), 83.26, 76.67 (C≡C), 41.33, 31.10, 29.89, 25.88, 24.48, 23.81, 11.89
8.6.4 Experimental Details of Polymers

**Synthesis of P1**

To a stirred mixture of \( \text{L1} \) (49 mg, 0.11 mmol) and \( \text{trans-}[\text{Pt}(\text{PBu}_3)_2\text{Cl}_2] \) (79.0 mg, 0.11 mmol) in freshly distilled triethylamine (20 mL) and \( \text{CH}_2\text{Cl}_2 \) (20 mL) solution was added CuI (5 mg). The solution was stirred at room temperature for 24 h under a nitrogen atmosphere. The solvents were removed on a rotary evaporator *in vacuo*. The residue was redissolved in \( \text{CH}_2\text{Cl}_2 \) and filtered through a short aluminium oxide column using the same eluent to remove ionic impurities and catalyst residue. After removal of the solvent, the crude product was washed with *n*-hexane three times followed by methanol three times and then repeated precipitation from \( \text{CH}_2\text{Cl}_2/n\)-hexane (or \( \text{CH}_2\text{Cl}_2/methanol \)) and drying *in vacuo* to afford polymer P1 (76.0 mg, 0.07 mmol, 71%) as a red solid.

**Spectral Data:** \(^1\text{H NMR} \) (400 MHz, CDCl₃): \( \delta = 7.94−7.93 \) (m, 2H, Ar), 7.48 (s, 2H, Ar), 6.91−6.90 (m, 2H, Ar), 4.79−4.76 (m, 2H, alkyl), 2.17−2.13 (m, 12H, alkyl), 1.64−1.50 (m, 12H, alkyl), 0.99−0.89 (m, 18H, alkyl) ppm. \(^{31}\text{P NMR} \) (161 MHz, CDCl₃): \( \delta = 3.35 \) \((^{1}J_{P-Pt} = 2315 \text{ Hz}) \) ppm.
Synthesis of **P2**: Deep red solid, yield: 55%.

*Spectral Data*: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.01–8.00$ (m, 2H, Ar), 7.58 (s, 2H, Ar), 7.25–7.05 (m, 4H, Ar), 6.77 (m, 2H, Ar), 4.82 (m, 2H, Ar), 2.20–2.11 (m, 20H, alkyl), 1.63–1.47 (m, 34H, alkyl), 0.99–0.92 (m, 6H, alkyl), 0.92–0.87 (m, 3H, alkyl) ppm. $^{31}$P NMR (161 MHz, CDCl$_3$): $\delta = 3.42$ ($^{1}J_{P-Pt} = 2314$ Hz) ppm.

Synthesis of **P3**: Brown solid, yield: 87%.

*Spectral Data*: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.11$ (s, 2H, Ar), 4.12–4.11 (m, 4H, alkyl), 1.60–0.95 (m, 78H, alkyl) ppm. $^{31}$P NMR (161 MHz, CDCl$_3$): $\delta = 3.42$ ($^{1}J_{P-Pt} = 2312$ Hz) ppm.

Synthesis of **P4**: Brown solid, yield: 81%.

*Spectral Data*: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.36$ (s, 2H, Ar), 7.09 (m, 2H, Ar), 6.78 (m, 2H, Ar), 4.14 (m, 4H, alkyl), 1.81–0.95 (m, 78H, alkyl) ppm. $^{31}$P NMR (161 MHz, CDCl$_3$): $\delta = 3.29$ ($^{1}J_{P-Pt} = 2310$ Hz) ppm.

8.6.5 Experimental Details for Model Compounds

Synthesis of **M1**

To a stirred mixture of **L1** (6.2 mg, 0.015 mmol) and trans-[Pt(PET$_3$)$_2$PhCl] (20.1
mg, 0.030 mmol) in freshly distilled triethylamine (6 mL) and CH₂Cl₂ (6 mL) was added CuI (2.0 mg). The solution was stirred at room temperature under nitrogen over a period of 24 h. After removal of the solvent, the crude product was purified by column chromatography on silica gel eluting with CH₂Cl₂ to give **M1** (15.0 mg, 0.01 mmol, 57%) as a brown solid.

**Spectral Data:**

\(^1\)H NMR (400 MHz, CDCl₃): δ = 7.86−7.85 (m, 2H, Ar), 7.39 (s, 2H, Ar), 7.26−7.19 (m, 4H, Ar), 6.92−6.74 (m, 8H, Ar), 4.73−4.69 (m, 2H, alkyl), 1.71−1.51 (m, 25H, alkyl), 0.82−0.80 (m, 46H, alkyl) ppm. \(^1^3\)C NMR (100 MHz, CDCl₃): δ = 141.08, 138.10, 135.35, 127.23, 126.34, 126.10, 122.19, 121.03, 120.34 (Ar), 30.23, 29.87, 28.94, 28.68, 25.37, 21.95, 12.67, 21.44, 14.38, 14.20, 14.03, 13.08, 12.98, 7.04 (alkyl). \(^3^1\)P NMR (161 MHz, CDCl₃): δ = 10.02 (\(^1J\)P−Pt = 2610 Hz) ppm.

**Synthesis of M2:** Brown solid, yield: 55%.

**Spectral Data:** \(^1\)H NMR (400 MHz, CDCl₃): δ = 8.00−7.99 (m, 2H, Ar), 7.72−7.56 (m, 3H, Ar), 7.16−7.04 (m, 3H, Ar), 6.99−6.97 (m, 4H, Ar), 6.95−6.81 (m, 4H, Ar), 6.78−6.77 (m, 4H, Ar), 4.84−4.69 (m, 2H, Ar), 2.22−2.17 (m, 28H, alkyl), 1.25−1.08 (m, 43H, alkyl) ppm. \(^1^3\)C NMR (100 MHz, CDCl₃): δ = 141.96, 139.07, 138.21, 137.86, 133.51, 130.91, 128.83, 127.92, 127.78, 127.38, 123.76, 123.58,
123.18, 122.27, 121.39 (Ar), 31.93, 31.24, 30.93, 30.06, 29.70, 26.30, 22.99, 22.70, 22.50, 15.33, 15.16, 14.98, 14.12, 14.03, 8.05 (alkyl). $^{31}$P NMR (161 MHz, CDCl$_3$): $\delta = 10.04$ ($^{1}J_{P-Pt} = 2612$ Hz) ppm.

**Synthesis of M3**: Red solid, yield: 56%.

*Spectral Data*: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.31$–7.30 (m, 4H, Ar), 7.11 (s, 2H, Ar), 6.99–6.95 (m, 4H, Ar), 6.83–6.79 (m, 2H, Ar), 4.08–4.07 (m, 4H, alkyl), 1.78–1.73 (m, 32H, alkyl), 1.25–1.15 (m, 42H, alkyl), 1.07–0.94 (m, 12H, alkyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 155.86$, 155.76, 142.67, 139.02, 131.67, 128.17, 127.37, 124.33, 124.19, 124.04, 121.38, 119.29 (Ar), 103.34 (C≡C), 40.59, 30.49, 29.70, 29.21, 23.85, 23.16, 15.29, 15.12, 14.95, 14.19, 11.33, 8.04 (alkyl). $^{31}$P NMR (161 MHz, CDCl$_3$): $\delta = 10.03$ ($^{1}J_{P-Pt} = 2618$ Hz) ppm.

