Towards conjugated polymers with low exciton binding energy
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Chapter 1

Introduction to polymer solar cells
1.1 Solar energy harnessing

Energy sustainability has become one of the most important global subjects over the past four decades. In response to the fact that conventional fossil fuels will run out eventually in the near future, scientists across the world have been actively searching for possibilities to make use of natural energy forms like wind, water, bioenergy. Another increasingly pursued energy source is what has promoted life evolution billions of years ago: sunlight. The total amount of solar energy reaching the earth is ~ 1.7×10^{17} Joules per second (3.15×10^7 seconds per year). Cultivated in an efficient way, solar energy may suffice the global energy need, knowing that the amount of energy consumed globally has been estimated to be 3.9×10^{20} Joules in the whole year of 2013.\(^1\)

Solar energy is exploited in several ways, either thermal-related or electricity-conversion-related. Thermal-related processing of solar energy is direct, but doesn’t offer general energy transportability (except for cases where electricity is generated on-the-spot by steam turbines with concentrated solar power). On the other hand, converting solar energy to electricity with photovoltaic cells has attracted significant scientific interest. In general, solar cells are divided into three generations. The first generation is primarily based on (monocrystalline or polycrystalline) silicon wafers, which can yield a power conversion efficiency over 20\(^%\). As a commercialized generation, they are widely installed on roofs, on land and in other applicable locations, even on water, lately. Despite its commercial success, mainly due to a very impressive lowering of production costs, in the long run, this generation of solar cells is considered not optimally cost-effective, ultimately, because of the relatively thick active layer (up to 200 micrometers of silicon is needed to absorb enough sunlight). The second generation of solar cells is represented mainly by thin-film amorphous silicon solar cells, CIGS (copper indium gallium selenide) and CdTe (cadmium telluride) solar cells. Different from the first generation of solar cells, the second generation takes advantage of thin film technologies due to the unique characteristics of the materials (only up to 2 micrometers of semiconductor is needed to absorb enough sunlight). This generation of solar cells is apparently more cost-effective than the first generation, although with a relatively lower power conversion efficiency of around 15\(^%\). Additionally, these type of thin-film solar cells are so thin that it is possible to make solar cells on flexible substrates. The issue with the second generation of solar cells is that its production still needs high-energy processes such as high vacuum and high temperature. Another drawback is related to the fact that some key elements in these solar cells are not environment-friendly and are also not abundant in nature.

The third generation of solar cells is represented by (dye or quantum-dot) sensitized solar cells, organic (small molecule or polymer) solar cells, up-conversion/down-conversion solar cells, and a few even more exotic types such as plasmonic solar cells based on novel materials. The distinct promise of the 3rd generation of solar cells lies in its relatively high performance with low production cost, in comparison with the first two generations. Currently, dye-sensitized solar cells and small-molecule
organic solar cells have marked research efficiencies of 15%\(^3\) and 9%\(^4\) in the lab, respectively, while polymer solar cells have reached ~11% in 2016\(^5\) and 13.1% in 2017.\(^6\) Recently, remarkable advances of perovskite-based solar cells have been reached with organic selective charge transport layers, affording power conversion efficiencies over 22%.\(^7\) Although the overall performance (power conversion efficiency and device stability) of third-generation solar cells is still inferior to that of the first two generations, it has been gaining improvement throughout the past two decades. With increased understanding of the fundamentals of the 3\(^{rd}\) generation of solar cells, a bright future may be in reach.

1.2 Introduction to polymer solar cells

The study of photovoltaic effects of conjugated polymer semiconductors dates back to the 1980s, when Weinberger and coworkers reported a junction with an internal conversion efficiency of 0.3% based on graphite/trans-polyacetylene/aluminum junctions.\(^8\) Early studies on such kind of single layer organic photovoltaic cells also include conjugated organic compounds such as poly(3-methylthiophene) (aluminum/poly(3-methylthiophene)/Pt junction)\(^9\) and poly(p-phenylene-vinylene) (PPV) (aluminum/PPV/ITO junction)\(^10\). The latter has afforded an open-circuit voltage of more than 1 V and a power conversion efficiency of about 0.1%, but in general these organic solar cells with only one semiconductor did not yield good photovoltaic performance. This is mainly due to the fact that most light-induced excitons cannot make their way to the electrodes of these devices. The electric field built by the work function difference between the two electrodes is far from enough to split the excitons, leading to marginal charge collection. This problem was partially solved with a bilayer device structure,\(^11\) where a material with high electron affinity (e.g., C\(_{60}\)) is used to form the second layer. A MEH-PPV/C\(_{60}\) bilayer device exhibited a small photoresponse as a result of photoinduced electron transfer across the heterojunction interface from the PPV to C\(_{60}\), giving a fill factor of 0.48 and a power conversion efficiency of 0.04% (under monochromatic illumination)\(^12\). Furthermore, with a ITO/PPV/C\(_{60}\)/aluminum device, a power conversion efficiency of 1% was achieved and an exciton diffusion length of 7 nm was modelled out, which significantly promoted the understanding of this system.\(^13\) This discovery, however, also exposed a potential problem of bilayer devices: To absorb enough light, the thickness of a polymer layer commonly needs to reach ~100 nm, which implies that only the small fraction of excitons generated near the bilayer interface can be split and contribute to the photocurrent. This problem is solved by a simple but elegant solution, blending the polymers (donor) and fullerenes (acceptor) to form the photoactive layer. With a proper film-forming process, the domain sizes of such a polymer:fullerene blend are within the exciton diffusion radius. Given appropriate donor/acceptor energy level alignment, such a bulk-heterojunction design allows most photoinduced excitons to split and contribute to the photocurrent.\(^14\)

Bulk-heterojunction polymer solar cells (BHJ-PSCs) have been under intensive research for the past two decades. Research has been focused on polymer design, side chain engineering, fullerene
innovations, novel electron acceptor design, etc. All these efforts have contributed to push the record power conversion efficiencies of single junction bulk-heterojunction polymer solar cells towards a higher regime.

1.2.1 Operating principle

Figure 1(a) shows the typical device structure of a BHJ polymer solar cell, which can be described as two electrodes sandwiching a heterojunction plus the electron/hole transporting layers. The heterojunction is formed by mixing the polymer (donor) and fullerene derivative (acceptor), following the spontaneous phase separation of these two materials. This process provides high surface area charge-separating heterojunction interface throughout the bulk photoactive blend. The device architecture in Figure 1(a) may be further translated into an energy diagram view, as shown in Figure 1(b). The operating principle of BHJ polymer solar cells is better explained with a combined view of Figure 1(a) and 1(b).

![Figure 1](image)

**Figure 1.** (a) A typical conventional device structure of polymer solar cells. The individual components are labeled as shown. (b) A simplified energy band diagram showing the energy transfer in bulk-heterojunction solar cells. Energy offsets are shown qualitatively. The yellow vertical oval represents a local exciton on the polymer which is at its excited state.

The photocurrent generation process starts with light absorption by the photoactive layer. Commonly the electron-donating conjugated polymer plays a major role in light absorption. Absorption
of a photon by the polymer promotes one electron from the HOMO to the LUMO (or a higher energy level), forming an excited state, usually called an exciton. To dissociate into free charges, these excitons need to diffuse (randomly within the bulk) to the heterojunction interface. This is accomplished by a Förster resonance energy transfer process which can be either intramolecular or intermolecular. The domain size of the polymer phase must be within the diffusion length of the excitons, which is around 5-10 nm as reported for a number of low bandgap conjugated polymers.\textsuperscript{15}

Excitons have short lifetimes (in the order of 1 ns), thus they need to split fast at the heterojunction interface before decaying occurs.\textsuperscript{16} Actually, the dissociation of excitons is one of the decisive processes during charge photogeneration in these devices. While controversies still exist over how excitons exactly dissociate into free charges, the formation of charge transfer states (CT states) has been reported. A CT state represents the state when an electron and hole are localized on the acceptor and donor material, respectively, but are still coulombically bound. Exciton binding energy plays a central role herein, as will be discussed in detail in later paragraphs. Free charges are obtained on the basis of CT states dissociation. After charge separation, the holes and electrons diffuse/drift via a hopping mechanism, in the polymer and fullerene phase, respectively, to the electrodes and furnish charge collection.

An important implication in Figure 1(b) rests with an energetic downhill for anode to cathode which is the fundamental requisite for the whole process, while certain energy alignment essentially determines important photovoltaic parameters such as the photovoltage.\textsuperscript{17} For example, an optimal energy offset between the LUMO energies of the donor and acceptor materials may provide sufficient driving force for electron transfer (same principle applies to HOMO energies offset in the case of hole transfer). Furthermore, the open-circuit photovoltage $V_{oc}$ may be briefly described as limited by the potential difference between the HOMO level of the donor and LUMO level of the acceptor. Improper energy alignment leads to lower energy conversion efficiency by various loss mechanisms.\textsuperscript{18}

**Figure 2.** An example of a current density – voltage (J - V) curve of a polymer solar cell. $J_{SC}$, $V_{OC}$, $MPP$, $J_{MPP}$, $V_{MPP}$ and FF refer to short-circuit current density, open-circuit voltage, maximum power point, current density at the maximum power point, voltage at the maximum power point and fill factor at the maximum power point.
Successful photocurrent generation certainly relies on efficient exciton dissociation, but it is also closely related to the overlap of the light absorption profile of the photoactive layer with the solar spectrum. A larger overlap generally benefits a larger photocurrent. To summarize, a high performance polymer solar cell thereby needs a very well balanced energy alignment that theoretically guarantees a high photovoltage and efficient charge separation, a good light absorption that could lead to high photocurrent, and good properties of the photovoltaic blend that would suppress charge recombination. The photon-to-electricity conversion capability of such a polymer solar cell is characterized by a current density-potential curve, as shown in Figure 2, where the open-circuit photovoltage, short-circuit photocurrent, and maximum power point are indicated. The power conversion efficiency (PCE) is defined by the following equation:

\[
PCE = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}}
\]

where \(P_{in}\) is incident solar power, and the fill factor \(FF\) is defined as the result of the maximum power output divided by \(V_{oc} \times J_{sc}\):

\[
FF = \frac{V_{MPP} \times J_{MPP}}{V_{oc} \times J_{sc}}
\]

The power conversion efficiency is measured under standard test conditions, which include the light intensity of 1 Sun (1000 W/m²) and the spectral distribution of sunlight (air mass 1.5), and the cell temperature at 25 °C.

### 1.2.2 Excitons and exciton-binding energies

Bulk-heterojunction polymer solar cells nest under a bigger solar cell category, the excitonic solar cells.¹⁹ Excitonic solar cells function on the premise of the formation and subsequent dissociation of excitons, which leads to free charges. More specifically, these excitons are named Frenkel excitons²⁰ due to the fact that they are formed within organic molecules in materials of relatively low dielectric constants, in contrast to Wannier excitons for inorganic semiconductors with large dielectric constants. For the case of organic solar cells, the lack of sufficient dielectric screening results in a need for a high energy to split the exciton, i.e. to overcome the exciton binding energy.

Specifically, two types of excitons are defined in polymer solar cells (thereby two types of exciton binding energy), depending on the different stages of the photocurrent generation process. These two types of excitons are schematically illustrated with the electronic state diagram in Figure 3.²¹
Figure 3. An electronic state diagram showing the charge carrier generation process in a bulk-heterojunction polymer solar cell. $S_0$ (donor) means the ground state of the polymer, and $S_1$ (donor) refers to the first excited singlet state of the polymer. CS (donor) represents the state when the hole and electron are separated on the polymer chain. CT$_1$ and CT$_n$ are the manifolds of the charge transfer state which involves both the donor (polymer) and the acceptor (fullerene derivative). CS$_{\text{donor-acceptor}}$ refers to the state when free charges are separated within the polymer/fullerene derivative blend and being transported in the respective phases. The red arrows indicate photoexcitation and energy transfer pathways. The excited-state exciton binding energy ($E_{b}^{\text{exc}}$) and the charge transfer exciton binding energy ($E_{b}^{\text{CT}}$) are shown explicitly.

Photoexcitation of conjugated polymers generates a singlet excited state, which can be considered as a coulombically bound hole-electron pair. This hole-electron pair initially resides on the conjugated polymer backbone. The exciton binding energy of such an excited state, $E_{b}^{\text{exc}}$, is thereby defined as the potential energy difference between the singlet excited state and a pair of fully separated hole and electron on the polymer chain (Figure 3). Given that the exciton survives diffusing to or was formed directly at the heterojunction interface, the electron of the local exciton may transfer to the other co-blended component with high electron affinity (such as fullerene derivatives). After the electron transfer reaction, the hole-electron pair remains coulombically bound in case of insufficient dielectric screening, since the donor polymer and acceptor fullerene molecules are physically adjacent to each other. This second type of exciton is termed as the charge transfer exciton, with binding energy $E_{b}^{\text{CT}}$, defined as the potential energy difference between the charge transfer excited state and a pair of fully separated hole and electron.

The role played by excitons in the charge photogeneration process is doubtlessly crucial. Efficient charge photogeneration is only possible when excitons can diffuse to the heterojunction interface within their lifetimes, and also quickly dissociate into free charges without geminate recombination. In this respect, quite some research effort has been dedicated to understand the properties of excitons, such as the exciton diffusion length and exciton binding energy. For example, by systematically varying the layer thickness of the electron donor material (PPV), T. Stuingera and W.
Brutting estimated the exciton diffusion lengths to be $12 \pm 3\,\text{nm}$ from the measured photocurrent spectra.\textsuperscript{30} Hummelen, Blom and coworkers accurately determined the exciton diffusion length of a PPV derivative to be $5 \pm 1\,\text{nm}$ with the help of time-resolved photoluminescence.\textsuperscript{31} By analytically studying the charge separation per incident photon profiles of a poly(3-hexylthiophene) (P3HT)/TiO$_2$ system, Warman and coworkers estimated the exciton diffusion length in P3HT to be $2.6 - 5.3\,\text{nm}$, depending on the formation site of excitons.\textsuperscript{32}

Quantifying the exciton binding energy has always been a highly valued theme. In virtue of the non-uniform and disordering nature of polymers, it has been difficult to reach consensus on the measurements. For a very simple and clear start, assuming that the coulombic force makes a major contribution to the exciton binding energy, one can attempt estimating the magnitude of the exciton binding energy with the following equation:

$$E = \frac{e^2}{4\pi\varepsilon_r\varepsilon_0 r}$$  \hspace{1cm} (1)

Taking typical values for the organic material dielectric constant, $\varepsilon_r = 4$, and a hole-electron distance $r = 0.5\,\text{nm}$, $e = 1.6\times10^{-19}\,\text{C}$, vacuum permittivity $\varepsilon_0 = 8.85\times10^{-12}\,\text{C/(Vm)}^{-1}$, and $1\,\text{C} = 6.24 \times 10^{18}$ electrons, eq. (1) gives $E_{b\text{CT}} \approx 0.72\,\text{eV}$, which is notably larger than the thermal energy $k_B T$ ($\approx 25\,\text{meV}$ at room temperature ($k_B = 8.617 \times 10^{-5}\,\text{eV K}^{-1}$, the Boltzmann constant). For the case of an intramolecular excited state exciton binding energy, $E_{b\text{exc}}$ probably is even larger because of the fact that the intramolecular hole-electron distance is even shorter. Note that this estimation is a most simple one that only takes into account Coulomb force, while the actual situation may involve an entropy contribution and other factors from the local physicochemical environment.