**Synthesis of M4**: Red solid, yield: 51%.

*Spectral Data*: $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.36$–7.25 (m, 6H, Ar), 7.09–6.79 (m, 10H, Ar), 4.15–4.14 (m, 4H, alkyl), 1.77–1.73 (m, 35H, alkyl), 1.09–0.97 (m, 51H, alkyl) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 143.81$, 139.03, 136.96, 133.43, 132.38, 130.81, 129.83, 128.99, 127.80, 127.65, 127.41, 126.98, 125.06, 121.42, 114.81 (Ar), 53.44, 40.67, 31.61, 30.47, 29.72, 29.24, 23.88, 23.22,
22.68, 15.30, 15.13, 14.96, 14.25, 14.14, 11.37, 8.05, 7.82 (alkyl). \( ^{31} \text{P NMR (161 MHz, CDCl}_3 \):} \( \delta = 10.05 (J_{\text{P-Pt}} = 2620 \text{ Hz}) \) ppm.
8.7 Experimental Details for Chapter 6

8.7.1 Experimental Details for Core Materials

*Synthesis of Br-FBT-DTS-FBT-Br*

**DTS** (2.0 g, 4.78 mmol) and 20 mL of anhydrous THF were put into a two-necked flask and cooled to −78 °C. Then, *n*-butyllithium (4.78 mL, 2.5 M in THF, 11.96 mmol) was added dropwise. After stirring at −78 °C for 30 min, trimethyltin chloride (2.85 g, 14.34 mmol) in THF (4 mL) solution was added dropwise, and then the cooling bath was removed. After the reaction temperature was warmed up to ambient temperature, the reaction was quenched by adding 15 mL deionized water, and the mixture was extracted with *n*-hexane (50 mL × 3), washed with deionized water (100 mL × 3) and dried over with anhydrous magnesium sulfate. 5,5’-Bis(trimethylstannyl)-3,3’-di-2-ethylhexylsilylene-2,2’-bithiophene was obtained as a sticky pale green oil (3.37 g, 4.53 mmol, 95%) and used in the next step without any further purification.

In a N₂ filled glove box a 20 mL glass tube was charged with **FBT** (830 mg, 2.65 mmol), 5,5’-bis(trimethylstannyl)-3,3’-di-2-ethylhexylsilylene-2,2’-bithiophene (800 mg, 1.07 mmol), Pd(PPh₃)₄ (75 mg, 0.06 mmol) and toluene (15 mL), and sealed with a Teflon® cap. The reaction mixture was heated to 80 °C for 48 h. Upon cooling, the
material was then loaded onto silica and purified by flash chromatography using an $n$-hexane/dichloromethane gradient. After fraction collection and solvent removal a red solid was obtained. Recovered yield: (677 mg, 0.76 mmol, 72%).

*Spectral Data:* $^1$H NMR (600 MHz, THF-d$_8$): $\delta = 8.36–8.35$ (t, $J = 7.86$ Hz, 2H, DTS), 8.00–7.98 (dt, $J = 10.44$ Hz, 2H, FBT), 1.55–1.61 (m, 2H, EH), 1.37–1.09 (m, 21H, EH), 0.81–0.75 (m, 11H, EH) ppm. $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta = 161.4$, 159.7, 154.1, 154.1, 151.2, 148.6, 145.6, 139.3, 139.3, 132.2, 132.1, 132.1, 127.4, 127.4, 114.9, 114.7, 95.5, 95.4 (Ar), 36.0, 35.8, 29.0, 23.0, 17.7, 14.2, 10.9 (EH) ppm.

**Synthesis of Br-FBT-DTG-FBT-Br**

DTG (2.0 g, 4.31 mmol) and 20 mL of anhydrous THF were put into a two-necked flask and cooled to $-78\,^\circ$C. Then, $n$-butyllithium (4.31 mL, 2.5 M in THF, 10.79 mmol) was added dropwise. After stirring at $-78\,^\circ$C for 30 min, trimethyltin chloride (2.28 g, 12.93 mmol) in THF (4 mL) solution was added dropwise, and then the cooling bath was removed. After the reaction temperature was warmed up to ambient temperature, the reaction was quenched by adding 15 mL deionized water, and the mixture was extracted with $n$-hexane (50 mL × 3), washed with deionized water (100 mL × 3) and dried over with anhydrous magnesium sulfate. 5,5'-Bis(trimethylstannyl)-3,3'-di-2-ethylhexyl germole-2,2'-bithiophene was
obtained as a sticky pale green oil (3.15 g, 3.99 mmol, 93%) and used in the next step without any further purification.

In a N\textsubscript{2} filled glove box, a 20 mL glass tube was charged with FBT (830 mg, 2.65 mmol), 5,5’-bis(trimethylstannyl)-3,3’-di-2-ethylhexylgermole-2,2’-bithiophene (843 mg, 1.07 mmol), Pd(PPh\textsubscript{3})\textsubscript{4} (75 mg, 0.06 mmol) and toluene (15 mL), and sealed with a Teflon® cap. The reaction mixture was heated to 80 °C for 48 h. Upon cooling, the material was then loaded onto silica and purified by flash chromatography using a \textit{n}-hexane/dichloromethane gradient. After fraction collection and solvent removal, a red solid was obtained. Recovered yield: (677 mg, 0.73 mmol, 72%).

\textit{Spectral Data:} \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): \(\delta = 8.20−8.18 (t, J = 4.29 \text{ Hz}, 2\text{H}, \text{DTS}), 7.70−7.68 (d, J = 10.10 \text{ Hz}, 2\text{H}, \text{FBT}), 1.60−1.54 (m, 4\text{H}, \text{EH}), 1.43−1.21 (m, 19\text{H}, \text{EH}), 0.85−0.79 (m, 12\text{H}, \text{EH}) \text{ ppm.}

\textbf{8.7.2 Experimental Details for Halide Precursors}

\textit{Synthesis of AT1-Br}

2-Hexylthiophene (2.0 g, 11.97 mmol) and 20 mL of anhydrous THF were put into a two-necked flask and cooled to \(-78 \text{ °C}.\) Then, \(n\)-butyllithium (5.26 mL, 2.5 M in THF, 13.16 mmol) was added dropwise. After stirring at \(-78 \text{ °C} \) for 30 min, trimethyltin chloride (3.57 g, 17.95 mmol) in THF (4 mL) solution was added.
dropwise, and then the cooling bath was removed. After the reaction temperature was warmed up to ambient temperature, the reaction was quenched by adding 15 mL deionized water, and the mixture was extracted with \( n \)-hexane (50 mL \( \times \) 3), washed with deionized water (100 mL \( \times \) 3) and dried over with anhydrous magnesium sulfate. 5,5′-Bis(trimethylstannyl)-3,3′-di-2-ethylhexylsilylene-2,2′-bithiophene was obtained as a pale yellow oil (3.80 g, 11.48 mmol, 96%) and used in the next step without any further purification.

_Spectral Data:_ \(^1\)H NMR (600 MHz, CDCl\(_3\)): \( \delta = 7.03−7.02 \) (d, \( J = 3.18 \) Hz, 1H, Ar), 6.91 (d, \( J = 3.18 \) Hz, 2H, Ar), 2.88–2.86 (t, \( J = 7.77 \) Hz, 2H, alkyl), 1.72–1.63 (m, 2H, alkyl), 1.35–1.30 (m, 5H, alkyl), 0.92–0.89 (m, 4H, alkyl), 0.40–0.31 (t, \( J = 27.51 \) Hz, 9H, SnMe\(_3\)) ppm.

In a N\(_2\) filled glove box, a 20 mL glass tube was charged with **FBT** (1 g, 3.20 mmol), (5-hexylthiophen-2-yl)trimethylstannane (1.16 g, 3.52 mmol), Pd(PPh\(_3\))\(_4\) (222 mg, 0.02 mmol) and toluene (15 mL), and sealed with a Teflon\textsuperscript{®} cap. The reaction mixture was heated to 80 °C for 48 h. Upon cooling, the material was then loaded onto silica and purified by flash chromatography using a \( n \)-hexane/dichloromethane gradient. After fraction collection and solvent removal, a yellow solid was obtained. Recovered yield: (640 mg, 1.60 mmol, 50%).
**Spectral Data:** $^1$H NMR (600 MHz, CDCl$_3$): $\delta = 7.92$ (d, $J = 6.90$ Hz, 1H, Ar), 7.59–7.57 (d, $J = 10.14$ Hz, 1H, FBT), 6.85 (d, $J = 3.72$ Hz, 1H, Ar), 2.86–2.84 (t, $J = 13.32$ Hz, 2H, alkyl), 1.74–1.69 (m, 2H, alkyl), 1.42–1.24 (m, 7H, alkyl), 0.89–0.87 (m, 3H, alkyl) ppm. $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta = 161.6, 159.9, 149.8, 148.9, 134.6, 134.6, 129.1, 127.9, 125.5, 115.5, 115.3$ (Ar), 31.5, 31.5, 30.3, 28.8, 22.5, 14.1 (alkyl) ppm.

**Synthesis of AT2-Br**

In a N$_2$ filled glove box, a 5 mL glass tube was charged with AT1-Sn (65 mg, 0.08 mmol), Br-FBT-DTS-FBT-Br (78 mg, 0.08 mmol), Pd(PPh$_3$)$_4$ (12 mg, 0.01 mmol) and toluene (3 mL), and sealed with a Teflon® cap. The reaction mixture was heated to 100 $^\circ$C for 1 minute, 120 $^\circ$C for 1 min, 140 $^\circ$C for 10 min, 150 $^\circ$C for 10 min, and 160 $^\circ$C for 40 min using a Biotage microwave reactor. Upon cooling, the material was then loaded onto silica, washed with methanol and purified by flash chromatography using an $n$-hexane/dichloromethane gradient. The product was recovered as a purple solid. Recovered yield: (58 mg, 0.04 mmol, 53%).

**Spectral Data:** $^1$H NMR (600 MHz, THF-d$_8$): $\delta = 8.46–8.44$ (t, $J = 3.23$ Hz, 1H, DTS), 8.46–8.44 (t, $J = 3.91$ Hz, 1H, DTS), 8.39 (s, 2H, Ar), 8.14–8.13 (d, $J = 3.65$ Hz, 1H, Ar), 8.09–8.06 (dt, $J = 13.37$ Hz, 1H, FBT), 7.96–7.94 (m, 2H, FBT), 6.97 (d,
$J = 3.65$ Hz, 1H, Ar), 2.91–2.88 (t, $J = 7.58$ Hz, 2H, alkyl), 2.76–2.73 (t, $J = 7.73$ Hz, 4H, alkyl), 1.78–1.70 (m, 16H, alkyl), 1.46–1.13 (m, 43H, alkyl), 0.83–0.79 (m, 8H, alkyl) ppm. $^{13}$C NMR (150 MHz, THF-$d_8$): $\delta =$ 161.5, 159.9, 159.8, 159.8, 158.2, 158.1, 154.0, 154.0, 153.1, 153.0, 153.0, 152.9, 151.8, 151.2, 149.5, 149.4, 149.1, 148.6, 145.1, 145.0, 144.9, 144.8, 142.2, 142.1, 140.3, 140.3, 139.3, 139.3, 135.3, 132.7, 132.6, 132.5, 132.0, 131.8, 131.8, 131.8, 131.8, 131.6, 131.6, 131.5, 131.5, 131.5, 131.2, 131.1, 130.5, 128.5, 127.3, 127.3, 126.1, 126.0, 125.6, 125.5, 125.2, 115.4, 114.5, 114.3, 110.3, 110.2, 110.0, 109.9, 95.2, 95.0 (Ar), 60.8, 36.0, 35.7, 31.9, 31.7, 31.6, 31.5, 30.8, 30.0, 29.6, 29.2, 29.0, 28.9, 28.8, 28.4, 26.4, 24.3, 24.2, 24.0, 22.9, 22.5, 22.5, 17.5, 13.6, 13.4, 10.2 (alkyl) ppm.

8.7.3 Experimental Details for Stannylated Precursors

**Synthesis of AT1-Sn**

In a 50 mL two-neck round bottom flask, 2-bromo-3-hexylthiophene (763.7 mg, 3.09 mmol), 2-(3-Hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1 g, 3.40 mmol), potassium fluoride (538.4 mg, 9.27 mmol), 2-dicyclohexylphosphino-2’,4’,6’-triisopropylbiphenyl (147 mg, 0.30 mmol), and palladium acetate (104 mg, 0.15 mmol) were added in THF/H$_2$O (9:1, v/v). The mixture was heated at 90°C for 2 h. Afterwards, the mixture was extracted with ethyl
acetate (20 mL × 3) and dried over with anhydrous magnesium sulfate. Then, the mixture was concentrated under reduced pressure. The residue was purified by chromatography on a silica gel column using n-hexane as eluent. The product 3-hexyl-2-(3-hexylthiophen-2-yl)thiophene was isolated as a colorless oil. Recovered yield: (868 mg, 2.59 mmol, 84%).

Spectral Data: $^1$H NMR (600 MHz, CDCl$_3$): $\delta = 7.28-7.21$ (d, $J = 5.28$ Hz, 2H, Ar), 6.96–6.95 (d, $J = 5.28$ Hz, 2H, Ar), 2.51–2.48 (t, $J = 7.74$ Hz, 4H, alkyl), 1.56–1.51 (m, 4H, alkyl), 1.27–1.21 (m, 12H, alkyl), 0.86–0.84 (m, 6H, alkyl) ppm.

$^{13}$C NMR (150 MHz, CDCl$_3$): $\delta = 142.3, 128.7, 128.5, 125.2$ (Ar), 31.6, 30.7, 29.1, 28.8, 22.6, 14.1 (alkyl) ppm.

At −78°C, to a solution of 3-hexyl-2-(3-hexylthiophen-2-yl)thiophene (664 mg, 1.98 mmol) in freshly distilled THF (20 mL) was added dropwise n-butyllithium solution (0.87 mL, 2.5 M in THF, 2.18 mmol) over 10 min under argon. The reaction mixture was stirred at −78°C for 1 h. Then trimethyltin chloride (593 mg, 2.97 mmol) in THF (2 mL) solution was added dropwise over 5 min. The resulting solution was allowed to stir at −78°C for 1 h. The reaction was quenched by adding 15 mL deionized water, and the mixture was extracted with n-hexane (50 mL × 3), washed with deionized water (100 mL × 3) and dried over with anhydrous magnesium sulfate.
Then, the solvent was removed under reduced pressure to give (4-hexyl-5-(3-hexylthiophen-2-yl)thiophen-2-yl)trimethylstannane as a pale yellow oil. Recovered yield: (728 mg, 1.46 mmol, 74%).

**Spectral Data:** $^1$H NMR (600 MHz, CDCl$_3$): $\delta = 7.28−7.27$ (d, $J = 5.28$ Hz, 1H, Ar), 7.04 (s, 1H, Ar), 6.97−6.96 (t, $J = 5.22$ Hz, 1H, Ar), 2.55−2.50 (m, 4H, alkyl), 1.59−1.53 (m, 4H, alkyl), 1.43−1.26 (m, 12H, alkyl), 0.87−0.85 (m, 6H, alkyl), 0.38−0.36 (m, 9H, SnMe$_3$) ppm.