Experimental determination of exciton binding energy has generated results ranging from $\approx 60\,\text{meV}$ to $\approx 1\,\text{eV}$. PPVs are the most studied species in this sense. For example, transient-photoconductivity decay measurements on PPV films by Heeger et al. have revealed an $E_{b\text{exc}}$ of $\approx 0.1\,\text{eV.}$\textsuperscript{33} Based on electric field and temperature-dependence studies, weakly bound excitons with $E_{b\text{exc}} \approx 0.06\,\text{eV}$ were extracted.\textsuperscript{34} These studies seem to suggest a rather small exciton binding energy for PPV. However, other investigations indicate a $E_{b\text{exc}}$ around $0.5\,\text{eV}$.\textsuperscript{35} Apart from the different nature of the measurements, these discrepancies also reflect the non-uniform and disordered nature of polymers, which leaves a difficult situation to precisely define and measure the exciton-related properties. The charge-transfer state exciton binding energy $E_{b\text{CT}}$ is expected to be smaller than $E_{b\text{exc}}$ according to eq. (1), since the hole and electron are now located on different species, thus the hole-electron distance should be increased. For instance, with electric field induced quenching of the photoluminescence of MDMO-PPV/PCBM films, Hallermann et al. determined a binding energy of $130\,\text{meV}$ for excitons in the charge-transfer state.\textsuperscript{36} Given that $E_{b\text{CT}}$ by definition is the potential energy difference between the charge transfer state and charge separated state, Janssen et al. estimated the energy of the charge transfer state of

\begin{equation*}
\frac{e^2}{4\pi\varepsilon_r\varepsilon_0 r} \geq 0.72\,\text{eV}.
\end{equation*}
P3HT/PCBM system to be 1.0 eV, and the energy of the charge separated state 0.7 eV, yielding an $E_{b}^{CT}$ of $\sim 0.3$ eV.\textsuperscript{37}

Photovoltaic systems with low exciton binding energies hold great significance for high-performance devices. In a recent investigation, Robin J. Nicholas and collaborators have demonstrated that the use of very high magnetic fields enables to accurately measure multiple excitonic transitions of the perovskite CH$_3$NH$_3$PbI$_3$, thus allowing to further study its spectroscopic properties precisely. They obtained an exciton binding energy of around 16 meV in the low temperature orthorhombic phase and a few millielectrovolts in the room temperature phase where solar cells operate.\textsuperscript{38}

To summarize, despite all the differences between different studies on the properties of excitons, one may extract an approximate numerical range for the exciton binding energy. The importance of constructing systems with low exciton binding energies has been valued from the beginning. In a practical sense, eq.(1) unambiguously shows that to decrease the exciton binding energy thus to effectively generate free charges from excitons, it is necessary to enhance the medium dielectric constant, and/or to increase the extent of excited state delocalization. Design of molecular systems along this direction may lead to considerable progress of solar cells based on molecular semiconductors.

### 1.3 Conjugated polymers

MDMO-PPV and regio-regular P3HT have been ground-breaking materials in the course of material development for polymer solar cells. As the understanding of the physicochemical fundamentals of PSCs gets increasingly deeper within the community, researchers have shifted the focus to conjugated polymers with an internal donor-acceptor alternating character, which was originally conceptualized for the purpose of bandgap reduction.\textsuperscript{39, 40} The past decade has witnessed a boom of new donor-acceptor alternating conjugated polymers for optoelectronic applications. This generation of polymers has provided much insight into important requirements of high-performance polymer solar cells, such as good energy level alignment with regard to the acceptor material for efficient energy transfer, proper bandgap for maximized light absorption, appropriate intermolecular packing for enhanced hole mobility, and sufficient compatibility with the acceptor material for good morphology. With contribution from every aspect, the design of novel polymers has become increasingly rational, boosting the solar cell power conversion efficiency to over 13% with a single junction device.\textsuperscript{6}

#### 1.3.1 One-dimensional conjugated polymers

Most reported alternating donor-acceptor conjugated polymers are one-dimensional in terms of the donor-acceptor configuration. Such a linear donor-acceptor alternation can quickly narrow down the bandgap due to donor-acceptor orbital hybridization,\textsuperscript{41} providing a relatively simple and efficient tuning of the frontier orbitals. From the rich library of various combinations of donors and acceptors monomer
units, as one can readily find in a number of review articles, we can highlight some existing popular donor and acceptor units according to their relative strength, as shown in Figure 4.

Figure 4. A collection of widely applied donor units (1 – 5) and acceptor units (6 – 14) in recent years. These structures are ranked from left to right roughly according to their electron-donating capabilities (increasing from 1 to 5) or their electron-withdrawing capabilities (increasing from 6 to 14). For cases where $X = N$, only one $R$ group is attached to $X$.

The choice of donor and acceptor decisively affects the light absorption capacity of the resulting polymer and the basic energy alignment with regard to the acceptor of choice. It may also influence the morphology of the photoactive blend in a subtle way. For example, weak donors such as fluorenes ($1, X = C$, Figure 4) and dibenzosilole ($1, X = Si$, Figure 4) are known to give relatively high $V_{oc}$ due to the low-lying HOMO levels of the corresponding polymers, but the poor orbital mixing with acceptor-type monomers in the chain generally results in polymers with relatively large bandgaps, resulting in an inherently low light absorption capacity. Stronger donors such as the dithienosilole ($5, X = Si$, Figure 4) on the other hand, could afford a preferred optical bandgap. Unquestionably, the design of OPV polymers relies on a rational combination of donor and acceptor moieties, but also in conjunction with understanding of the relationship between structure and morphology. This may be exemplified by the development of the PTB series of polymers, as shown in the schematics of Figure 5.
Figure 5. The development of the PTB series of polymers may be viewed as a typical developing route for benchmark polymers, i.e., from structure definition to fine tuning of the physicochemical properties of the polymeric material. PCE means power conversion efficiency. The PV results were obtained in combination with [70]PCBM as the acceptor material, except PTB5 which was studied in conjugation with [60]PCBM.

Figure 5 shows the development of the PTB series of polymers with selected structures. One can see the influence of what seems as a subtle structural change on the photovoltaic performance. The initial structural change of a single fluorine atom from PTB5 to PTB4 caused about 0.1 eV difference in the HOMO levels, which played an important role in the efficiency gain of PTB4.42 Furthermore, change of the $R_1$ in PTB4 from n-octyl to 2-ethylhexyl ($R_2$) improved the solubility and morphology, pushing the efficiency to 7.4%.43 Cao and coworkers enhanced the light absorption capacity as well as increased hole mobility of PTB7 by synthesizing high-molecular weight materials, obtaining efficiencies up to 8.5%.44 Yu et al. initiated the concept of using thienyl side groups on the PTB series of polymers,45 which was later followed by optimization of a number of other conjugated polymers.46,47

1.3.2 Two-dimensional conjugated polymers

A second type of donor-acceptor conjugated polymers has a distinct character of two-dimensional conjugation, as presented below by some representative structures shown in Figure 6.48 The early development of this class of polymers was based on the P3HT main chain, but provided with thienylenevinylene side chains (1 in Figure 6). These polymers were reported to show enhanced light absorption in the visible region relative to P3HT, and the reported photovoltaic performance is basically similar to that of P3HT.49 Some out-of-the-box explorations showed that with a proper extent (~2%) of cross linking of polythiophenes with thienylenevinylene chains, it is possible to see an increase of hole mobility relative to the non-cross-linked counterpart (2 in Figure 6).50 In addition, some researchers attached electron-donating side groups such as triphenylamine to the thiophene backbone (3 in Figure 6), aiming to tune the hole mobilities of these materials.51
Figure 6. A collection of selected structures with distinct two-dimensional conjugations. $m$ and $n$ in the structures are numbers between 0 and 1 (For details, please refer to the specific citations). Notice that the groups pendant to the electron-rich backbone can either be electron-donating or electron-withdrawing.

In recent years, with the booming investigations of donor-acceptor alternating conjugated polymers, this class of 2-D polymers was extended with various kinds of electron-withdrawing side groups (3–6 in Figure 6). For example, in 2008, regioregular polythiophenes tethered with 90 mol% of phenanthrenyl-imidazole (4 in Figure 6) has led to a ~0.1 eV reduction of the bandgap in comparison to P3HT, in conjunction with a doubled electron transfer probability as found in polymer:PCBM blend studies. These two features of the new polymer contributed to much higher external quantum efficiencies (thus higher photocurrents) than those of P3HT:PCBM, as well as enhanced solar cell efficiencies of 3.45%.52

A popular strategy to design two-dimensional conjugation polymers was to incorporate triphenylamine into the polymer backbone, such as in structure 5 (Figure 6).53,54,55,61 Such a design has endowed the polymer with a decent hole mobility and power conversion efficiency of 4.37% when applied in solar cells in combination with [70]PCBM,53 which may indicate room for improvement, given the fact that the phenyl-phenyl connection tends to destroy the planarity of the polymer backbone, which is not beneficial to intermolecular packing. In the later years, along with the worldwide enthusiastic research on donor-acceptor alternative conjugated polymers, new 2-D polymers have emerged with better light-harvesting capability and higher intermolecular packing potential, continuously pushing up the solar cell efficiencies.58,59,60,61,62 For example, by systematically investigating the acceptor and side-chain effect, Peng et al. have reported an efficiency of 5.65% for 6 in combination with [70]PCBM (Figure 6), which is attributed to its good light absorption, improved carrier mobility and well-defined phase compared to its analogues.52
To summarize, the investigation of the above 2-D polymers is mainly promoted by two motivations: (i) To enhance the light absorption capacity with two conjugations in the \( \pi \)-system (donor-donor conjugation and donor-acceptor conjugation), and (ii) to make use of intramolecular charge transfer (from donor to acceptor) thus improving electron transfer to fullerene acceptors in polymer solar cells. In terms of the detailed structural design, some researches directly used the 3-position of thiophene to furnish a donor-pendant acceptor configuration (this may introduce some torsion between adjacent thiophenes, yet the detailed effect remains unevaluated), while others employed an ethylenic linker as the \( \pi \)-bridge between the donor backbone and pendant acceptors. An ethylenic linker is an excellent choice to minimize the steric hindrance between neighboring conjugation moieties, especially when the acceptor group is bridged onto the 3-position of thiophene. Note that these ethylenic linkers also extend the overall \( \pi \)-conjugation. On the other hand, it should be noted that most of these 2-D polymers were prepared using the Wittig-Horner reaction to introduce the ethylenic segment. The stereochemistry of this particular alkene-generating reaction however depends on multiple factors and varies with different substrates, leaving a possible challenge to control the regio-regularity of the resulting polymers.

1.3.3 Polymer quality as an important theme

The search for new donor-acceptor conjugated polymers has always been one of the most attended subjects, paving the road for efficiency enhancement. On the other hand, the community has been facing an increasing challenge to further push up the power conversion efficiency. Unquestionably, ground-breaking design principles are needed to go to the next generation of polymer solar cells. Some researchers however, have sensed the necessity to exploit the limit of the current generation of polymers by improving the quality of these synthetic materials from a chemistry perspective, given the fact that currently almost every OPV polymer is synthesized by Stille copolymerization without specific optimization.

The quality of conjugated polymers in general embodies a manifold of characters, such as the molecular weight, degree of regio-regularity, polydispersity index, end-group control, and even precise control of intermolecular interactions by manipulating key atoms on the polymer. These characteristics impose an obvious but important impact on crucial requisites for high performance solar cells, such as a maximized light harvest (extent of conjugation), balanced morphology (domain size), and good hole
mobility (intermolecular packing). A collection of representative studies on the detailed properties of donor-acceptor conjugated polymers is listed below.

Table 1. Some examples of various perspectives on understanding the influence of specific physicochemical properties of conjugated polymers on device performances.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polymer structure</th>
<th>Point of discussion</th>
<th>Major conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image" alt="Molecular weight" /></td>
<td>Molecular weight</td>
<td>Higher molecular weight led to better light absorption and carrier mobility.</td>
</tr>
<tr>
<td>2</td>
<td><img src="image" alt="End-capping" /></td>
<td>End-capping</td>
<td>Uniform end-capping benefitted fill factor.</td>
</tr>
<tr>
<td>3</td>
<td><img src="image" alt="Fractionated polymers" /></td>
<td>Fractionated polymers</td>
<td>Yielded higher current densities.</td>
</tr>
<tr>
<td>4</td>
<td><img src="image" alt="Effect of Palladium" /></td>
<td>Effect of Palladium as impurity</td>
<td>Residual Pd caused adverse effect.</td>
</tr>
<tr>
<td>5</td>
<td><img src="image" alt="Atomic direction" /></td>
<td>Atomic direction</td>
<td>Specific F-H interaction enhanced backbone planarity.</td>
</tr>
</tbody>
</table>

Tuning (mostly increasing) of the molecular weight is by far the most studied subject regarding the quality of conjugated polymers. For example, Reinhold and coworkers have shown that the molecular weight of P3HT affects the mechanical properties of the corresponding devices by increasing the cohesive energy, and that a proper increase of molecular weight can afford higher PCEs. Cao et al. have studied the effect of the molecular weight of PTB7 on solar cell performance (Entry 1, Table 1). It was shown that PTB7 with increased molecular weight (obtained with longer polymerization time) enhanced the light absorption capacity, which significantly contributed to the eventual power conversion efficiency in combination with [70]PCBM.

Heeger et al. specifically studied the effect of end capping effect in conjugated polymers (Entry 2, Table 1), given the fact that routine Stille copolymerizations may lead to polymer chains with various end groups including stannanes, bromine or hydrogen atoms, or even methyl groups transferred from
catalyst ligands. It was shown that while there is no morphological difference between devices based on non-capped and H-capped polymers, the existing tin-capping and Br-capping adversely affects the fill factor and device stability. Another important parameter regarding polymers is the parameter $D$ (also known as polydispersity index), the influence of which has also been studied in a number of works by Manca$^{71}$, McCulloch$^{72}$, and Sivula$^{73}$ et al. For instance, by purifying indacenodithiophene polymers with recycling size-exclusion chromatography, McCulloch et al. demonstrated efficiency improvements of up to 30% with respect to the non-purified polymers (Entry 3, Table 1).$^{72}$ Seth B. Darling and coworkers artificially added Pd(PPh$_3$)$_4$ into PTB7/[70]PCBM blends and studied the device performance and photophysics of these systems (Entry 4, Table 1).$^{74}$ It was found that the presence of more residual palladium apparently deteriorated the cell performance, which was attributed to increased trap-assisted charge recombination.

Stille polycondensation potentially produces main chain complexity when asymmetrical dibrominated monomers are involved. The exact relative configuration of building blocks therefore may play a role in device performance. Jen et al. conducted a quantitative analysis of the polymerization towards PTB7 (Entry 5, Table 1).$^{75}$ It was revealed that a routine PTB7-Th synthesis was not regio- or chemo-selective, resulting in two distinctly different segments in terms of relative donor/acceptor configuration. Furthermore, only one of the configurations with specific fluorine atom direction contributes to the superior absorption, packing order, and charge mobility in the corresponding polymers. The unique structure–property relationships are the result of cooperative molecular arrangements of the key segment and noncovalent interactions between the fluoro atoms and the aromatic protons on the thiophene side-chains of the polymers.