In a N$_2$ filled glove box, a 20 mL glass tube was charged with (4-hexyl-5-(3-hexylthiophen-2-yl)thiophen-2-yl)trimethylstannane (1.15 g, 2.32 mmol), 4-bromo-5-fluoro-7-(5-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (927 mg, 2.32 mmol), Pd(PPh$_3$)$_4$ (161 mg, 0.14 mmol) and toluene (15 mL), and sealed with a Teflon® cap. The reaction mixture was heated to 100 °C for 1 min, 120 °C for 1 min, 140 °C for 10 min, 150 °C for 10 min, and 160 °C for 40 min using a Biotage microwave reactor. Upon cooling, the material was then loaded onto silica, washed with methanol and purified by flash chromatography using a $n$-hexane/dichloromethane gradient. 5-Fluoro-4-(4-hexyl-5-(3-hexylthiophen-2-yl)thiophen-2-yl)-7-(5-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole was recovered as a red oil. Recovered yield: (1.01 g, 1.54 mmol, 67%).
**Spectral Data:** $^1$H NMR (600 MHz, CDCl$_3$): $\delta = 8.14$ (s, 1H, Ar), 7.91–7.90 (d, $J$ = 4.56 Hz, 1H, Ar), 7.60–7.58 (d, $J$ = 12.36 Hz, 1H, FBT), 7.33–7.32 (d, $J$ = 5.28 Hz, 1H, Ar), 7.00 (d, $J$ = 5.28 Hz, 1H, ar), 6.84–6.83 (d, $J$ = 3.60 Hz, 1H, Ar), 2.87–2.85 (t, $J$ = 7.62 Hz, 2H, alkyl), 2.62–2.60 (t, $J$ = 7.80 Hz, 3H, alkyl), 1.76–1.71 (m, 2H, alkyl), 1.67–1.58 (m, 4H, alkyl), 1.44–1.39 (m, 2H, alkyl), 1.34–1.26 (m, 16H, alkyl), 0.92–0.83 (m, 10H, alkyl) ppm. $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta = 159.8$, 158.1, 153.3, 153.3, 149.6, 149.1, 142.5, 135.3, 131.6, 131.6, 128.6, 128.5, 128.3, 125.9, 125.8, 125.5, 125.4, 116.1, 115.9 (Ar), 31.7, 31.6, 31.5, 30.8, 30.8, 30.3, 29.2, 29.2, 29.0, 29.0, 28.8, 22.6, 22.6, 14.1, 14.1 (alkyl) ppm.

At $-78 \, ^{\circ}C$, to a solution of 5-fluoro-4-(4-hexyl-5-(3-hexylthiophen-2-yl)thiophen-2-yl)-7-(5-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (578 mg, 0.88 mmol) in freshly distilled THF (10 mL) was added dropwise lithium diisopropylamide (LDA) solution (0.9 mL, 2 M in THF, 1.85 mmol) over 10 min under argon. The reaction mixture was stirred at $-78 \, ^{\circ}C$ for 1 h. Then trimethyltin chloride (194 mg, 0.97 mmol) in THF (2 mL) solution was added dropwise over 5 min. The resulting solution was allowed to stir at $-78 \, ^{\circ}C$ for 1 h and at 25 °C for another 3 h. The reaction was quenched by adding 15 mL deionized water, and the mixture was extracted with n-hexane (50 mL × 3), washed with deionized water (100
mL × 3) and dried over with anhydrous magnesium sulfate. Then, the solvent was removed under reduced pressure to give 5-fluoro-4-(4-hexyl-5-(3-hexyl-5-(trimethylstannyl)thiophen-2-yl)thiophen-2-yl)-7-(5-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole as a red oil. Recovered yield: (624 mg, 0.76 mmol, 87%).

*Spectral Data:* $^1$H NMR (600 MHz, CDCl$_3$): $\delta = 8.14$ (s, 1H, Ar), 7.92–7.91 (d, $J = 3.66$ Hz, 1H, Ar), 7.63–7.61 (d, $J = 13.02$ Hz, 1H, FBT), 7.06 (s, 1H, Ar), 6.84 (d, $J = 3.60$ Hz, 1H, Ar), 2.87–2.85 (t, $J = 7.28$ Hz, 2H, alkyl), 2.62–2.59 (m, 4H, alkyl), 1.75–1.58 (m, 8H, alkyl), 1.42–1.28 (m, 25H, alkyl), 0.43–0.34 (m, 9H, SnMe$_3$) ppm.

**Synthesis of AT3-Sn**

At −78 °C, to a solution of 3-hexyl-2-(3-hexylthiophen-2-yl)thiophene (664 mg, 1.98 mmol) in freshly distilled THF (20 mL) was added dropwise $n$-butyllithium solution (2.37 mL, 2.5 M in THF, 5.94 mmol) over 10 min under argon. The reaction mixture was stirred at −78 °C for 1 h. Then trimethyltin chloride (1.40 mg, 7.92 mmol) in THF (2 mL) solution was added dropwise over 5 min. The resulting solution was allowed to stir at −78 °C for 1 h. The reaction was quenched by adding 15 mL deionized water, and the mixture was extracted with $n$-hexane (50 mL × 3), washed with deionized water (100 mL × 3) and dried over with anhydrous magnesium sulfate.
Then, the solvent was removed under reduced pressure to give (4-hexyl-5-(3-hexylthiophen-2-yl)thiophen-2-yl) trimethylstannane as a pale yellow oil. Recovered yield: (728 mg, 1.10 mmol, 74%).

*Spectral Data:* $^1$H NMR (600 MHz, CDCl$_3$): $\delta = 7.04$ (s, 2H, Ar), 2.55–2.50 (m, 4H, alkyl), 1.59–1.53 (m, 4H, alkyl), 1.43–1.26 (m, 12H, alkyl), 0.87–0.85 (m, 6H, alkyl), 0.38–0.36 (m, 18H, SnMe$_3$) ppm.

**Synthesis of AT5-Sn**

In a N$_2$ filled glove box, a 20 mL glass tube was charged with AT1-Br (488.6 mg, 1.22 mmol), tributyl(thiophen-2-yl)stannane (502 mg, 1.34 mmol), Pd(PPh$_3$)$_4$ (85 mg, 0.07 mmol) and toluene (15 mL), and sealed with a Teflon® cap. The reaction mixture was heated to 100 °C for 1 min, 120 °C for 1 min, 140 °C for 10 min, 150 °C for 10 min, and 160 °C for 40 min using a Biotage microwave reactor. Upon cooling, the material was then loaded onto silica, washed with methanol and purified by flash chromatography using a $n$-hexane/dichloromethane gradient. 5-Fluoro-7-(5-hexylthiophen-2-yl)-4-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole was recovered as a yellow solid. Recovered yield: (417 mg, 1.03 mmol, 85%).

*Spectral Data:* $^1$H NMR (600 MHz, THF-d$_8$): $\delta = 8.25$ (d, $J = 3.60$ Hz, 1H, Ar), 7.93–7.92 (d, $J = 3.60$ Hz, 1H, Ar), 7.69–7.67 (d, $J = 13.38$ Hz, 1H, FBT), 7.57–7.56
(d, \( J = 5.03 \text{ Hz}, 1H, \text{ Ar})\), 7.16–7.14 (t, \( J = 3.83 \text{ Hz}, 1H, \text{ Ar})\), 6.80–6.79 (d, \( J = 3.54 \text{ Hz}, 1H, \text{ Ar})\), 2.83–2.81 (t, \( J = 7.67 \text{ Hz}, 2H, \text{ alkyl})\), 1.72–1.67 (m, 3H, alkyl), 1.33–1.25 (m, 6H, alkyl), 0.90–0.88 (m, 2H, alkyl) ppm. \(^{13}\)C NMR (150 MHz, THF-\(d_8\)): \( \delta = 159.7, 158.0, 153.1, 153.1, 149.4, 148.9, 135.2, 135.2, 132.5, 132.5, 129.7, 129.6, 128.4, 127.5, 127.5, 126.6, 126.0, 126.0, 125.1, 115.3, 115.1, 110.2, 110.1 (\text{ Ar})\), 31.6, 31.4, 29.9, 28.8, 22.5, 13.5 (alkyl) ppm.

At −78 °C, to a solution of 5-fluoro-7-(5-hexylthiophen-2-yl)-4-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (337 mg, 0.83 mmol) in freshly distilled THF (10 mL) was added dropwise lithium diisopropylamide (LDA) solution (1 mL, 2 M in THF, 2.07 mmol) over 10 min under argon. The reaction mixture was stirred at −78 °C for 1 h. Then trimethyltin chloride (183 mg, 0.92 mmol) in THF (2 mL) solution was added dropwise over 5 min. The resulting solution was allowed to stir at −78 °C for 1 h and at 25 °C for another 3 h. The reaction was quenched by adding 15 mL deionized water, the mixture was extracted with \( n \)-hexane (50 mL × 3), washed with deionized water (100 mL × 3) and dried over with anhydrous magnesium sulfate. Then, the solvent was removed under reduced pressure to give AT5-Sn as a red oil. Recovered yield: (624 mg, 1.10 mmol, 87%).

Spectral Data: \(^1\)H NMR (600 MHz, THF-\(d_8\)): \( \delta = 8.28 (d, J = 3.35 \text{ Hz}, 1H, \text{ Ar})\),
7.92–7.91 (d, $J = 3.65$ Hz, 1H, Ar), 7.65–7.63 (d, $J = 12.90$ Hz, 1H, FBT), 7.31–7.30 (d, $J = 2.63$ Hz, 1H, Ar), 6.85–6.84 (d, $J = 3.65$ Hz, 1H, Ar), 2.87–2.85 (t, $J = 7.65$ Hz, 2H, alkyl), 1.75–1.70 (m, 2H, alkyl), 1.43–1.31 (m, 6H, alkyl), 0.91–0.88 (m, 3H, alkyl), 0.48–0.38 (t, $J = 28.74$ Hz, 9H, SnMe$_3$) ppm.

**Synthesis of AT6-Sn**

In a N$_2$ filled glove box, a 20 mL glass tube was charged with 2-bromo-3-hexylthiophene (1 g, 4.04 mmol), (E)-1,2-bis(trimethylstannyl)ethene (980 mg, 1.61 mmol), Pd(PPh$_3$)$_4$ (280 mg, 0.24 mmol) and toluene (15 mL), and sealed with a Teflon® cap. The reaction mixture was heated to 100 ºC for 1 min, 120 ºC for 1 min, 140 ºC for 10 min, 150 ºC for 10 min, and 160 ºC for 40 min using a Biotage microwave reactor. Upon cooling, the material was then loaded onto silica, washed with methanol and purified by flash chromatography using a $n$-hexane/dichloromethane gradient. 3-Hexyl-2-((E)-2-(3-hexylthiophen-2-yl)vinyl) thiophene was recovered as a yellow solid. Recovered yield: (411 mg, 1.14 mmol, 70%).

**Spectral Data:** $^1$H NMR (600 MHz, CDCl$_3$): $\delta = 7.08–7.07$ (d, $J = 4.68$ Hz, 1H, Ar), 7.03 (s, 1H, Ar), 6.86–6.85 (d, $J = 4.74$ Hz, 1H, Ar), 2.69–2.66 (t, $J = 7.49$ Hz, 4H, alkyl), 1.63–1.60 (m, 4H, alkyl), 1.38–1.29 (m, 12H, alkyl), 0.91–0.89 (m, 6H,
alkyl) ppm. $^{13}$C NMR (150 MHz, CDCl$_3$): 140.7, 136.3, 129.8, 122.5, 119.4 (Ar), 31.7, 30.9, 29.1, 28.4, 22.6, 14.1 (alkyl) ppm.

At $-78 \, ^{\circ}C$, to a solution of 3-hexyl-2-((E)-2-(3-hexylthiophen-2-yl)vinyl) thiophene (411 mg, 1.13 mmol) in freshly distilled THF (20 mL) was added dropwise n-butyllithium solution (0.50 mL, 2.5 M in THF, 1.25 mmol) over 10 min under argon. The reaction mixture was stirred at $-78 \, ^{\circ}C$ for 1 h. Then trimethyltin chloride (340 mg, 1.70 mmol) in THF (2 mL) solution was added dropwise over 5 min. The resulting solution was allowed to stir at $-78 \, ^{\circ}C$ for 1 h. The reaction was quenched by adding 15 mL deionized water, and the mixture was extracted with n-hexane (50 mL $\times$ 3), washed with deionized water (100 mL $\times$ 3) and dried over with anhydrous magnesium sulfate. Then, the solvent was removed under reduced pressure to give (4-hexyl-5-((E)-2-(3-hexylthiophen-2-yl)vinyl)thiophen-2-yl)trimethylstannane as a light brown oil. Recovered yield: (599 mg, 1.14 mmol, 82%).

Spectral Data: $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.08$–$7.07$ (d, $J = 5.15$ Hz, 1H, Ar), 7.04–7.03 (d, $J = 4.35$ Hz, 2H, Ar), 6.95 (s, 1H, Ar), 6.86–6.85 (d, $J = 5.15$ Hz, 1H, Ar), 2.70–2.67 (t, $J = 7.72$ Hz, 4H, alkyl), 1.66–1.59 (m, 4H, alkyl), 1.42–1.33 (m, 12H, alkyl), 0.94–0.91 (m, 6H, alkyl), 0.46–0.34 (t, $J = 28.12$ Hz, 9H, SnMe$_3$) ppm.
In a N$_2$ filled glove box, a 20 mL glass tube was charged with (4-hexyl-5-((E)-2-(3-hexylthiophen-2-yl)vinyl)thiophen-2-yl)trimethylstannane (599 mg, 1.14 mmol), AT$_1$-Br (380 mg, 0.95 mmol), Pd(PPh$_3$)$_4$ (80 mg, 0.06 mmol) and toluene (15 mL), and sealed with a Teflon® cap. The reaction mixture was heated to 100 °C for 1 min, 120 °C for 1 min, 140 °C for 10 min, 150 °C for 10 min, and 160 °C for 40 min using a Biotage microwave reactor. Upon cooling, the material was then loaded onto silica, washed with methanol and purified by flash chromatography using a n-hexane/dichloromethane gradient. 5-Fluoro-4-(4-hexyl-5-((E)-2-(3-hexylthiophen-2-yl)vinyl)thiophen-2-yl)-7-(5-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole was recovered as a yellow solid. Recovered yield: (505 mg, 0.74 mmol, 78%).