### 1.3.4 Polymers towards low exciton-binding energy

The significance of developing conjugated polymers that would help build low exciton binding energy systems is doubtless. Yet, compared to conventional structural studies targeted on bandgap engineering and morphology tuning, etc., the area of dedicated research for low exciton binding energy polymers remains largely unexplored. In a practical sense, eq. (1) serves as an intuitive guide to identify design principles for polymers that may afford low $E_b$: increase the dielectric constant of the polymer as a material, and increase the hole-electron distance on the excited state. Specifically, since only one material (the polymer) is within consideration, $E_b$ herein refers to $E_b^{\text{exc}}$.

In terms of the material dielectric constant, the relevant reports are within a handful, while some of them are based on third-component doping, others on designing novel organic structures. For example, Ma et al. blended B,O-chelated azadipyrromethene with a high dielectric constant camphoric anhydride to form donor films, which show increased permittivity relative to non-doped cases.$^{76}$ Subsequent photophysical investigation suggests that the use of camphoric anhydride has likely reduced the exciton
binding energy. Another report used lithium bis(trifluoromethylsulfonyl)imide as the dopant for a polymer/PCBM blend, has lead to increased low-frequency permittivity, as well as improved charge transport and suppressed charge recombination,\textsuperscript{77} backing the positive effect of enhancing the dielectric constant of the photoactive blend.

Despite these reported successes, the use of third-component additives can possibly adversely affect the light absorption and charge mobility for obvious reasons. This makes it very important to develop organic semiconductors with intrinsic properties that may lead to low exciton binding energies. Early researchers utilized \(2-(2-(2\text{-methoxyethoxy})\text{ethoxy})\text{ethyl}\) groups to achieve this.\textsuperscript{78} In this work, Breselge \textit{et al.} replaced the methoxy group and/or the \(-\text{OC}_{10}\text{H}_{21}\) chain in MDMO-PPV with \(2-(2-(2\text{-methoxyethoxy})\text{ethoxy})\text{ethyl}\) to afford \(7a\)–\(7c\) (Figure 7(a)), achieving a dielectric constant of 4.1, 4.0 and 5.5 for \(7a\), \(7b\), and \(7c\), respectively, compared to 3.01 for MDMO-PPV. Subsequent device physics studied by Blom and coworkers\textsuperscript{79} showed that a blend of \(7b\) and a PCBM derivative exhibited an enhanced charge dissociation efficiency of 72\%, in conjunction with improved charge separation distance.

![Figure 7](image_url)

\textbf{Figure 7.} (a) Structural change on MDMO-PPV with \(2-(2-(2\text{-methoxyethoxy})\text{ethoxy})\text{ethyl}\) chains leads to new material with higher permittivity. (b) Introducing cyano groups on the end of the side chains also leads to an increase of the dielectric constant.

In a recent work, cyano groups were introduced at the end of the solubilizing side chains of PIDT-DPP-Alkyl, resulting in a dielectric constant increase from 3.9 to 5.0. Jen and coworkers found out that such a dielectric constant enhancement has led to suppressed geminate recombination, which is likely
responsible for the higher $V_{oc}$, $J_{sc}$ and FF of PIDT-DPP-CN than the alkyl counterpart.\textsuperscript{80} The other implication from eq.(1), i.e., to increase the hole-electron distance of the excited state, however, has received no dedicated attention. This thesis will exploit the possibility to increase the hole-electron distance, \textit{via} designing and synthesizing novel conjugated polymers, as will be explained in the following chapters.
1.4 Thesis outline

The scientific goal of this thesis is part of a research programme which aims at enhancing solar energy-to-electricity conversion efficiency, by using novel polymers and fullerene derivatives that would contribute to a decreased exciton-binding energy. A proper understanding of the relationship between exciton-binding energy and photovoltaic performance of molecular semiconductors is absolutely necessary, as already indicated in some of our early studies. The design of novel conjugated polymers is based on theoretical propositions on possible ways to reduce the exciton binding energy. In the meantime, we are also interested in exploring non-conventional polymerization strategies in pursuit of polymers of enhanced chemical quality.

Chapter 2 sets a goal in obtaining high-quality donor-acceptor conjugated polymers. This chapter describes a one-pot Suzuki-Miyaura homopolymerization, which involves in-situ borylation/cross coupling of dibrominated donor-acceptor conjugated macromonomers, in comparison to the standard Stille copolymerization of electron-rich dithienosilole and electron-deficient isoindigo monomers. Quantum chemical calculations and MALDI-TOF measurements are used to extract structural characteristics of these two polymers which are compared. A brief comparison of the photovoltaic performance is also conducted.

There are generally two possible strategies to reduce the exciton binding energy of a polymeric material, i.e. (i) enhance its dielectric constant with chemical modification for more effective charge screening, and (ii) consider increasing the excited-state hole-electron distance of the polymer, so as to facilitate charge separation. Chapter 3 specifically focuses on the second perspective, by investigating two-dimensional (2-D) donor-acceptor conjugated polymers. In these conjugated polymers, the acceptor moieties are configured as pendant groups of the donor backbone, via a distinct cross conjugation. We conceive that a conjugated backbone consisting of pure donor moieties introduces an enhanced delocalization of the highest occupied molecular orbital (HOMO) of the polymer, while cross-conjugated acceptors lead to a well localized lowest unoccupied molecular orbital (LUMO). Furthermore, these features might synergistically yield an increased hole-electron distance, which could result in a relatively low exciton binding energy when compared to a conjugated analogue with linear donor-acceptor (D-A) conjugation. To this end, this chapter first discusses structural optimization based on theoretical calculations on a series of monomers. In the end, we also directly compared the exciton-binding energy characteristics of a prototypical donor-acceptor cross-conjugation dimer and its linear-conjugation counterpart.

Chapter 4 attempts to lay a general ground work for the synthesis of thieno[3,4-b]thiophene-based two-dimensional donor-acceptor cross-conjugated polymers, where the acceptor units are perpendicularly attached to the thiophene-based backbone, while 2,5,8,11-tetraoxadodecyl (TEG) side-
groups are used as solubilizing chains with an additional purpose of increasing the dielectric constant of the resulting polymer. It is found that in spite of efficient chain growth, the as-presented one-pot Suzuki-Miyaura homopolymerization (context of Chapter 2) persistently introduces unassignable impurities to the polymer (P1). Although an exact explanation is not pursued, it is hypothesized that the oxygen atoms in the TEG chains chelate the boron atoms in the system of Suzuki-Miyaura homopolymerization. This hypothesis is supported by an experiment with a control polymer (P2) where alkyl chains were employed as solubilizing side chains, where the problem with P1 was well eliminated, as evidenced by our mass spectra analysis. Stille copolymerization is used to yield the desired 2-D conjugated polymer (CC1). The present work hints to important aspects of bis(pinacolato)diboron-promoted homopolymerization regarding its potential drawbacks, which might limit its application scope

The previous chapters have paved the way for the synthesis of a 2-D polymer featuring a distinct cross conjugation between the thiene[2,3-c]pyrrole-4,6-dione acceptor and the thieno[3,4-b]thiophene donor moieties, with thiophene spacers in the backbone. This enabled us to actually study the influence of donor-acceptor cross conjugation on the exciton-binding energy characteristics of conjugated polymers. Chapter 5 describes a combined device physics and quantum chemical study of such a 2-D polymer, with a special focus on exciton binding energy. Preliminary evaluation of the external quantum efficiency of this polymer (CC1) suggested, to our surprise, that the exciton binding energy is unambiguously higher than that of the typical linearly-conjugated polymers. This experimental observation is supported by extensive quantum chemical calculations on a series of cross- and linear-conjugated dimers. Furthermore, quantum chemical calculations suggest that the higher exciton binding energy of cross-conjugated polymers is most likely related to strong electron localization in their excited state, leading to a shorter hole-electron distance.
1.5 References


Chapter 2

High-quality conjugated polymers via one-pot Suzuki-Miyaura homopolymerization*

ABSTRACT This chapter describes a one-pot Suzuki-Miyaura homopolymerization that involves in-situ borylation/cross coupling of dibrominated donor-acceptor conjugated macromonomers, in contrast to the standard Stille copolymerization of dithienosilole and isoindigo monomers. Reaction kinetics investigation reveals that bis(pinacolato)diboron promotes an efficient polymerization. The homopolymer showed blue-shifted absorption compared to the Stille copolymer, which is rationalized by quantum chemical calculations of a series of oligomers containing various donor-acceptor configurations. The calculations suggest that the homopolymerization of asymmetrical macromonomers likely introduced both acceptor-acceptor and donor-donor segments into the backbone. The acceptor-acceptor segment is found to contribute mostly to the blue-shift of the maximum absorption wavelength. Furthermore, detailed analysis of MALDI-TOF (matrix-assisted laser-desorption ionization-time of flight) spectra of these two polymers indicated that while the homopolymer is well defined, the Stille copolymer is end-capped mostly with the dithienosilole moieties and/or methyl groups, implicating that destannylation and methyl transfer are the most-likely chain-termination pathways that limit high molecular weight. This is in sharp contrast to the homopolymerization, where chain-terminators are required to control the molecular weight for obtaining soluble material. The photovoltaic performance of bulk-heterojunction solar cells based on these polymers is compared.

2.1 Introduction

The Stille cross-coupling promoted copolymerization has been the method of choice for the development of donor-acceptor alternating conjugated polymers for a host of applications such as polymer solar cells, polymer light-emitting diodes, thin-film transistors and even polymer-based sensors. Such popularity is largely due to its remarkable tolerance for many functional groups, which enables the design of a variety of functional polymers. Yet, the convenience of Stille cross-coupled polymerization comes at a cost in terms of the unavoidable toxicity and the difficulty to purify the organostannanes that are necessary to achieve high molecular weights, as well as possible synthetic complications due to tin-tin homocouplings when certain catalysts and/or organostannanes are used. These drawbacks may pose limitations on the molecular weights and structural integrity of the resulting polymers. In this sense, a number of researches has set out to reach better copolymers from Stille copolymerization. Results suggest that high molecular weight, low polydispersity and better structure integrity can contribute to enhanced light absorption and improved morphology, which translate to better overall device performance.

Along with the popularity of the Stille cross-coupled copolymerization, the Suzuki cross-coupling has been widely used to synthesize high molecular weight copolymers. However, the monomer scope of Suzuki copolymerization is primarily limited to electron-neutral / mildly electron-rich building blocks such as carbazoles and fluorenes, which is probably due to the tendency towards deborylation of the boronic acid/esters of such moieties. These challenges highlight the significance of developing one-pot reactions that eliminate the necessity to acquire purified boronic acid/ester. To this end, a handful of researches have investigated the scope of one-pot synthesis of biaryls in terms of catalyst, base and aryl halides. Early discoveries have shown that bis(pinacolato)diboron could be used as a condensation reagent for the one-pot synthesis of low to moderate molecular weight poly(arylene)s, and that certain bases such as K$_2$CO$_3$ may lead to oligomer formation in biaryl formation systems. In 2009, Reynold et al. revisited this synthetic pathway and specifically studied the effect of CsF on the homopolymerization of fluorenes. Furthermore, with one of our earlier contributions, it has been shown that with symmetrical model systems, in-situ borylation/cross-coupling demonstrates a general superiority over the Stille copolymerization in terms of end-group control.

In this work, we further develop the chemistry of one-pot borylation/cross-coupling polymerization. Instead of employing simple, head-to-tail symmetrical, relatively electron-neutral monomers, we constructed a head-to-tail non-symmetrical donor-acceptor conjugated macromonomer that was subjected to homopolymerization. Particularly, we compare the as-obtained homopolymer with a copolymerized counterpart synthesized from the standard Stille cross-coupling, in terms of the optoelectronic properties and structural integrity.
2.2 Results and discussion

2.2.1 Synthesis of polymers

Scheme 1. Synthesis of polymers. Reagents: (i) \(\text{Pd}_2(\text{dba})_3\) (CHCl\(_3\) adduct, recrystallized from acetone), P(o-tol), toluene; (ii) 3, \(\text{Pd}_2(\text{dba})_3\) (CHCl\(_3\) adduct), P(o-tol), toluene; (iii) NBS, THF; (iv) bis(pinacolato)diboron, K\(_3\)PO\(_4\), \(\text{Pd(dppf)Cl}_2\) (CH\(_2\)Cl\(_2\) adduct), toluene/DMF (v/v = 4/1). P-Stille refers to the polymer obtained from a standard Stille copolymerization, while P-BiPi is the polymer synthesized with the BiPi promoted polycondensation. BiPi means bis(pinacolato)diboron.

Scheme 1 presents the synthesis of the two polymers P-Stille and P-BiPi, where P-Stille is the copolymerization result of the dibrominated compound 1 and the distannyl dithienosilole 2 and P-BiPi is the polymer obtained by the homopolymerization method. The obtainable molecular weight of the P-Stille product is maximized by gently refluxing the polymerization mixture for 24 h, giving a \(M_n\) and \(M_w\) of 11 and 16 KDa \((D = 1.45)\), respectively. On the other hand, after a successful synthesis of the dibrominated macromonomer 5, an initial attempt to homopolymerize this macromonomer 5 overnight at 100 °C led to a 97% yield of an intractable black solid, which could either be due to cross-linking or a very high molecular weight. The possibility of cross-linking under the given conditions was readily excluded with the high purity of 5 determined from its HPLC absorption trace (Figure 1), excluding significant over-bromination of compound 4. Furthermore, infrared spectroscopy measurements of 5 and the insoluble material showed overlapping spectra (Figure 2), unambiguously indicating that the intractable material comprises ultra-high molecular weight polymer chains, based on macromonomer 5. These observations underscore the capacity of the \textit{in-situ} borylation/cross coupling route to yield high molecular weight polymeric materials.
Figure 1. (a) $^1$H NMR spectrum of the macromonomer which was used for the one-pot polymerization. Peaks of hydrogen atoms attached to aromatic carbon atoms are numbered and assigned. (b) HPLC trace @ 360 nm of the same macromonomer measured in toluene. This trace is indicative of the purity of the macromonomer.

Figure 2. FT-IR spectra of the macromonomer 5 and the intractable black powder obtained from the initial polymerization attempt, as described in the manuscript. This comparison confirms the pure organic nature of the insoluble material, as well as the fact that the insoluble material is of the same chemical structure as the monomer.
To better control the molecular weight, we further studied the kinetics of this specific homopolymerization by monitoring the molecular weight and light absorption changes over time, as shown in Figure 3(a). It can be seen that the polymerization was notably fast, with the absorption saturating ~ 4 h after the reaction was started at room temperature. The consecutively red-shifting absorptions suggest a continuous growth of the polymer chains. This observation is further correlated with the GPC results shown in Figure 3(b), which indicate that polymers with $M_n = 9.3$ KDa are obtained after a reaction period of 4.5 h. Further prolonging the reaction time quickly led to insoluble product. Moreover, Figure 3(b) shows a strong attenuation in the growth of the molecular weight over time (and over the conversion of monomers). Additionally, the fact that P-BiPi becomes completely intractable in a small time window after the initial polymerization period hints to cross coupling of long oligomers, leading to long and insoluble polymer chains that precipitate. The kinetic study suggests that with the specific macromonomer, the one-pot SM polymerization yields molecular weights comparable to that of the standard Stille copolymerization. Since molecular weight is not our pursuit within the current chemical investigation, no further optimization on molecular weights was conducted. Note that the above analysis does not provide direct insight into the polymerization mechanism (step-growth or chain-growth), but a highly efficient polymerization of dibrominated donor-acceptor macromonomers is indeed observed. In terms of controlling the molecular weight, an efficient way is to pre-mix chain-terminators with the starting materials at the very beginning, such that part of the bifunctional monomers will be partially deactivated towards further reaction. Indeed, when using compound 4 as the chain-terminator for reaction (iv), we were able to isolate CHCl$_3$-soluble polymers with a yield of 70%. Compound 4 was chosen as the chain-terminator because it shows the same reactivity as the macromonomer, ensuring a proper and efficient chain termination. The molecular weight of the polymer is limited by the chain terminator, which is reflected by increased product solubility in our case. An initial attempt of adding 5% of chain terminator (molar percentage relative to macromonomer) did not allow a satisfactory isolation of CHCl$_3$-soluble polymers, even when the reaction time was limited. Isolation of soluble polymers was possible when the chain terminator percentage was increased to ~10%.
Figure 3. (a) Normalized UV-vis absorptions and (b) molecular weight changes over time for the homopolymerization. The black bar in (b) means the reaction product has already become intractable.

Figure 4. UV-Vis absorption spectra of the Stille copolymer P-Stille and Suzuki-Miyaura homopolymer P-BiPi.
2.2.2 Optoelectronic properties

With the insights obtained from the kinetic study, we were able to synthesize soluble polymeric materials for characterization. We first measured the UV-vis absorption spectra of polymers P-Stille and P-BiPi in chloroform, as shown in Figure 4. Interestingly, while the cut-off wavelengths of the two absorptions are close, there is a 75 nm blue shift of the maximum absorption wavelength from P-Stille (737 nm) to P-BiPi (662 nm). P-BiPi also showed apparently enhanced absorption of high energy photons (an absorption band peaking around 410 nm) compared to P-Stille. These observations indicate a significant structural difference between P-Stille and P-BiPi. Considering the fact that both the Miyarau and Suzuki catalytic cycles involve oxidative insertion as the first step, which preferably takes place on the isoindigo end due to its electron deficiency, this structural difference is most likely related to the cross coupling of two isoindigo ends (forming an A-A segment). The resulting oligomers ending with donor moieties may then lead to donor-donor cross-couplings (forming a D-D segment), in addition to the normal donor-acceptor cross-coupling (forming a D-A segment).

To understand the structural origin of these absorption features, we considered a series of oligomers containing different conjugation segments, and calculated their absorption characteristics by time-dependent DFT (TD-DFT). We first calculated the absorption bands of DADA, DAAD and ADDA segments. These results are shown in Figure 5. It is clear that an ADDA fragment enables the absorption of low-energy photons, while a DAAD fragment absorbs the higher energy photons more amongst these three oligomers. We note that these three dimers were minimized in a coplanar conformation. In this sense, the calculated absorptions of these dimers are fairly qualitative. Nevertheless, the assessment between theory and measurement suggests that the existence of DAAD segments in the backbone will promote the absorption of high-energy photons, which is in accord with the observation shown in Figure 3. This phenomenon is also present in the calculated absorption bands of DADADADA and ADDAADDADA tetramers, the latter of which contains both AA and DD segments (Figure 6). On the basis of these observations, we further calculated the electronic transitions of the ADDAADDADA DA-tetramer, for which an absorption spectrum was calculated as shown in Figure 6(B). Despite the differences, it is clear that the calculated spectrum tends to replicate the absorption peaks of the experimental counterpart. This result provides indirect evidence that the as-presented in-situ borylation/cross coupling polymerization has introduced DD, AA and DA segments into the backbone, probably in a random pattern.
Figure 5. Calculated absorption bands of a series of dimers in the case of P-BiPi.

Figure 6. (A) Calculated absorption bands of two planarized DA-tetramers, DADADADA and ADDAADDA. (B) A comparison of the calculated absorption spectrum of a ADDAADDA tetramer, and the measured absorption spectra of the P-BiPi.
These random donor-acceptor configurational patterns introduce structural disorder in the backbone of homopolymerized P-BiPi, which is further reflected in several optoelectronic properties of the material. For example, as shown in Figure 7(a), while the Stille copolymer P-Stille shows a Stokes shift of 0.18 eV in chloroform solution, the Stokes shift of the homopolymer P-BiPi is notably increased to 0.35 eV. As noted by several authors, this might indicate that the structural disorder gives rise to a broader density of states, with emission occurring after relaxation towards low energy sites. Moreover, as seen in Figure 7(b), while P-Stille clearly showed a mono-exponential photoluminescence decay with a fitted excitonic lifetime of 313 ps, the photoluminescence decay of P-BiPi is bimodal exponential, suggesting a multi-pathway decay with lifetimes of 41 ps and 5 ps. Although the detailed mechanism of this phenomenon is beyond the scope of this work, these observations seem to suggest that the existence of AA and/or DD segments in conjugated polymers adversely affects exciton lifetimes, and may also lead to significant fluorescence quenching as shown by the photoluminescence intensities in Figure 7(B).

![Figure 7](image_url)

**Figure 7.** (a) Normalized absorption (black lines) and emission (red lines) spectra of P-Stille and P-BiPi measured in chloroform. (b) Photoluminescence spectra of P-Stille and P-BiPi in CHCl₃ solutions. The red lines are mono-exponential (P-Stille) or bimodal-exponential (P-BiPi) fits.
2.2.3 Mass spectrometry

MALDI-TOF has been widely applied to polymers both with saturated backbones and with conjugated backbones, to infer structural information \cite{28,29,30}. Due to the soft-ionization nature of MALDI-TOF, the chemical composition of the polymers remains largely intact (absent of fragmentation). Therefore, given preliminary structural information and proper sample preparations, the analysis of MALDI-TOF spectra can be straightforward and reliable, although it does not give adequate quantitative information regarding the average molecular weight of the polymer sample.

Figure 8. (A) Comparison of the MALDI-TOF spectra of P-Stille and P-BiPi. Peaks of interest are marked with numbers. Peaks 1–4 (peak-to-peak interval: 900 Da) of polymer P-BiPi correspond to dimer to pentamer with hydrogen end groups as the homopolymerization result. Peaks 5, 7, 9 of polymer P-Stille correspond to peaks 2–4 of P-BiPi. The peak-to-peak interval of 5-to-6, 7-to-8 and 9-to-10 is 416, which indicates the presence of an extra donor moiety in the backbone. Other peaks are not convincingly assignable. Dithranol is used as the matrix for both spectra. (B) A zoom-in of peaks 2 and 5. The zoom-in reveals that in the case of the Stille copolymerization, there are peaks representing polymers+methyl group. This is mostly likely due to methyl transfer from the trimethyltin monomer. Residual bromo end groups are visible.
The MALDI-TOF spectra of P-Stille and P-BiPi are shown in Figure 8. Note that due to the relatively poor solubility of P-BiPi in CHCl₃, the hexane fraction instead of the CHCl₃ fraction of the homopolymerization product was used to maintain a sufficient concentration at room temperature. As seen in Figure 8(A), the in-situ borylation/cross coupling polymerization yielded samples showing a clean repetition of peaks, with a repetition interval of 900 Da, in accord with the mass of a D-A repeating unit. Additionally, no obvious residual Br or boronic ester end groups were observed in the case of P-BiPi. This is most likely due to the fact that a H-capped chain terminator (compound 4 in Scheme 1) was used. There are some side-peaks which are of slightly higher m/z values following the major peaks, as shown in Figure 8(B). One of them might be a polymer chain with hydroxyl groups transferred from the dithranol matrix. The structural origin of the other lower peaks is not clear.

In contrast to the clean and simple mass spectrum of P-BiPi, a very different scenario was recorded for the Stille-copolymerized P-Stille. Although well-defined repetitions are found for all major peaks, only some of them can be sensibly assigned to corresponding structures. As shown in Figure 8(A), oligomeric molecules of the same chemical composition can be found for P-Stille and P-BiPi. Yet, it is interesting to notice that compared to the dihydro-terminated oligomers based on the same number of donor and acceptor moieties (as defined by the P-BiPi spectrum of Figure 8(A)), all peaks with the highest intensity in the P-Stille spectrum are 416 Da (mass of a repeating donor moiety) higher (5 → 6, 7 → 8, and 9 → 10). This indicates two possibilities: (i) a majority of the resulted polymerized molecules are ended with a donor moiety; (ii) this extra donor moiety is incorporated into the backbone through tin-tin homocoupling. Since the spectrum is free of polymer chains with trimethyltin end groups, the first possibility further implies that destannylation behaves as a major pathway for chain termination, impeding further chain growth. The origin of destannylation was not investigated specifically, but we hypothesize that destannylation is more likely to occur when electron-rich heteroarylstannanes are involved. Destannylation as a side reaction is expected to imbalance the stoichiometry of the original monomer ratio, leading to polymer chains with residual reactive Br end groups, which are clearly visible in the MALDI-TOF spectrum. Although homocoupling of organostannanes in conjugated polymer formation has been highlighted elsewhere, we did not have a direct observation in our case. We note that homocoupling of organostannanes should not be a noticeable problem in this case, primarily owing to the usage of a Pd(0) instead of a Pd(II) catalyst. Upon zooming in peaks 2 and 5, methyl transfer from trimethyltin is evidenced with a clear peak, as shown in Figure 8(B). This highlights the drawbacks of routine Stille copolymerizations that potentially hinder the achievement of high quality conjugated polymers. Future synthetic effort should be dedicated to diminish these structural flaws.
2.2.4 Photovoltaic characterizations

**Figure 9.** Current–Voltage curves of the P-Stille and P-BiPi-based bulk heterojunction solar cells with DIO additive, under AM1.5 solar illuminations.

The photovoltaic performance of these two polymers was compared by fabricating bulk heterojunction solar cells under the same conditions, with a device structure of ITO/PEDOT:PSS/polymer:[60]PCBM/LiF/Al. AFM pictures (Figure 10) of the active layer indicate that both polymers can be mixed with [60]PCBM without noticeable phase separation, though P-Stille seems to be slightly aggregated in the blend. Despite the better chemical integrity of the homopolymerized P-BiPi, the random donor-acceptor configuration has notably reduced the absorption of the incoming light spectrum, which is indicated by the drastically lower molar extinction coefficient per repeating unit for P-BiPi than for P-Stille, from 550 nm on (Figure 11). We believe this is largely responsible for its lower photocurrent of 1.08 mA cm$^{-2}$, compared to the 3.34 mA cm$^{-2}$ of the P-Stille device, as shown in Figure 9. The random donor-acceptor configurations in P-BiPi likely impair effective intermolecular packing, resulting in a lower hole mobility of 5×10$^{-8}$ cm$^2$V$^{-1}$s$^{-1}$, compared to that of 6×10$^{-6}$ cm$^2$V$^{-1}$s$^{-1}$ in the P-Stille case, as measured by space charge limited current measurements (Figure 12). Note that the studied polymers were not optimized for high mobility, as it is well-known that a variety of structural variations may pose notable effects on this physical parameter. While the present research demonstrates the capacity of one-pot homopolymerization in producing polymers of enhanced chemical integrity, its translation into improved physical characteristics should be achieved in conjunction with dedicated consideration of physical aspects. Overall, with a low photovoltage of 0.6 V and fill factor of 29%, the P-BiPi-based device showed a power conversion efficiency of 0.99%, while P-Stille generated a power conversion efficiency of 1.66% with a photovoltage of 0.79 V and a fill factor of 44%.
Figure 10. AFM height images of thin films of polymer:[60]PCBM blends for P-Stille (left) and P-BiPi (right).

Figure 11. Comparison of the molar extinction coefficients of P-BiPi and P-Stille per repeating unit. The measurements were conducted on CHCl₃ solutions at 2.9 and 3.2 μg/mL for P-BiPi and P-Stille, respectively. The molar extinction coefficients per repeating unit were calculated using these mass concentrations, the molar mass of repeating units, and the measured absorbance. It is clear that P-Stille exhibits a much higher absorptivity from 550 nm on.
Figure 12. $J$–$V$ curves of the space-charge limited current (SCLC) devices for measuring the hole mobility of P-BiPi and P-Stille. The data were fitted to the modified Mott–Gurney equation:\textsuperscript{33}

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu_0 n \exp \left( 0.891 y_n \sqrt{\frac{V_{\text{int}}}{L}} \right) \frac{V_{\text{int}}^2}{L^3}$$

where $J$ is the SCL current density, $\epsilon_0$ and $\epsilon_r$ are the electric permittivity of free space and the relative dielectric constant of the active layer respectively, $\mu_0 n$ is the charge carrier mobility, $L$ is the thickness of the device and $y_n$ is the electric field-activation factor. The voltage on the active layer, $V_{\text{int}}$, is given by $V_{\text{int}} = V - V_{\text{bi}} - V_{rs}$, where $V$ is the applied voltage, $V_{\text{bi}}$ the built-in voltage and $V_{rs}$ is the voltage drop due to the series resistance of the contacts.
2.3 Conclusions

In conclusion, we have extended the concept of homopolymerization based on *in-situ* borylation/cross-coupling. This polymerization route is appealing in the sense that it not only completely eliminates the necessity to synthesize high-purity boron agents, but also can potentially produce high molecular weight polymeric materials through efficient polymerization, which is evidenced by our kinetic investigation. Yet, when applied to head-to-tail asymmetrical donor-acceptor macromonomers rather than simple, symmetrical monomers, such homopolymerizations tend to introduce donor-donor and acceptor-acceptor segments into the polymer backbone, apart from the expected alternating donor-acceptor structure. This type of structural complication was shown to occur in the homopolymerization by correlating the experimental UV-vis absorptions with calculated absorptions from TD-DFT. Nevertheless, MALDI-TOF measurements showed the capacity of this homopolymerization in producing polymers with improved structural integrity compared to the standard Stille copolymerization which suffers from destannylation and/or methyl transfer, affording moderate molecular weights even with prolonged reaction time. This work is to lead to new strategies for the synthesis of high-quality donor-acceptor conjugated polymers, which shall feature improved chemical integrity and high molecular weights.
2.4 Experimental

General
All reagents and solvents were purchased from commercial sources and were used without further purification unless indicated otherwise. UV/Vis measurements were carried out on a Perkin Elmer Lambda 9000 spectrometer in 1-cm quartz cuvettes with concentrations of 0.03–0.1 mg/mL in CHCl₃. MALDI-TOF spectra were taken on a Biosystems Voyager apparatus. Samples were prepared by mixing the matrix (~10 mg/mL in THF) and polymer sample (~1 mg/mL in THF or CHCl₃) at room temperature in a 3:1 volume ratio. All measurements were performed in positive ion mode. NMR spectra were measured using a Varian AMX400 (400 MHz) instrument at 25 °C. FT-IR spectra were recorded on a Nicolet Nexus FT-IR fitted with a Thermo Scientific Smart iTR sampler. GPC measurements were done on a Spectra Physics AS 1000 series machine equipped with a Viskotek H-502 viscometer and a Shodex RI-71 refractive index detector. The columns (PLGel 5m mixed-C) (Polymer Laboratories) were calibrated using narrow disperse polystyrene standards (Polymer Laboratories). Samples were made in CHCl₃ at a concentration of 2–3 mg/mL.