*Spectral Data:* $^1$H NMR (600 MHz, CDCl$_3$): $\delta = 8.03$ (s, 1H, Ar), 7.95 (d, $J =$ 3.65 Hz, 1H, Ar), 7.67–7.65 (d, $J =$ 13.19 Hz, 1H, FBT), 7.16–7.03 (m, 3H, Ar), 6.87–6.85 (m, 2H, Ar), 2.89–2.86 (t, $J =$ 7.55 Hz, 2H, alkyl), 2.74–2.69 (m, 4H, alkyl), 1.76–1.58 (m, 6H, alkyl), 1.42–1.31 (m, 18H, alkyl), 0.90–0.87 (m, 9H, alkyl) ppm. $^{13}$C NMR (150 MHz, CDCl$_3$): 159.7, 158.0, 153.1, 153.0, 149.5, 148.8, 141.1, 141.0, 138.7, 138.6, 136.6, 135.4, 135.3, 132.7, 132.6, 129.8, 129.7, 129.7, 128.3, 125.3, 125.2, 125.2, 122.8, 119.8, 119.1, 115.7, 115.5, 110.4, 110.3 (Ar), 31.8, 31.8, 31.7, 31.4, 31.0, 30.3, 29.3, 29.2, 29.0, 28.5, 28.5, 14.2, 14.2 (alkyl) ppm.
At −78 °C, to a solution of 5-fluoro-4-(4-hexyl-5-((E)-2-(3-hexylthiophen-2-yI)vinyl)thiophen-2-yI)-7-(5-hexylthiophen-2-yI)benzo[c][1,2,5]thiadiazole (326 mg, 0.41 mmol) in freshly distilled THF (10 mL) was dropwise lithium diisopropylamide (LDA) solution (0.5 mL, 2 M in THF, 1.02 mmol) over 10 min under argon. The reaction mixture was stirred at −78 °C for 1 h. Then trimethyltin chloride (90.3 mg, 0.45 mmol) in THF (2 mL) solution was added dropwise over 5 min. The resulting solution was allowed to stir at −78 °C for 1 h and at 25 °C for another 3 h. The reaction was quenched by adding 15 mL deionized water, and the mixture was extracted with n-hexane (50 mL × 3), washed with deionized water (100 mL × 3) and dried over with anhydrous magnesium sulfate. Then, the solvent was removed under reduced pressure to give AT5-Sn as a red oil. Recovered yield: (337 mg, 0.40 mmol, 97%).

*Spectral Data:* $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 7.98 (d, $J = 1.02$ Hz, 1H, Ar), 7.59–7.57 (d, $J = 4.13$ Hz, 1H, Ar), 7.90–7.89 (d, $J = 13.26$ Hz, 1H, FBT), 7.13–6.93 (m, 3H, Ar), 6.85–6.82 (m, 1H, Ar), 2.85–2.83 (t, $J = 7.65$ Hz, 2H, alkyl), 2.71–2.67 (m, 4H, alkyl), 1.74–1.56 (m, 8H, alkyl), 1.40–1.30 (m, 14H, alkyl), 0.92–0.88 (m, 11H, alkyl), 0.42–0.32 (t, $J = 28.17$ Hz, 9H, SnMe$_3$) ppm.
**Synthesis of AT7-Sn**

In a N₂ filled glove box a 20 mL glass tube was charged with 2-bromo-3-hexylthiophene (1 g, 4.04 mmol), 2,5-bis(trimethylstannyl)thieno[3,2-b]thiophene (753 mg, 1.61 mmol), Pd(PPh₃)₄ (280 mg, 0.24 mmol) and toluene (15 mL), and sealed with a Teflon® cap. The reaction mixture was heated to 100 °C for 1 min, 120 °C for 1 min, 140 °C for 10 min, 150 °C for 10 min, and 160 °C for 40 min using a Biotage microwave reactor. Upon cooling, the material was then loaded onto silica, washed with methanol and purified by flash chromatography using a n-hexane/dichloromethane gradient. 2,5-Bis(3-hexylthiophen-2-yl)thieno[3,2-b]thiophene was recovered as a light yellow solid. Recovered yield: (627 mg, 1.32 mmol, 79%).

**Spectral Data:**

^1^H NMR (600 MHz, CDCl₃): δ = 7.26 (s, 2H, Ar), 7.22–7.21 (d, J = 5.27 Hz, 2H, Ar), 6.98–6.97 (d, J = 5.28 Hz, 2H, Ar), 2.84–2.81 (t, J = 7.95 Hz, 4H, alkyl), 1.71–1.66 (m, 4H, alkyl), 1.44–1.32 (m, 12H, alkyl), 0.93–0.91 (m, 6H, alkyl) ppm. ^13^C NMR (150 MHz, CDCl₃): δ = 140.2, 139.2, 137.7, 130.8, 130.1, 124.3, 118.0 (Ar), 31.7, 30.8, 29.3, 22.7, 14.2 (alkyl) ppm.

At −78 °C, to a solution of 2,5-bis(3-hexylthiophen-2-yl)thieno[3,2-b] thiophene (607 mg, 1.28 mmol) in freshly distilled THF (20 mL) was added dropwise
n-butyllithium solution (0.56 mL, 2.5 M in THF, 1.41 mmol) over 10 min under argon. The reaction mixture was stirred at −78 °C for 1 h. Then trimethyltin chloride (383 mg, 1.92 mmol) in THF (2 mL) solution was added dropwise over 5 min. The resulting solution was allowed to stir at −78 °C for 1 h. The reaction was quenched by adding 15 mL deionized water, and the mixture was extracted with \( n \)-hexane (50 mL × 3), washed with deionized water (100 mL × 3) and dried over with anhydrous magnesium sulfate. Then, the solvent was removed under reduced pressure to give (4-hexyl-5-(2-(3-hexylthiophen-2-yl)thieno[3,2-b]thiophen-5-yl)thiophen-2-yl)trimethylstannane as a yellow oil. Recovered yield: (765 mg, 1.20 mmol, 93%).

**Spectral Data:** \(^1\)H NMR (600 MHz, CDCl\(_3\)): \( \delta = 7.22−7.19 \) (m, 3H, Ar), 7.03–6.99 (m, 2H, Ar), 2.80–2.76 (m, 4H, alkyl), 1.68–1.63 (m, 4H, alkyl), 1.37–1.24 (m, 12H, alkyl), 0.88–0.86 (m, 6H, alkyl), 0.42–0.33 (t, \( J = 28.23 \) Hz, 9H, SnMe\(_3\)) ppm.

In a N\(_2\) filled glove box, a 20 mL glass tube was charged with (4-hexyl-5-(2-(3-hexylthiophen-2-yl)thieno[3,2-b]thiophen-5-yl)thiophen-2-yl)trimethylstannane (751 mg, 1.81 mmol), AT1-Br (314 mg, 0.78 mmol), Pd(PPh\(_3\))\(_4\) (81 mg, 0.05 mmol) and toluene (15 mL), and sealed with a Teflon\(^\circledR\) cap. The reaction mixture was heated to 100 °C for 1 min, 120 °C for 1 min, 140 °C for 10 min, 150 °C
for 10 min, and 160 °C for 40 min using a Biotage microwave reactor. Upon cooling, the material was then loaded onto silica, washed with methanol and purified by flash chromatography using a n-hexane/dichloromethane gradient. 5-Fluoro-4-(4-hexyl-5-(2-(3-hexylthiophen-2-yl)thieno[3,2-b]thiophen-5-yl)thiophen-2-yl)-7-(5-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole was recovered as a red solid. Recovered yield: (400 mg, 0.51 mmol, 65%).