Synthesis
Compounds 1, 34 2 and 3 35,36 were synthesized according to literature methods. The dithienosilole precursors for 2 and 3 were synthesized with a modified procedure based on a literature method.36 The synthetic steps towards the two polymers are shown in Scheme 1.

P-Stille. A 25 mL, flame-dried two neck flask, filled with dry N₂, was charged with 1 (100 mg, 0.155 mmol) and 2 (118 mg, 0.16 mmol), followed by the addition of Pd₂(dba)₃ (CHCl₃ adduct, recrystallized from acetone) (4 mg), P(o-tol)₃ (16 mg). Degassed dry toluene was then introduced into the reaction flask via a cannula. The reaction was then set at 100 °C for 24 h. Afterwards, the reaction mixture was allowed to cool to room temperature, and added dropwise into 500 mL of methanol. The precipitate was collected with a cellulose thimble, which was then subjected to Soxhlet extraction with methanol for 24 h, acetone for 7 h, hexane for 5 h, and CHCl₃ for 3 h, subsequently. The chloroform fraction was obtained as a purple-blue solid after precipitation in methanol (128 mg, ~85%). ¹H NMR (400 MHz, CDCl₃) δ 9.08 (2 H, br), 7.54 (1 H, br), 7.43 (1 H, br), 6.51 (1 H, br), 3.74 (4 H, br), 2.94 (1 H, br), 1.22 (34 H, br), 0.79 (30 H, br). IR (cm⁻¹): 2954, 2920, 2853, 1689, 1608, 1453, 1376, 1352, 1170, 1102, 1073, 1013, 874, 817, 739.

Compound 4. A 50 mL, flame-dried three neck flask, filled with dry N₂, was charged with 1 (500 mg, 0.776 mmol) and 3 (480 mg, 0.83 mmol), followed by the addition of Pd(PPh₃)₄ (45 mg). Degassed dry toluene was then introduced into the reaction flask via a cannula. The reaction was then stirred at 100 °C overnight. After cooling to room temperature, most of the solvent of the resulting mixture was removed under reduced pressure. The resulting purple oil was subjected to silica gel chromatography with toluene/hexanes (v/v = 1/3) as the eluent. Compound 4 was obtained as a purple oil (450 mg, 60%
yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.13 ($d, J = 8$ Hz, 1 H), 9.02 ($d, J = 8$ Hz, 1 H), 7.40 (s, 1 H), 7.27 ($dd, J = 8$ Hz, 1 H), 7.17 ($dd, J = 8$ Hz, 1 H), 7.08 ($d, J = 4$ Hz, 1 H), 6.92 ($d, J = 1$ H), 6.86 ($d, J = 1$ H), 3.62 ($m, 4$ H), 1.84 ($m, 2$ H), 1.35 ($m, 20$ H), 1.18 ($m, 10$ H), 0.93 ($m, 20$ H), 0.80 ($m, 12$ H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 168.59, 168.20, 149.84, 148.59, 145.94, 145.79, 144.51, 144.38, 143.31, 138.71, 133.19, 130.61, 130.55, 130.44, 130.01, 127.38, 126.12, 125.82, 124.85, 120.65, 120.35, 118.83, 111.30, 104.62, 44.30, 44.10, 37.77, 37.45, 35.92, 35.64, 30.81, 30.59, 28.87, 28.60, 24.28, 24.00, 22.97, 17.63, 14.17, 10.82.

**Compound 5.** A 50 mL round-bottom flask was charged with 4 (320 mg, 0.33 mmol) and THF (20 mL). NBS (70.5 mg, 0.396 mmol) was added all at once. After 2h, the product mixture was extracted with diethyl ether, and the organic phase was collected and dried under reduced pressure. The resulting purple oil was subjected to silica gel chromatography with toluene/hexanes (v/v = 1/3) as the eluent, yielding 245 mg of 5 (70% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.14 ($d, J = 8$ Hz, 1 H), 9.03 ($d, J = 8$ Hz, 1 H), 7.37 (s, 1 H), 7.26 ($dd, J = 8$ Hz, 1 H), 7.16 ($dd, J = 8$ Hz, 1 H), 7.03 (s, 1 H), 6.93 ($d, J = 1$ H), 6.89 ($d, J = 1$ H), 3.64 ($m, 4$ H), 1.85 ($m, 2$ H), 1.37 ($m, 24$ H), 1.17 ($m, 10$ H), 0.96 ($m, 16$ H), 0.79 ($m, 12$ H).

**Reaction for P-BiPi kinetics.** A 50 mL, flame-dried two neck flask, filled with dry N$_2$, was charged with 5 (80 mg, 0.0755 mmol) and then Pd(dppf)Cl$_2$ (CH$_2$Cl$_2$ adduct) (5 mg), K$_3$PO$_4$ (64 mg) and bis(pinacolato)diboron (19 mg, 0.0775 mmol). Degassed toluene/DMF (v/v = 4/1) (15 mL) was introduced into the reaction flask via a cannula. The reaction was set at 80 °C. A sample of ~1 mL was taken from the reaction flask at given time spots for UV-vis and GPC measurements.

**P-BiPi.** A 25 mL, flame-dried two neck flask, filled with dry N$_2$, was charged with 4 (11 mg, 0.0113 mmol), 5 (100 mg, 0.0943 mmol) and then Pd(dppf)Cl$_2$ (CH$_2$Cl$_2$ adduct) (4 mg), K$_3$PO$_4$ (80 mg) and bis(pinacolato)diboron (25 mg). Degassed toluene/DMF (v/v = 4/1) (10 mL) was introduced into the reaction flask via a cannula. The reaction was set at 80 °C overnight. Afterwards, the reaction mixture was cooled to room temperature, and added dropwise into 500 mL of methanol. The precipitate was collected with a cellulose thimble, which was subjected to Soxhlet extraction with methanol for 24 h, acetone for 7 h, hexane for 5 h, and CHCl$_3$ for 5 h, respectively. The chloroform fraction was obtained as a purple-blue solid after precipitation in methanol (70 mg, ~70%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.22 (1 H, br), 9.19 (1 H, br), 7.41 (1 H, br), 7.31 (2 H, br), 7.03 (1 H, br), 7.00 (2 H, br), 3.74 (4 H, br), 1.93 (2 H, br), 1.25 (34 H, br), 0.83 (28 H, br). IR (cm$^{-1}$): 2954, 2920, 2853, 1689, 1608, 1453, 1376, 1352, 1170, 1102, 1073, 874, 817, 739.

**Density functional theory calculations.** Geometries of dimers (DAAD, DADA and ADDA) and tetramers (DADADADA and ADDAADDA) were optimized using Density Functional Theory (DFT) (B3LYP/6-311G*) with ORCA$^7$ without any symmetry constraints. Subsequently, the vertical excitation energies were calculated using time-dependent DFT (TD-DFT) (B3LYP/6-311G*). The lowest 10 excited states were calculated for the tetramers.
**Photoluminescence measurements.** Photoluminescence measurements were carried out on solutions contained in quartz cuvettes (2 mm path length) in transmission mode. The excitation source was the second harmonic (approximately 400 nm) of a mode-locked Ti:Sapphire laser (Mira 900, Coherent) delivering 150 ps pulses at a repetition rate of 76 MHz. The laser power was adjusted using neutral density filters; and the excitation beam was spatially limited by an iris. The beam was focused with a 150 mm focal length lens onto a spot of approximately 50 µM. Steady state spectra were collected into a spectrometer with a grating of 50 lines/mm and recorded with an em-CCD array (Hamamatsu, ImagEM) sensitive between 400 nm and 900 µm. For time resolved measurements, the same pulsed excitation source was used. Spectra were collected on a Hamamatsu streak camera (Hamamatsu, Japan) working in Synchroscan mode (time resolution ~ 2ps) with a cathode sensitive in the visible. All spectra were corrected for the spectral response of the setup using a calibrated lamp.

**Solar Cell Device Fabrications and Measurements.** Indium tin oxide (ITO) coated glass substrates were precleaned with deionized water, CMOS grade acetone, and then isopropanol, each for 15 min. Possible organic residues were removed by UV-ozone cleaning for 20 min. A layer of PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate), VP Al4083, H. C. Stark) (thickness ~ 60 nm) was spin-cast on top at 1500 rpm for 50 s. After being baked at 140 °C for ~10 min, the substrates were transferred into a nitrogen-filled glovebox (<0.1 ppm of O₂ and H₂O). Atop that, active layers of polymer:[60]PCBM (99.5%, Solenne B.V.) (D/A weight ratio = 1:4) were spin-coated in a N₂-filled glovebox from o-DCB solution with 3% (v/v) 1,8-diiodooctane (DIO, Sigma Aldrich) at 600 rpm for 5 s and 400 rpm for 120 s. The donor-to-acceptor total concentration was 30 mg/mL. The thickness of the photoactive layers was about 100 nm. Finally, LiF/Al (1 nm and 100 nm, respectively) were thermally evaporated at a pressure of < 10⁻⁶ Torr on top of the organic layer to make the sandwiched structure ITO/PEDOT:PSS/active layer/LiF/Al. The active area of the device was 0.04 cm². The current–voltage characteristics of all solar cell devices were measured with a Keithley 2400 source meter and were conducted in a nitrogen-filled glovebox. An AM 1.5G solar simulator (AAA grade, XES-70S1) was used as the light source. The light intensity of the solar simulator was calibrated to be 100 mW/cm² (at the position of sample) using a standard silicon reference solar cell (area 20 × 20 mm², the certification of the reference cell is accredited by NIST to the ISO-17025 standard). Hole-only devices were fabricated on bare glass substrates which were carefully cleaned by washing with detergent solution and ultrasonication in acetone and isopropyl alcohol, followed by UV-ozone treatment. A Cr(1 nm)/Au(30 nm) anode was then thermally evaporated onto the substrate, followed by the coating of a 60-nm thick film of PEDOT-PSS. The film was then baked at 120 °C for 10 min. Subsequently, polymer:fullerene blends were deposited by spin-coating from o-dichlorobenzene solutions under N₂. The hole-only devices were finished by thermal evaporation of a Pd(20 nm)/Au(80 nm) top contact.
2.5 References

Chapter 3

Theoretical evaluation of the influence of donor-acceptor cross-conjugation on the exciton binding energy of conjugated polymers

ABSTRACT There are generally two possible strategies to reduce the exciton binding energy of a polymeric material, i.e. (i) enhance its dielectric constant with chemical modification for more effective charge screening, and (ii) consider increasing the excited-state hole-electron distance of the polymer, so as to facilitate charge separation. This chapter specifically focuses on the second perspective, by investigating two-dimensional (2-D) donor-acceptor conjugated polymers. In these conjugated polymers, the acceptor moieties are configured as pendant groups of the donor backbone, via a distinct cross conjugation. We conceive that a conjugated backbone consisting of pure donor moieties introduces an enhanced delocalization of the highest occupied molecular orbital (HOMO) of the polymer, while cross-conjugated acceptors lead to a well localized lowest unoccupied molecular orbital (LUMO). Furthermore, these features might synergistically yield an increased hole-electron distance, which could result in a relatively low exciton binding energy when compared to a conjugated analogue with linear donor-acceptor (D-A) conjugation. To this end, this chapter first discusses structural optimization based on theoretical calculations on a series of monomers. A chosen structure is then subjected to a preliminary evaluation of the exciton binding energy.
3.1 Introduction

3.1.1 Motivation

Bulk-heterojunction polymer solar cells currently receive intensive research interest in the new energy field. The past decade has witnessed encouraging performance progress, thanks to the tremendous effort devoted to optimizing the electronic structures of photoactive materials, and controlling the morphology of the photoactive blend. Further performance improvement, however, has been proven to be challenging. A recent simulation study revealed that by lowering the exciton binding energy ($E_b$), it is possible to bring the solar cell efficiency to a new regime.\(^1\) The exciton-binding energy is the minimum energy required to split an exciton, \textit{i.e.} a bound hole-electron pair, which is formed within a molecule or a fragment of a polymer chain upon photon excitation. While the exact formula towards $E_b$ is under discussion,\(^2\) $E_b$ has been described by some researchers as the Coulombic attraction between two charges in a dielectric medium with a relative permittivity $\varepsilon_r$:\(^3,4\)

$$E_b = \frac{e^2}{4\pi\varepsilon_r\varepsilon_0 r} \quad (1)$$

wherein $e$ is the elementary charge, $\varepsilon_0$ is the permittivity of vacuum, and $r$ is the hole-electron distance. Obviously, increasing the dielectric constant of the photoactive blend favors the dissociation of the bound hole-electron pair into free charges, which may be further translated into enhanced solar cell performance.\(^5\) Herein, we explore the possibilities to reduce the exciton binding energy by introducing an increased hole-electron distance ($r$) for conjugated polymers. As intuitively indicated by eq (1), increasing $r$ has exactly the same influence on $E_b$. To achieve this, we hypothesize to design the donor-acceptor conjugated polymer in such a way, that (i) it constructs the linear-conjugated polymer backbone with solely donor moieties, and (ii) it installs the acceptor moiety as the pendant groups on the donor backbone. With this donor-acceptor configuration, it is expected that the HOMO of the polymer would be delocalized along an extended part of the chain, enabling a chain-like behavior for the hole. On the other hand, the electron part of the exciton is localized on the electron-withdrawing moiety, which may allow readily transfer it to electron acceptors such as fullerenes given a proper energy alignment. Because of the chain-like feature of the hole and a localized electron, we may anticipate an increased hole-electron distance.

The current chapter particularly provides a quantum chemical point of view, with an attempt to validate the feasibility of reducing exciton-binding energy with an increased hole-electron distance. We conduct quantum chemical calculations on specifically designed cross-conjugated donor-acceptor monomeric structures for the analysis of structure-dependent frontier orbitals, polarizabilities, as well as exciton binding energies.
3.1.2 Two-Dimensional donor-acceptor conjugated polymers

Conjugated polymers for optoelectronic purposes, featuring pendant conjugated moieties in general, are not a new perspective. Though relatively limited in examples, previous studies highlight the significance of molecular engineering in organic photovoltaics (OPV).

**Figure 1.** A collection of selected structures with distinct two-dimensional conjugations. \( m \) and \( n \) in the structures are numbers between 0 and 1 (For details, please refer to the specific citations). Notice that pendant attachments to the electron-rich backbone could either be electron-donating or electron-withdrawing.

Figure 1 presents some representative structures. Polythiophenes with pendant high-electron-affinity functional groups have been used as active materials in electrochemical capacitors since the 1980s, thanks to their decent dopability.\(^6\)\(^7\) Such polymers (1 in Figure 1) showed that nitrobenzene units act as traps for electrons at the excited state, delaying the recombination of charge carriers. By installing vinylthienyl groups on the 3-positions of the backbone thiophene units (2 in Figure 1), enhanced light absorption in the visible range was obtained when compared to P3HT. Early examples of this class of polymers are mostly analogues of P3HT, with thienylenevinylene side chains (3 in Figure 1). These polymers show apparently enhanced light absorption in the visible region relative to P3HT, and the resulting photovoltaic performance is basically comparable to that of P3HT.\(^8\) Some out-of-the-box explorations found that with a proper extent (~2%) of cross linking of polythiophenes with thienylenevinylene chains, it is possible to obtain an increase of hole mobility relative to the non-cross-linked counterpart (4 in Figure 1).\(^9\) In addition, some researchers attached electron-donating side groups such as triphenylamine to the thiophene backbone (5 in Figure 1), aiming to tune the hole mobilities of
these materials.\textsuperscript{10} In recent years, concurrent with the booming investigations of conjugated alternating donor-acceptor co-polymers, 2-D polymers start to employ various kinds of electron-withdrawing side groups (5–8 in Figure 1). For example, in 2008, regioregular polythiophenes tethered with 90 mol\% of phenanthrenyl-imidazole (6 in Figure 1) has led to a ~0.1 eV shrinkage in bandgap in comparison to P3HT, in conjunction with a doubled electron transfer probability as found in polymer:[70]PCBM blend studies. These two features of the new polymer has contributed to much higher external quantum efficiencies (thus higher photocurrents) than those of P3HT, as well as enhanced solar cells efficiencies of 3.45\% (compared to 2.9\% of P3HT).\textsuperscript{11} A popular strategy to design two-dimensional conjugated polymers has incorporated triphenylamine into the polymer backbone,\textsuperscript{12,13,14,15,16} yielding structures such as 7 (Figure 1). Such a design has endowed the polymer with a decent hole mobility and power conversion efficiency of 4.37\% when applied in solar cells,\textsuperscript{17} which may indicate room for improvement, given that diphenylamine may not promote intermolecular packing. Recently, new 2-D polymers have emerged with enhanced light-harvesting capability and higher intermolecular packing potential, continuously pushing up the solar cell efficiencies\textsuperscript{18,19,20,21} For example, by systematically investigating the acceptor and side-chain effect, Peng et al. have reported an efficiency of 5.65\% for 8 (Figure 1), which is attributed to its good light absorption and improved carrier mobility compared to its analogues.\textsuperscript{22}

To summarize, the investigation of D-A cross-conjugated 2-D polymers is generally promoted by two motivations: (i) To enhance visible light absorption with two conjugations (donor-donor linear-conjugation and donor-acceptor cross-conjugation), and (ii) to make use of intramolecular charge transfer (from donor to acceptor) which might facilitate electron transfer to acceptors in polymer solar cells. The structural design of the precedent polymers may be categorized as: (i) directly using the 3-position of thiophene to furnish a donor-pendant acceptor configuration (this may introduce some torsion between adjacent thiophenes, yet the detailed effect remains unevaluated), and (ii) employing an ethylenic linker as the $\pi$-bridge between the donor backbone and pendant acceptors. An ethylenic linker is a good choice in consideration of minimizing the steric hindrance between neighboring conjugation moieties, especially when the acceptor group is bridged onto the 3-position of thiophene, and it should also be noted that these ethylenic linkers extend the overall $\pi$-conjugation. However, it should be mentioned as well that for most of these 2-D polymers the Wittig-Horner reaction was used to introduce the ethylenic segment. The stereochemistry of this particular alkene-generating reaction can vary with different substrates, leaving a possible challenge to control the regio-regularity of the resulting polymers.
3.2 Structural design

This chapter specifically focuses on the electronic characteristics of 2-D monomers/oligomers from a theoretical perspective. To do this, we first formulate appropriate structures for extended analysis. The previous studies on 2-D polymers have disclosed a few possible donor-acceptor constructions, i.e. (i) installing the acceptor directly on the 3-position of thiophene, (ii) bridging acceptors and the thiophene backbone with an ethylenic linker, and (iii) using the natural branching of triphenylamine to install acceptors. All these constructions have their unique advantages. Herein, we propose an alternative route, where the ethylenic linker is “fused” into another thiophenic ring:

Scheme 1. Structural change from the vinylthienyl moiety (left) to a thieno[3,4-b]thiophene-based building block (right, abbreviated as T34bT hereafter).

The utilization of T34bT minimizes adjacent steric hindrance upon installing an acceptor. Furthermore, the virtually fully-controllable thiophene chemistry readily allows direct coupling of acceptors. Note that in polymer 8 (Figure 1), two electron-rich thiophene rings were placed on the two sides of benzothiadiazole, which benefits the synthesis but may weaken the electron-withdrawing capability of the chosen acceptor group. This can be well avoided if the T34bT building block is employed. The structure evolution in Scheme 1 promotes a similar design with even improved coplanarity and \( \pi \)-conjugation:

Scheme 2. Structural evolution from the thieno[3,4-b]thiophene-based building block (left) to a benzotriothiophene (BTT)-based building block with extended conjugation.

BTT with larger \( \pi \)-conjugation area may lead to stronger intermolecular \( \pi-\pi \) stacking and thus to improved charge carrier mobility. Also, its enhanced \( \pi \)-conjugation would probably increase the polarizability, which may help the delocalization of charges.

The choice of solubilizing chains has always been an interesting topic in the design of conjugated polymers. Proper alkylation of polymers improves processability, but is also widely used to tune the morphology of polymer:fullerene blends. Introduction of solubilizing side chains, such as TEGs, may
also contribute specifically to other interesting properties, such as an increased dielectric constant for the resulting material. Note that an increased dielectric constant contributes to a reduced exciton binding energy as well. To this end, TEG chains are also employed in constructing the novel 2-D polymers, as exemplified by the following structures:

![Scheme 3](image)

**Scheme 3.** Prototypical polymer structures (1 and 2) based on the above discussion.

Such a design announces a few features: (i) The acceptor is directly installed on the backbone without thiophene spacing, which exploits the full electron-withdrawing capacity of the acceptor group and also eliminates possible chemical complexity of the ethylenic linker; (ii) The acceptor is in cross conjugation to the polymer backbone; (iii) The donor backbone is in good conjugation with a fairly coplanar character; (iv) TEG-chains were installed on the inner side of the flanking thiophenes; While this will not necessarily be included in the quantum calculations, TEG chains will be included in the synthesis of 2-D polymers (Chapters 4 & 5).

### 3.3 Quantum chemical calculations

2-D polymers have received relatively less concerted research attention compared to 1-D conjugated polymers, despite their unique characteristics such as isotropic charge transport. The lack of systematic quantum chemical evaluations further delayed the development of this type of photoactive materials. Here we have designed a series of monomeric structures with a distinct configuration of donor-acceptor cross conjugation, based on the above-discussed choices of two donor-acceptor bridges (T34bT and benzotrithiophene) and various types of acceptors. While the donor backbones are mostly thiophene-based, some are structurally modified for specific tuning of electronic structures.

Regarding the ground-state study, we attempt to provide a guideline for future design of 2-D polymers with properly engineered frontier orbitals. Evaluation focus is also upon the relationship
between structure and isotropic polarizability. Note that polarizability as a quantifiable parameter can indicate multiple physical properties: (i) a higher polarizability is indicative for a larger dipole moment induced by an electric field, which can be beneficial for intermolecular charge transfer, and (ii) a higher polarizability may arise from enhanced $\pi$-conjugation, thereby can imply improved charge mobility. On the basis of a computational analysis of monomers, we study the ground-state orbitals of oligomers between the 1-D donor-acceptor conjugation and its 2-D counterpart where the acceptors are positioned as the pendant group. Finally, we choose a promising dimer structure and preliminarily compare the exciton binding energies, thus to obtain a starting understanding of the charge separation properties.

**Computational details**

Geometries of all structures were optimized using DFT (B3LYP$^{24}/6-31G^{**}$) with the program GAMESS-UK.$^{25}$ Polarizabilities of all structures were calculated using DFT (B3LYPg/aug-cc-pVTZ) with the program DALTON.$^{26}$ Reported HOMO/LUMO energies were taken from the B3LYPg/aug-cc-pVTZ (DALTON) calculations. Vertical excitation energies (the lowest 10) were calculated using time-dependent DFT (TD-DFT, B3LYPg/aug-cc-pVTZ) with DALTON.
3.4 Results and discussion

Table 1 presents the computational result of 22 monomeric structures in their ground state, in terms of frontier orbitals and polarizabilities. Various types of acceptors and donors were included in these structures. The frontier orbital levels data are collected in Figure 2 and referenced to the frontier orbitals of [60]PCBM, and the polarizability data are shown as a bar graph in Figure 4.

Table 1. Computational results of monomeric structures. Note that the LUMO, HOMO (vs. vacuum) and bandgap possess a unit of eV. The polarizabilities are recorded on all three principal axes (x, y and z) for each structure. The polarizabilities are then averaged over three axes and further over all the electrons of each structure, to give the isotropic polarizability per electron. N.D. means not determined.

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3.4.1 On the frontier orbitals

The fundamental requirement of the frontier orbitals of the polymer is the need to properly align with fullerene acceptors (e.g. [60]PCBM). Note that all calculations reported here are with monomeric structures. Due to the difference between monomers and polymers, the analysis conducted here is qualitative. As a starting point, structures 3 is found to show a rather high LUMO and HOMO of $-2.76$ and $-4.70$ eV, respectively. This unambiguously indicates that the methoxylated thiophenes are providing an enhanced electron-donating capacity, ensuring the necessity to remove the thiophene-contacting oxygen atoms, as seen with all following structures.

Donor-acceptor linear conjugation is known to be capable of quickly narrowing the bandgap. This effect was however not observed with our 2-D configuration, as revealed by some initial quantum chemical calculations on donor-acceptor cross-conjugated monomers and the corresponding tetramers. These calculations indicated a very small bandgap reduction from monomer to tetramer. This is likely due to the fact that the acceptor is cross-conjugated to the donor backbone. In this respect, it is important to design monomers with fairly low-lying frontier orbitals and relatively narrow bandgaps. Figure 2 presents an overview of the LUMO and HOMO levels of the first 21 structures, with a comparison of the frontier orbitals of PCBM. It should be noted that for all structures, the HOMO and LUMO are appreciably localized on the donor and acceptor moieties, respectively, which is critical for efficient intra-molecular charge separation.

![Figure 2](image.png)

**Figure 2.** An overview of the frontier orbitals of the first 21 structures in Table 1 and PCBM[60]. All red lines are energy levels of LUMO, and all black lines HOMO. The gray lines are drawn as a guide to the eyes.
It can be seen that most structures show LUMO levels around $-3$ eV, while all structures containing two cyano groups on the acceptor moieties (4, 7, 20, 23) are likely to afford insufficient driving forces for electron transfer to PCBM due to low-lying LUMO levels. Additionally, these structures with low-lying LUMOs also have relatively low-lying HOMOs, which is important for the establishment of decent $V_{oc}$ (open-circuit photovoltage). This suggests the necessity for a different electron acceptor with higher LUMO levels in order to maintain efficient electron transfer. On the other hand, all structures without methoxy substitution on donor backbones show HOMO levels around $-5$ eV, which gives sufficient driving force for hole transfer. Specifically, a few routes to yield low-lying HOMO levels can be noted from Table 1 and Figure 2: (i) bringing down the electron-richness of the T34bT bridge by introducing a fluorine atom (structure 17) without sacrificing the coplanarity; (ii) increasing the structural density of acceptor groups along the polymer chain by eliminating one thiophene moiety (structure 19, note that this may lead to a virtually regio-regular polymer); (iii) employing relatively electron deficient donor structures such as dibenzosilole (structure 20).

Figure 3. Comparison of the HOMO & LUMO delocalization of the trimers based on the same donor and acceptor moieties. The gray ellipse in 3(a) indicates the acceptor that interrupts the HOMO delocalization.
Recall that our design of the above 2-D structures specifically aims at obtaining a more delocalized HOMO, which might lead to an increased hole-electron distance in the excited state of the polymer. Thereby, we choose structure 8 in Figure 2 to construct the corresponding trimers for a direct comparison with the donor-acceptor alternating counterpart, and the result of the calculation is presented in Figure 3. It can be seen that there is a major difference between the HOMO distributions. Specifically, for the donor-acceptor alternating trimer, both the HOMO and HOMO–1 are apparently interrupted by acceptor moieties, impeding the long-range orbital delocalization. In contrast, the HOMO of the 2-D trimer delocalizes substantially.

3.4.2 On the polarizabilities

Unlike the dielectric constant, which is a material (bulk) property, polarizability is a molecular property, depicting the ability of a molecule to form instantaneous dipoles in an electric field. A higher polarizability may imply multiple features of a polymer: (i) A higher molecular polarizability is directly translated into a stronger ability to form a dipole, which may assist the splitting of a bound hole-electron pair; (ii) A higher dielectric constant of the polymer can be expected according to the Clausius–Mossotti relation, which could offer benefits including but not limited to reduced recombination, decreased exciton-binding energy, lower reorganization energy and decreased Coulomb attraction within the exciton. Thereby, it is valuable to gain a preliminary understanding of the relationship between chemical structure and polarizability. To this end, we further calculated the polarizabilities of some of the structures in Table 1. Figure 4 presents the average isotropic polarizabilities of structures 3 – 23:

![Figure 4](image)

**Figure 4.** An overview of the average isotropic polarizabilities of the 21 structures in Table 1. The light blue area is drawn as a guide to the eyes, indicating that a majority of the presented polarizabilities statistically fall in the range of 2.0 ± 0.2.
Apparently most of the structures possess an average isotropic polarizability of $2.0 \pm 0.2$ (10% variation). Still it can be seen that some structures (21) gives an obviously lower value, while some other structures (7, 14–16, 18, 23) are apparently much more isotropically polarizable. These structures generally possess acceptor moieties with fairly strong electron-withdrawing capabilities. Note that structure 21 is the only one with two thiophene-phenyl bonds, which make a dihedral angle of 20°. This observation indicates that structural planarity is a major contributor to isotropic polarizability. As a word of summary, we found that generally, differences in donor-acceptor combinations do not affect the isotropic polarizability in a striking manner, as long as the structure planarity is ensured.

### 3.4.3 On the exciton binding energies

Quantum calculation allows a direct and convenient comparison of the exciton binding energies of oligomers featuring cross vs. linear donor-acceptor conjugation. On the basis of the above study on the ground state properties as well as some extra consideration on potential synthetic challenges, the following set of dimers were chosen for the preliminary quantum chemical study on the influence of donor-acceptor cross conjugation upon exciton binding energy:

![Figure 1. Structures of 2-D cross conjugated configuration (top) and linear conjugated configuration (down) subjected to exciton binding energy calculations.](image)

For the comparison, we take the vertical exciton binding energy $(E_{b}^{exc})_{vert}$ as the observable, defined by eq.(1) which is derived in consideration of the reaction $D^+ + D \rightarrow D^+ + D^-$, where $D^+$, $D$, $D^+$ and $D^-$ refer to the excited-state, ground-state, cation and anion forms of molecule $D$, respectively:

$$(E_{b}^{exc})_{vert} = E(D^+) + E(D^-) - E(D^+) - E(D)$$

(1)

where $E(D^+)$, $E(D^-)$, $E(D^*)$ and $E(D)$ represent the total energies of the vertical cationic state, vertical anionic state, vertical first excited state and vertical ground state of the subject molecule. The calculation results are included in Table 2.
Table 2. Calculated total energies of the vertical cationic state, vertical anionic state, vertical first excited state and vertical ground state of the subject dimers. The resulting exciton binding energies are also included. Units of all total energies are atomic unit. Unit of \(E_{\text{exc}}^{ \text{vert}}\) is eV (converted from atomic unit).