Spectral Data: \( ^1H \) NMR (600 MHz, THF-d8): \( \delta = 8.18 \) (s, 1H, Ar), 8.02–8.01 (d, J = 3.41 Hz, 1H, Ar), 7.80–7.78 (d, J = 13.44 Hz, 1H, FBT), 7.46 (s, 1H, Ar), 7.35 (s, 1H, Ar), 7.31–7.30 (d, J = 5.09 Hz, 1H, Ar), 6.98–6.97 (d, J = 5.16 Hz, 1H, Ar), 6.87–6.86 (d, J = 3.18 Hz, 1H, Ar), 2.90–2.80 (m, 6H, alkyl), 1.76–1.64 (m, 9H, alkyl), 1.47–1.31 (m, 18H, alkyl), 0.90–0.87 (m, 6H, alkyl) ppm. \( ^{13}C \) NMR (150 MHz, THF-d8): \( \delta = 159.9, 158.2, 153.0, 152.9, 149.5, 149.1, 139.9, 139.6, 139.4, 137.9, 137.2, 135.3, 133.3, 133.2, 132.9, 132.8, 131.1, 131.0, 130.6, 129.8, 128.5, 126.0, 125.9, 125.1, 124.3, 117.9, 117.8, 115.3, 115.0, 109.7 (Ar), 31.7, 31.7, 31.6, 31.4, 30.7, 30.6, 30.0, 29.3, 29.2, 29.1, 28.8, 22.6, 22.5, 22.5, 13.5, 13.4 (alkyl) ppm.

At −78 °C, to a solution of 5-fluoro-4-(4-hexyl-5-(2-(3-hexylthiophen-2-yl)thieno[3,2-b]thiophen-5-yl)thiophen-2-yl)-7-(5-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (165 mg, 0.20 mmol) in freshly distilled THF (10 mL) was dropwise lithium
diisopropylamide (LDA) solution (0.4 mL, 2 M in THF, 0.80 mmol) over 10 min under argon. The reaction mixture was stirred at −78 °C for 1 h. Then trimethyltin chloride (45.70 mg, 0.22 mmol) in THF (2 mL) solution was added dropwise over 5 min. The resulting solution was allowed to stir at −78 °C for 1 h and at 25 °C for another 3 h. The reaction was quenched by adding 15 mL deionized water, and the mixture was extracted with n-hexane (50 mL × 3), washed with deionized water (100 mL × 3) and dried over with anhydrous magnesium sulfate. Then, the solvent was removed under reduced pressure to give AT5-Sn as a red oil. Recovered yield: (202 mg, 0.19 mmol, 94%).

*Spectral Data:* $^1$H NMR (600 MHz, THF-d₈): δ = 8.26 (s, 1H, Ar), 8.10−8.09 (d, $J = 3.65$ Hz, 1H, Ar), 7.90−7.87 (d, $J = 13.44$ Hz, 1H, FBT), 7.53 (s, 1H, Ar), 7.38 (s, 1H, Ar), 7.11 (s, 1H, Ar), 6.94 (d, $J = 3.59$ Hz, 1H, Ar), 2.97−2.86 (m, 6H, alkyl), 1.42−1.32 (m, 19H, alkyl), 0.97−0.91 (m, 14H, alkyl), 0.46−0.37 (t, $J = 28.50$ Hz, 9H, SnMe₃) ppm.

### 8.7.4 Experimental Details for Small Molecules

**Synthesis of AT1**

In a N₂ filled glove box, a 5 mL glass tube was charged with AT1-Sn (143 mg, 0.17 mmol), Br-FBT-DTS-FBT-Br (78 mg, 0.08 mmol), Pd(PPh₃)₄ (12 mg, 0.01 mmol)
mmol) and toluene (3 mL), and sealed with a Teflon® cap. The reaction mixture was heated to 100 °C for 1 minute, 120 °C for 1 min, 140 °C for 10 min, 150 °C for 10 min, and 160 °C for 40 min using a Biotage microwave reactor. Upon cooling, the material was then loaded onto silica, washed with methanol and purified by flash chromatography using a n-hexane/dichloromethane gradient in duplicate. After fraction collection and solvent removal, a purple solid was obtained. The solid was slurried in a 3:1 mixture of methanol and n-hexane, sonicated for 1 hour and stirred overnight. The suspension was filtered, washed with acetone and dried in vacuo. The product was recovered as a purple solid. Recovered yield: (91 mg, 0.04 mmol, 52 %).

*Spectral Data*: $^1$H NMR (600 MHz, THF-d$_8$): $\delta = 8.46$−$8.44$ (t, $J = 6.90$ Hz, 2H, DTS), 8.39 (s, 2H, Ar), 8.37 (s, 2H, Ar), 8.14−8.13 (d, $J = 3.60$ Hz, 2H, Ar), 8.09−8.06 (dt, $J = 13.32$ Hz, 2H, FBT), 7.96−7.94 (d, $J = 13.32$ Hz, 2H, FBT), 6.97 (d, $J = 3.66$ Hz, 2H, Ar), 2.97−2.95 (t, $J = 13.32$ Hz, 4H, alkyl), 2.81−2.78 (t, $J = 13.32$ Hz, 6H, alkyl), 2.46 (s, 2H, alkyl), 1.87−1.76 (m, 24H, alkyl), 1.65−1.61 (m, 4H, alkyl), 1.52−1.18 (m, 50H, alkyl), 0.97−0.84 (m, 24H, alkyl) ppm. $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta = 159.6$, 158.1, 158.0, 153.0, 152.9, 152.9, 152.8, 151.3, 149.4, 149.2, 149.0, 144.9, 144.9, 144.8, 142.0, 141.9, 140.2, 140.2, 135.3, 135.2, 132.6, 132.5, 132.5, 131.7, 131.6, 131.5, 131.5, 131.3, 131.3, 131.2, 128.4, 125.9, 125.8, 125.4, 125.3, 125.1, 115.2, 115.1, 115.0, 114.8, 110.1, 110.0, 109.9 (Ar), 36.0, 35.7, 31.6,
31.6, 31.5, 31.4, 30.8, 29.9, 29.6, 29.2, 29.0, 28.9, 28.7, 24.5, 24.4, 24.3, 24.1, 24.0, 23.0, 22.5, 17., 13.6, 13.4, 13.4, 10.2 (alkyl) ppm. FD-TOF MS: Calculated for C_{108}H_{126}F_{4}N_{8}S_{12}Si: 2022.6. Found: 2023.4 (M^{+}), 1012.3 (M^{2+}), 674.9 (M^{3+}).

Synthesis of AT2: Yield: 85%; purple solid.