<table>
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<th>(E(D^-))</th>
<th>(E(D^*)</th>
<th>(E(D))</th>
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The calculated \(E_{\text{exc}}\) values fall in the eV scale, generally higher than some reported exciton binding energies in the meV range for polymers. This is probably due to the fact that these calculations were performed in vacuum, lacking environmental stabilization. Also note that the calculations deployed dimers instead of longer oligomers, the latter being more representative for a real polymer where orbital delocalization is more significant. In spite of the qualitative nature of these calculations, they surprisingly indicate that the exciton binding energy of the cross conjugated dimer is higher than that of its linear counterpart. These results may have a few implications: (i) A delocalized hole plus a localized electron do not necessarily contribute to an increased hole-electron distance, at least for the two-dimensional structures under investigation (on the contrary, it may lead to an even shorter hole-electron distance, as will be discussed in Chapter 5); (ii) in view of the delocalization nature of charges in photovoltaic systems, the hole-electron distance itself does not have a clear physical definition; in this respect, the “effective” hole-electron distance may strongly depend on how the charge delocalizes.
3.5 Conclusions

From a theoretical perspective, we have studied a D-A conjugated polymer configuration, where the backbone is constructed purely with linearly conjugated electron-rich moieties, and the acceptors are installed as cross-conjugated pendant groups of the donor backbone. Specifically, we evaluated the influence of donor-acceptor cross conjugation on the exciton binding energy of conjugated polymers. Our preliminary investigation indicates that cross conjugation results in a higher exciton binding energy than donor-accepter linear conjugation. Such observation likely implies that a delocalized hole plus a localized electron do not necessarily contribute to an increased hole-electron distance, at least for the two-dimensional structures under investigation. A more detailed study is necessary to properly understand these results.
3.6 References

Chapter 4

Synthesis of thieno[3,4-b]thiophene-based 2-D conjugated polymers featuring a donor backbone and pendant acceptor groups

ABSTRACT Control of the chemical quality of conjugated polymers offers fundamental support for the development of photovoltaic materials. The successful utilization of new design/synthesis strategies may need dedicated chemistry exploration. This chapter discusses the synthesis of a two-dimensional conjugated polymer comprising a polythiophene backbone, a pendant thieno[2,3-c]pyrrole-4,6-dione acceptor, and a thieno[3,4-b]thiophene bridge. 2,5,8,11-Tetraoxadodecy (TEG) side-chains are used as solubilizing side chains. It is found that in spite of efficient chain growth, the as-presented one-pot Suzuki-Miyaura homopolymerization (see Chapter 2) persistently introduces unassignable impurities to the polymer (P1). Although an exact explanation is not pursued, it is hypothesized that the oxygen atoms in the TEG chains chelate the boron atoms in the reaction system of Suzuki-Miyaura homopolymerization. This hypothesis is supported by an experiment with a control polymer (P2) where alkyl chains were employed as solubilizing side chains, where the problem with P1 was well eliminated, as evidenced by our mass spectra analysis. Stille copolymerization is used to yield the desired 2-D conjugated polymer (CC1). The present work hints to important aspects of bis(pinacolato)diboron-promoted homopolymerization regarding its potential drawbacks, which might limit its application scope.
4.1 Introduction

Two-dimensional (2-D) conjugated polymers have been studied as candidates for organic photovoltaics in the past two decades, alternative to one-dimensional donor-acceptor conjugated polymers. In these 2-D polymers, the acceptors are configured perpendicularly to the donor backbone. On the basis of precedent developments, 2-D photovoltaic polymers may fall into the following categories (for examples of structures, see Figure 6 in Chapter 1 and Figure 1 in Chapter 3): (i) Polythiophene backbones with pendant groups ranging from thiophenic or phenyl moieties,\textsuperscript{1,2,3} with an ethylenic linker between the backbone and the pendant groups. (ii) Polythiophene backbones with pendant groups such as phenanthrenyl-imidazole, with the pendant groups directly installed on the 3-position of the backbone thiophenes;\textsuperscript{4,5,6,7,8} (iii) Fluorene and triphenylamine based backbones with various pendant acceptors,\textsuperscript{9,10,11,12,13,14} where an ethylenic linker is used as the backbone-pendant group bridge; (iv) A backbone based on more extensively conjugated moieties (e.g. benzothiadiazole) in conjugation to ethylenic linker bridged acceptors on thiophene units,\textsuperscript{15,16,17,18,19} The synthesis of these polymers is generally done by Suzuki or Stille cross-coupling promoted copolymerization of two bifunctional monomers. In cases where acceptors such as malononitrile were employed,\textsuperscript{10} authors take the advantage of Knoevenagel condensation by preparing a polymer precursor, which is then functionalized with the corresponding acceptors.

The present chapter discusses the design and synthesis of a two-dimensional conjugated polymer based on a thieno[3,4-b]thiophene bridge between a polythiophene backbone and a thieno[2,3-b]pyrrole-4,6-dione acceptor, as shown in the following figure:

![Figure 1](image_url)

**Figure 1.** Chemical structure of polymer CC1 comprising a polythiophene backbone, thieno[2,3-c]pyrrole-4,6-dione acceptor, and a thieno[3,4-b]thiophene bridge.

Originally, the pursued structure was one similar to CC1, but absent of the thiophene ring on the right side of the repeating unit. It starts with the convergent synthesis of the monomer with cross-conjugated thieno[3,4-b]thiophene and thieno[2,3-b]pyrrole-4,6-dione. Motivated by the work presented in Chapter 2, a homopolymerization of the cross-conjugated monomer was conducted. Structural characterization of the polymer indicated the problem of bis(pinacolato)diboron-promoted homopolymerization of
monomers containing TEG side chains being hindered by these substituents. Although polymers of improved chemical integrity are attainable with Stille copolymerization, the presented synthetic work provides strong evidence that the application of bis(pinacolato)diboron promoted homopolymerization might be side-chain sensitive. To this end, we proposed and executed the strategy which used one extra thiophene to furnish a Stille cross-coupling polycondensation, yielding CC1 with decent chemical quality.

4.2 Synthesis

4.2.1 Monomer synthesis

Scheme 1 presents the synthesis of the monomer for the construction of the two-dimensional conjugated polymers.

Intermediate 4 was synthesized in four steps from 3,4-dibromothiophene. Compound 2 was found to be rather susceptible to oxidation, even at low temperatures. Therefore, double TMS protection (3) was necessary before further chemical manipulation. Compound 3 was obtained through a one-pot reaction, without removal of the possible mono TMS-protected impurity. In the last step, compound 3 was converted to the target compound 4 by lithiation and subsequent quenching with trimethyltin chloride. The acceptor unit 8 was synthesized according to literature methods, starting from 2,3-dibromothiophene. While compound 11 appeared to be fairly stable to ambient conditions and normal purification processes, the resulting key intermediate 12 turned out to be quite unstable, making it impossible to purify it by column chromatography (both silica and Al₂O₃ were tried as stationary phases). In the case of brominating 11 with N-bromosuccinimide (NBS), compound 12 was formed in high yield, but the removal of succinimide residue proved to be rather difficult as a result of the incompatibility of 12 with column chromatography. We also found that these succinimide residues tend to adversely affect the subsequent Stille cross-coupling between 12 and 10, which gave 13 only in extremely low yields. Fortunately, switching from NBS to bromine for the bromination of 11 afforded high quality of 12 in good yield, using a simple water-washing procedure and eliminating the need for any other purification procedure. Compound 13 was thus synthesized from the cross-coupling of 10 and 12 in a decent yield. Compound 13 was readily converted into the final target monomer 14 by double bromination with NBS.
### 4.2.2 Synthesis of 2-D conjugated polymers

The successful one-pot homopolymerization of dibrominated monomers in Chapter 2 offered a motivation to synthesize a homopolymer with bis(pinacolato)diboron as the condensation reagent, as shown in Scheme 2.

**Scheme 2.** One-pot Suzuki-Miyaura homopolymerization of monomer 14 to polymer P1.

The above polymerization proceeded overnight at toluene/DMF refluxing temperature to yield a purple-blue viscous solution. Soxhlet extraction with methanol, acetone and then hexane removed low-molecular weight fractions and impurities. Finally, soxhlet extraction with chloroform yielded a deep purple product showing an exceptional solubility, not only in chloroform, but also in less polar solvents such as THF. This solubility feature is likely to be caused by the installation of TEG chains. The UV-vis absorption spectrum of a solution of P1 in chloroform is shown in Figure 2.

**Figure 2.** UV-vis absorption spectrum of the homopolymerization result from monomer 14.
Different from a typical donor-acceptor alternating conjugated polymer, the as-obtained 2-D polymer showed a strong and broad absorption covering the entire visible spectrum from 400 to 700 nm, with an optical bandgap of 1.69 eV. Note that other 2-D conjugated polymers were reported to show narrower absorptions but similarly possess strong absorptions in the visible region. Furthermore, a HOMO energy level of −5.0 eV was derived from cyclic voltammetry measurements (Figure 3). In conjunction with the optical bandgap, this yields a LUMO energy level of −3.31 eV. These preliminary results indicated that this material has the right frontier orbital energies for application in polymer solar cells with fullerene derivatives as the electron acceptor.

**Figure 3.** Cyclic voltammogram (oxidative cycle) of polymer P1 as a drop-cast film. The film was dropcast from a THF solution (~1 mg/mL). A 0.1 M solution of tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile was used as the electrolyte. Scan rate: 50 mV/s.
One of the major advantages of the bis(pinacolato)diboron promoted homopolymerization is that it can generate high quality polymers with well-controlled end groups. In order to check whether such a clean homopolymerization had also occurred for polymer P1, we performed MALDI-TOF experiments on the as-obtained polymer, with 2-((4-hydroxyphenyl)diazenyl)benzoic acid as the matrix. The spectrum is shown in Figure 4.

**Figure 4.** MALDI-TOF spectrum of homopolymer P1, with 2-((4-hydroxyphenyl)diazenyl)benzoic acid as the matrix. Peaks 1-6 refer to oligomers comprising 3-8 repeating units.

Figure 4 reveals a number of things regarding the bis(pinacolato)diboron-mediated homopolymerization: (i) The polymerization has proceeded successfully; (ii) There are clearly “regularly repeating” peaks (1 – 6), suggesting oligomers of different lengths; (iii) Most importantly, all sets of peaks appear as a cluster of peaks absent of sufficient peak-to-peak resolution, notably different from what one would expect from a *normal* mass spectrum; (iv) the resolution of each peak is different from each other, i.e., the first peak is resolvable in terms of the multiple side peaks, but as soon the molecular weight increases, the limited resolution tends to diminish further; (v) the width of a set of peaks can be as wide as 700 Da (peak 4), (vi) assuming each broad set of peaks is based on one oligomer, for example, peak 1 contains multiple peaks, and each of these peaks is a trimer attached with a different amount of *exotic* species. Then, as the molecular weight increases, the deviation between the center of the broad peak and the expected molecular weight of the corresponding oligomer keeps increasing.

The MALDI-TOF measurements suggest a successful polymerization with efficient chain growth, which indicates the backbone growth has been proceeding as expected. The results also reveal a complex situation regarding the chemical quality of the polymer obtained by this method. It is speculated that TEG chains are attracting a species from the reaction medium. With a longer polymer chain, the presence
of increasingly more TEG chains in a single polymer is able to attract more of this species. The exact identity of this species is unknown within the current study scope, but it should be either potassium ions, or the boronate side product which is produced within each Suzuki cycle. The first possibility with K\(^+\) may be eliminated based on the simple isotope composition of potassium, thus not expected to create such a broad cluster of peaks (Figure 4). Also note that by treating the polymer with crown ether 18-crown-6, no change to the quality of the polymer sample was observed. This further puts the second possibility of binding with boronate to the front. This may be plausible with an oxygen–boron interaction. We did not design further experiments to prove if these broad clusters of peaks are caused by the adsorption of boronate species by the oxygen atoms in the TEG chains.

Nevertheless, the MALDI-TOF results tend to suggest that the as-presented homopolymerization is unfortunately not compatible with monomers containing TEG chains. In order to get evidence for this hypothesis, we designed a control polymer P\(_2\), which was obtained from the homopolymerization of a similar monomer with the same backbone of 14, but all TEG chains are replaced with alkyl chains. Scheme 3 shows the synthetic details of P\(_2\):

![Scheme 3. Synthesis of control polymer P\(_2\).](image)

The synthesis of P\(_2\) started from obtaining the key intermediate 18. Compound 18 was synthesized with 3 steps starting from 3-bromothiophene (15), which was first transformed to 3-decylthiophene (16) by coupling with the corresponding Grignard reagent. 16 was then brominated into 17, which offered selective lithiation for the generation of 18.\(^{20}\) Compound 18 was then coupled with 12 with the same procedures used for the synthesis of compound 14, and this eventually led to the synthesis of dibrominated monomer 20. Finally, 20 was subjected to a bis(pinacolato)diboron-mediated homopolymerization, giving the homopolymer P\(_2\). P\(_2\) was purified by a conventional Soxhlet extraction procedure, in which methanol and acetone were first used as extraction solvents to remove low-
molecular weight fractions, and then hexane and chloroform were used in sequence to collect samples for mass spectra characterization. The MALDI-TOF spectrum of P2 is presented in Figure 5.

![MALDI-TOF spectrum of homopolymer P2](image)

**Figure 5.** MALDI-TOF spectrum of homopolymer P2 (chloroform fraction), with trans-3-indoleacrylic acid as the matrix.

As shown in Figure 5, the employment of alkyl chains immediately eliminated the peak broadening phenomenon in Figure 4, despite the presence of other minor impurities. This contrast suggest that TEG chains can be problematic for bis(pinacolato)diboron mediated polymerizations, at least with the given structure design. To this end, Stille copolymerization was brought forward, in order to obtain the 2-D polymer with decent chemical purity. To do this, we polymerized monomer 14 with one thiophene unit, as shown in Scheme 4.

![Scheme 4](image)

**Scheme 4.** Copolymerization of monomer 14 and bis-stannyalted thiophene to copolymer CC1.
This copolymerization gave polymer \textbf{CC1} as a deep-purple solid in a decent yield of 85%. As mentioned before, homopolymer \textbf{P1} from the homopolymerization showed a remarkable solubility in THF at room temperature. It is worth noting that adding one repeating thiophene unit into the backbone with Stille cross-coupling copolymerization, however, has \textit{completely} eliminated the THF-solubility of the polymer, even at elevated temperatures. This observation might serve as an indirect proof that the impurity in Figure 4 is related to boronate species, which would confer many more methyl groups for better solubility. The copolymer resulted from the above polymerization is characterized with MALDI-TOF for chemical integrity, as shown in Figure 6 (top).

\textbf{Figure 6.} MALDI-TOF spectrum (top) of \textbf{CC1} synthesized from Stille copolymerization and a zoom-in of peak 1 (bottom). The peak sets A–D represents oligomers based on sequentially increasing numbers of repeating unit 13 (see \textbf{Scheme 1}). The highest peaks in all peak sets are assigned to oligomers end-capped with a thiophene on each side, based on the m/z values. The other side peaks represent oligomers of various end-cappings, such as Br, SnMe$_3$, and/or thiophene on one side. Dithranol was used as the matrix (top).
The spectrum of the resulting copolymer is clearly free of broadened peaks. Each set of peaks consists of 3 peaks (for example, the first set of peaks contains 1, 2 and 3, the second set of peaks contains 4, 5 and 6.). A, B, C and D are regular repetitions after the first two sets of peaks. While Stille polymerization is known for its poor control of end groups, peaks 1-6 are readily assigned to oligomers of different end groups including hydrogen and bromine atoms and trimethyltin groups. Note that methyl transfer is also observed (Figure 6, bottom), in good accordance with the observation described in Chapter 2.