Spectral Data: \(^1\)H NMR (600 MHz, THF-d8): \(\delta = 8.45\text{--}8.42\) (dt, \(J = 3.29\) Hz, 2H, DTS), 8.37\text{--}8.36 (d, \(J = 3.06\) Hz, 2H, Ar), 8.30 (d, \(J = 3.89\) Hz, 1H, Ar), 8.13 (d, \(J = 3.65\) Hz, 1H, Ar), 8.04\text{--}7.99 (m, 2H, FBT), 7.95\text{--}7.93 (d, \(J = 14.82\) Hz, 1H, FBT), 7.30\text{--}7.29 (d, \(J = 2.94\) Hz, 1H, Ar), 7.20 (d, \(J = 3.48\) Hz, 1H, Ar), 6.97\text{--}6.96 (d, \(J = 3.65\) Hz, 1H, Ar), 6.81\text{--}6.80 (m, \(J = 3.48\) Hz, 1H, Ar), 2.97\text{--}2.94 (t, \(J = 7.59\) Hz, 2H, alkyl), 2.89\text{--}2.86 (t, \(J = 7.59\) Hz, 2H, alkyl), 2.81\text{--}2.78 (m, 4H, alkyl), 1.65\text{--}1.62 (m, 3H, alkyl), 1.50\text{--}1.18 (m, 42H, alkyl), 0.97\text{--}0.88 (m, 16H, alkyl) ppm. \(^{13}\)C NMR (150 MHz, THF-d8): \(\delta = 159.9, 159.7, 159.4, 158.2, 158.0, 157.8, 153.1, 153.0, 152.8, 152.7, 152.7, 151.4, 149.5, 149.2, 149.2, 149.1, 145.5, 144.8, 144.8, 142.1, 142.0, 140.2, 140.2, 140.1, 140.0, 140.0, 135.3, 135.3, 134.6, 132.6, 132.6, 131.7, 131.7, 131.6, 131.6, 131.4, 131.4, 131.3, 131.3, 130.9, 130.8, 130.7, 130.6, 128.5, 126.0, 126.0, 125.4, 125.4, 125.2, 125.0, 124.9, 123.4, 122.7, 115.4, 115.1, 110.2, 110.1, 110.0, 109.9 (Ar), 53.9, 36.0, 35.7, 31.7, 31.7, 31.6, 31.5, 31.5, 30.9, 30.8, 30.8, 30.0, 29.9, 29.2, 29.2, 29.1, 29.1, 28.9, 28.8, 28.7, 24.8, 24.6, 24.5, 23.0, 22.6, 22.5, 17.6, 13.6,
13.5, 13.4, 10.2 (alkyl) ppm. FD-TOF MS: Calculated for C_{86}H_{99}F_{3}N_{6}S_{10}Si: 1620.4
Found: 1621.3 (M^+) 810.7 (M^{2+}).

**Synthesis of AT3:** Yield: 85%; dark red solid.

*Spectral Data:* $^1$H NMR (600 MHz, THF-d$_8$): $\delta = 8.32$ (s, 2H, Ar), 8.06–8.05 (d, $J = 3.12$ Hz, 2H, Ar), 7.84–7.82 (d, $J = 13.32$ Hz, 2H, FBT), 6.92–6.91 (d, $J = 2.63$ Hz, 2H, Ar), 2.93–2.91 (t, $J = 7.40$ Hz, 4H, alkyl), 2.80–2.77 (t, $J = 7.55$ Hz, 4H, alkyl), 1.80–1.76 (m, 10H, alkyl), 1.47–1.35 (m, 22H, alkyl), 0.95–0.89 (m, 12H, alkyl) ppm. $^{13}$C NMR (150 MHz, THF-d$_8$): $\delta = 161.8, 160.1, 154.9, 154.9, 151.4, 151.0, 144.0, 137.2, 134.6, 134.5, 133.5, 133.5, 133.0, 133.0, 130.4, 128.0, 127.9, 127.1, 117.2, 117.0, 111.9, 111.8 (Ar), 33.5, 33.4, 33.4, 32.7, 31.8, 31.0, 30.9, 30.6, 24.4, 24.3, 15.3 (alkyl) ppm. FD-TOF MS: Calculated for C_{52}H_{60}F_{2}N_{4}S_{6}: 2022.6.
Found: 2023.2 (M^+), 1011.1 (M^{2+}).

**Synthesis of AT4:** Yield: 68%; purple solid.

*Spectral Data:* $^1$H NMR (600 MHz, THF-d$_8$): $\delta = 8.41–8.40$ (t, $J = 3.06$ Hz, 2H, DTS), 8.33 (s, 2H, Ar), 8.31 (s, 2H, Ar), 8.08 (d, $J = 3.65$ Hz, 2H, Ar), 7.99–7.96 (dt, $J = 16.01$ Hz, 2H, FBT), 7.90–7.88 (d, $J = 13.32$ Hz, 2H, FBT), 6.92 (d, $J = 3.66$ Hz, 2H, Ar), 2.92–2.90 (t, $J = 7.58$ Hz, 4H, alkyl), 2.76–2.74 (t, $J = 7.73$ Hz, 8H, alkyl),
1.50–1.25 (m, 62H, alkyl), 0.92–0.81 (m, 38H, alkyl) ppm. FD-TOF MS: Calculated for C\textsubscript{106}H\textsubscript{126}F\textsubscript{4}GeN\textsubscript{8}S\textsubscript{12}: 2068.5. Found: 2069.2 (M\textsuperscript{+}), 1034.6 (M\textsuperscript{2+}).

**Synthesis of AT5:** Yield: 48%; dark blue solid.

*Spectral Data:* \textsuperscript{1}H NMR (600 MHz, 1,1,2,2-tetrachloroethane-d\textsubscript{2}): \(\delta = 8.16–8.05\) (m, 6H, Ar), 7.80 (s, 2H, Ar), 7.52–7.50 (m, 4H, Ar), 6.73 (s, 2H, Ar), 2.77 (s, 4H, alkyl), 1.49–1.32 (m, 32H, alkyl), 0.97–0.88 (m, 24H, alkyl) ppm. FD-TOF MS: Calculated for C\textsubscript{76}H\textsubscript{74}F\textsubscript{4}GeN\textsubscript{8}S\textsubscript{10}: 1568.2. Found: 1568.2 (M\textsuperscript{+}), 784.1 (M\textsuperscript{2+}).

**Synthesis of AT6:** Yield: 43%; greenish blue solid.

*Spectral Data:* \textsuperscript{1}H NMR (600 MHz, 1,1,2,2-tetrachloroethane-d\textsubscript{2}): \(\delta = 8.11–8.05\) (m, 4H, Ar), 7.92 (s, 2H, Ar), 7.69–7.61 (m, 4H, Ar), 7.29 (s, 2H, Ar), 7.13 (s, 4H, Ar), 6.86 (s, 2H, Ar), 2.86–2.78 (m, 12H, alkyl), 1.72–1.50 (m, 30H, alkyl), 1.50–1.25 (m, 46H, alkyl), 0.97–0.88 (m, 24H, alkyl) ppm. FD-TOF MS: Calculated for C\textsubscript{112}H\textsubscript{130}F\textsubscript{4}GeN\textsubscript{8}S\textsubscript{12}: 2120.6. Found: 2120.4 (M\textsuperscript{+}), 1060.2 (M\textsuperscript{2+}).

**Synthesis of AT7:** Yield: 42%; purple solid.

*Spectral Data:* \textsuperscript{1}H NMR (500 MHz, 1,1,2,2-tetrachloroethane-d\textsubscript{2}): \(\delta = 8.17–8.14\) (m, 6H, Ar), 8.00–7.99 (m, 2H, Ar), 7.80–7.68 (m, 4H, Ar), 7.45–7.42 (m, 4H, Ar),
6.92–6.91 (m, 2H, Ar), 2.95–2.87 (m, 12H, alkyl), 1.45–1.23 (m, 44H, alkyl),
0.94–0.84 (m, 52H, alkyl) ppm. FD-TOF MS: Calculated for C_{120}H_{130}F_4GeN_8S_16:

2344.5. Found: 2345.4 (M^+) 1172.6 (M^{2+}).
References:


CURRICULUM VITAE

Biographical item on the author of the thesis, Miss Lai Laifan:

- Received the degree of Bachelor of Science in Applied Chemistry from Hong Kong Baptist University, July 2010.

October 2013

List of Publication:


for Dye-sensitized Solar Cells”