4.3 Discussion

Thieno[3,4-b]thiophene has been employed as the bridge between the acceptor and donor segments in the conjugated polymer CC1. Such a design is less likely to cause notable backbone torsion in comparison to the installation of acceptor moieties directly on the third position of thiophene units, as seen in previous reports on 2-D conjugated polymers. While bis(pinacolato)diboron promoted polycondensation has enabled an efficient polymerization of a dibrominated monomer, it unfortunately yielded a polymer with unassignable impurities, as discussed in previous paragraphs. Although the detailed mechanism of the peak broadening in Figure 3 is not scrutinized, one plausible reason is that TEG chains have adsorbed some boronate species from the reaction medium. It would be interesting to precisely understand the chemistry involved here in the future. We would like to note that despite its well-known problem of poor-end group control, Stille copolymerization has proven to be a preferable synthetic route for conjugated polymers featuring TEG chains.
4.4 Conclusions

A complete understanding of a new design/synthetic strategy, both on its upside and downside, is highly valuable to the progress of material evolution. Here, we have studied the synthetic challenges when bis(pinacolato)diboron-mediated homopolymerization meets TEG chains. The unique merits brought by installing TEG chains on molecules have now been well seen and widely applied. In our design of a 2-D conjugated polymer, TEG chains are included as solubilizing side chains. While bis(pinacolato)diboron has promoted an effective polycondensation of the macromonomers, we also spotted unassignable impurities. The apparent existence of these impurities was visualized by the unusually broad peaks in MALDI-TOF spectra of the as-obtained polymer. While the exact nature of the impurities is not clear yet, we postulate that it has likely originated from the oxygen-boron interaction between TEG chains and boronates. This postulate is supported by a control experiment where peak-broadening is completely eliminated, when TEG chains were replaced with conventional alkyl chains. In this sense, conventional Stille copolymerization was employed to produce the 2-D conjugated polymer, with slight structure modification to the originally designed polymer structure.
4.5 Experimental

Materials and methods

All reagents and solvents were purchased from commercial sources and used without further purification, unless otherwise indicated. UV/Vis measurements were carried out on a Jenway 6715 spectrometer in 1-cm fused quartz cuvettes with concentrations of 0.03–0.1 mg/mL in CHCl₃. MALDI-TOF spectra were taken on a Biosystems Voyager apparatus. Samples were prepared by mixing the matrix (~ 10 mg/mL in THF) and polymer sample (~ 1 mg/mL in THF or CHCl₃) at room temperature in a 3:1 volume ratio. All measurements were performed in positive ion mode. NMR spectra were measured using a Varian AMX400 (400 MHz) instrument at 25 °C. Cyclic voltammetry measurements were carried out with an Autolab PGSTAT100 potentiostat in a three-electrode configuration. The working electrode was a glass carbon electrode, the counter electrode was a platinum wire, and the pseudoreference was an Ag/AgCl wire externally calibrated against ferrocene (Fc/Fc⁺). Polymer films were dropcast from a THF solution at a concentration of ~1 mg/mL on the working electrode and allowed to dry.

Synthesis

((4-Bromothiophen-3-yl)ethynyl)trimethylsilane (1) A flame-dried, 250-mL, three-neck flask equipped with a water cooler was loaded with Pd(PPh₃)₄ (500 mg, 0.43 mmol) and CuI (150 mg), followed by sufficient degassing. Dry THF (100 mL) and distilled triethylamine were mixed with 3,4-dibromothiophene (7 mL, 63 mmol) and trimethylsilylacetylene (11 mL, 72 mmol) in a separate Schlenk flask, which was briefly degassed at −20 °C. After warming up to room temperature, the as-degassed solvent/reactant mixture was transferred into the three-neck flask via cannula. The reaction was then allowed to slowly warmed up to 80 °C and stirred overnight. After cooling down to room temperature, the solvent was removed under reduced pressure and the oil-like residue was dissolved in diethyl ether (250 mL) and washed with water (250 mL). The organic phase was collected and concentrated, and the residue was subjected to silica gel chromatography with pentane as eluent, yielding ((4-bromothiophen-3-yl)ethynyl)trimethylsilane (1) as a colorless oil (10 g, 67% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, J = 4 Hz, 1H), 7.21 (d, J = 4 Hz, 1H), 0.26 (s, 9H).

Thieno[3,4-b]thiophene (2) A 250 mL, three-neck Schlenk flask was flamed, and equipped with a solid-addition arm charged with elemental sulfur (0.789 g, 24.61 mmol). Compound 1 (5.8 g, 22.37 mmol) was then added to the flask, followed by the transfer of dry diethyl ether (100 mL). The system was then allowed to cool down in an ethanol/liquid nitrogen cold bath, after which the system was briefly degassed. n-BuLi (24.61 mmol, 10 mL) was then added dropwise into the reaction flask. The sulfur was poured into the reaction system 1 hour after the addition of n-BuLi. The reaction was maintained in the cold bath for 70 min, during which period the cold bath slowly warmed up to 30 °C. The reaction
mixture was then poured into a separation funnel with ice-cooled brine (200 mL). After a quick washing, the aqueous phase was collected and placed on a heater at 70 °C for 1 h. This aqueous system was then extracted with diethyl ether (250 mL), and the organic phase was collected and concentrated. The residue was purified with silica gel chromatography (pentane as eluent) to yield thieno[3,4-b]thiophene as a colorless oil (3.14 g, 82%). 1H NMR (400 MHz, CDCl3) δ 7.34 (d, J = 8 Hz, 1 H), 7.33 (s, 1 H), 7.25 (dd, J = 8 Hz, 1 H), 6.93 (dd, J = 8 Hz, 1 H). 13C NMR (101 MHz, CDCl3) δ 147.59, 139.32, 132.38, 116.75, 111.59, 110.57.

(Thieno[3,4-b]thiophene-4,6-diyl)bis(trimethylsilane) (3) A flame-dried, 100 mL, three-neck flask was charged with thieno[3,4-b]thiophene (1.25 g, 8.91 mmol) and dry THF (50 mL). The reaction flask was then cooled down to −80 °C using an ethanol/liquid N2 cold bath. n-BuLi (2.5 M, 3.92 mL) was then added dropwise. The reaction was kept below −50 °C for 1 h, afterwards chlorotrimethylsilane (1.25 mL) was added all at once. The cold bath was then removed. After 1 h, the reaction mixture was poured into water (250 mL) and extracted with diethyl ether (200 mL). The organic phase was collected and thoroughly concentrated to give a yellowish oil, which was further purified by silica gel chromatography, affording the product as a colorless oil (1.8 g, 71%). 1H NMR (400 MHz, CDCl3) δ 7.44 (d, J = 8 Hz, 1H), 7.03 (d, J = 8 Hz, 1H), 0.41 (s, 9H), 0.40 (s, 9H).

13C NMR (101 MHz, CDCl3) δ 137.88, 132.52, 129.08, 128.28, 125.36, 117.52, 0.22, −0.51.

(2-(Trimethylstannyl)thieno[3,4-b]thiophene-4,6-diyl)bis(trimethylsilane) (4) (Thieno[3,4-b]thiophene-4,6-diyl)bis(trimethylsilane) (0.853 g, 3 mmol) was transferred into a flame-dried, 100 mL, three-neck flask, which was connected to a nitrogen Schlenk line. Dry THF (50 mL) was then added via a cannula into the reaction flask. An ethanol/liquid nitrogen cold bath was used to cool down the reaction system to −80 °C. n-BuLi (3.3 mmol) was then added dropwise. After 15 min, chlorotrimethylstannane (3.3 mmol) was added into the reaction flask via a syringe, after which the cold bath was removed. After 15 min, the reaction mixture was poured into water (200 mL), and washed with diethyl ether (250 mL). The organic phase was collected and dried over Na2SO4. After filtering, the filtrate was concentrated under vacuum to yield (1.34 g, 97% yield) 4 as yellow oil. 1H NMR (400 MHz, CDCl3) δ 7.03 (d, J = 8 Hz, 1H), 0.40 (s, 9H), 0.39 (s, 9H). 13C NMR (101 MHz, CDCl3) δ 157.47, 152.68, 148.15, 130.20, 128.00, 124.79, 0.27, −0.51, −8.53.

Thiophene-2,3-dicarboxylic acid (5) 2,3-Dibromothiophene (5 g, 20.67 mmol) and dry THF (50 mL) were loaded into a flame-dried, 250-mL, three-neck flask, which was then cooled to −80 °C with an ethanol/liquid N2 cold bath. Two balloons filled with dry CO2 (2 L, 1 atm) were sealed and connected to the reaction flask. n-BuLi (12.92 mL, 20.67 mmol) was then added dropwise within 3 min. After 40 min, CO2 was released into the reaction flask. The cold bath was then removed. After 1 h, the reaction mixture was poured into water with an excess of aqueous HCl. The mixture was then extracted with diethyl ether (250 mL). The organic phase was collected and dried over Na2SO4. The ether solution was
filtered and thoroughly concentrated under vacuum. The as-obtained white solid (4.25 g, yield 99%) was immediately transferred into a flame-dried, 250 mL, three-neck flask. Following the same protocol as above except for the usage of 2.2 equivalents of n-BuLi, the intermediate was lithiated at – 80 °C for 40 min, and quenched with CO$_2$ (2 L, 1 atm). After 1 h, the resulting reaction mixture was worked-up in the same way as described above, yielding 2,3-dicarboxylic acid thiophene (5) as a white solid (3.5 g, 95% yield), which is used without further purification.

5-Decyl-4-H-thieno[2,3-c]pyrrole-4,6(5-H)-dione (7) A flame-dried, 100-mL, three-neck flask was charged with 5 (3.5 g, 20.33 mmol), followed by the addition of dry toluene (20 mL) and 0.05 mL of DMF. Oxalyl chloride (8.13 mL, 81 mmol) was added under vigorous stirring. Afterwards the reaction was set at 100 °C. After 50 min, the solvent in the reaction flask was removed with a strong N$_2$ flow. The intermediate compound 6 was then obtained as a brown oil. Decylamine (4.06 mL, 20.33 mmol) was then added all at once. The reaction was then stirred at 100 °C overnight. The resulting brown mixture was then poured into water (150 mL) and extracted with dichloromethane (200 mL). The as-obtained solid was subjected to silica gel chromatography using an eluent of dichloromethane/hexane (v/v = 1:2), affording 7 as a colorless oil (3.2 g, 55% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.74 (d, J = 4 Hz, 1H), 7.29 (d, J = 4 Hz, 1H), 3.58 (t, J = 8 Hz, 2H), 3.56 (q, J = 8 Hz, 2H), 1.62 (t, J = 8 Hz, 2H), 1.30–1.24 (m, 14H), 0.86(t, J = 8 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 163.91, 162.71, 144.66, 140.81, 137.23, 121.04, 38.46, 31.84, 29.49, 29.47, 29.26, 28.79, 26.78, 22.65, 14.10.

2-Bromo-5-decyl-4H-thieno[2,3-c]pyrrole-4,6(5H)-dione (8) Compound 7 (2 g, 6.8 mmol) was dissolved in CF$_3$COOH (20 mL). NBS (1.24 g, 7 mmol) was then added, followed by the addition of concentrated H$_2$SO$_4$ (2 mL). After stirring at room temperature for 7 h, the mixture was poured into water (150 mL) and extracted with CH$_2$Cl$_2$ (200 mL). The organic phase was collected and concentrated under reduced pressure to afford a brown solid, which was subjected to silica gel chromatography with CH$_2$Cl$_2$/hexane (v/v = 1/1) as eluent, yielding product 8 as a yellow solid (2.4 g, 95% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.30 (s, 1H), 3.57 (t, J = 8 Hz, 2H), 1.62 (t, J = 8 Hz, 2H), 1.30–1.25 (m, 14H), 0.87 (t, J = 8 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 162.80, 161.80, 143.69, 140.27, 125.22, 123.64, 38.53, 31.72, 29.36, 29.34, 29.13, 29.01, 28.56, 26.62, 22.53, 13.98.

1-(Thiophen-3-yl)-2,5,8,11-tetraoxadodecane (9) A 100-mL, three-neck flask equipped with water cooler was flame-dried and charged with NaH (1.471 g, 36.8 mmol, 60%wt in mineral oil). Dry THF (50 mL) was then introduced via a cannula. 3-Thienylmethanol (2.1 g, 18.39 mmol) was then added into the NaH suspension dropwise. As soon as the H$_2$ evolution ended, diethylene glycol 2-bromoethyl methyl ether (5.01 g, 22.07 mmol) was added via syringe, all at once. The reaction mixture was then gently refluxed overnight. After cooling to room temperature, the resulting solution was poured into water (150 mL) and extracted with dichloromethane (200 mL). The organic phase was collected and
concentrated, and the residue was subjected to silica gel chromatography with dichloromethane as eluent. The product 9 was obtained as a colorless oil (3.1 g, 65% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.29–7.27 (m, 1 H), 7.22–7.21 (m, 1 H), 7.08–7.06 (m, 1 H), 4.57 (s, 2 H), 3.66–3.62 (m, 10 H), 3.56–3.53 (m, 2 H), 3.37 (s, 3 H). \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 139.39, 127.28, 125.81, 122.72, 71.86, 70.56, 70.54, 70.44, 69.24, 68.35, 58.91.

\(3-(2,5,8,11\text{-Tetraoxadodecyl})\text{thiophen-2-yl}trimethylstannane\) (10) A flame-dried, 100-mL, three-neck flask was charged with 1-(thiophen-3-yl)-2,5,8,11-tetraoxadecane (0.6 g, 2.305 mmol), followed by the transfer of dry diethyl ether. The reaction system was cooled down using an ethanol/liquid nitrogen bath. n-BuLi (1.584 mL, 2.54 mmol) was then added dropwise. After keeping the reaction mixture at \(-80^\circ C\) for 40 min, chlorotrimethylstannane (2.76 mmol, 1 M THF solution) was added into the reaction mixture all at once. The cooling bath was then removed, and the solution was stirred for 3 h. The resulting solution was poured into water (150 mL), and extracted with diethyl ether (200 mL). The organic phase was collected and dried over NaSO\(_4\), and filtered. The filtrate was then thoroughly concentrated to afford 10 as a brownish oil (960 mg, 99% yield). No further purification was processed. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.54 (d, \(J = 4\) Hz, 1H), 7.16 (d, \(J = 4\) Hz, 1H), 4.58 (m, 2H), 3.65 (m, 12H), 3.37 (s, 3H), 0.36 (s, 9H). \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 146.46, 135.04, 130.68, 128.93, 71.91, 70.59, 70.55, 70.51, 70.08, 69.52, 59.01, −7.59.

\(2-(4,6\text{-Bis(trimethylsilyl)thiophen-2-yl})\text{decyl-4H-thieno}[2,3-c]pyrrole-4,6(5H)-dione\) (11) To a flame-dried, 100-mL, three-neck flask was added (2-(trimethylstanny)thieno[3,4-b]thiophene-4,6-diyi)bis(trimethylsilane) (0.75 g, 1.676 mmol), 2-bromo-5-decyl-4-H-thieno[2,3-c]pyrrole-4,6(5-H)-dione (0.624 g, 1.676 mmol) and Pd(PPh\(_3\))\(_4\) (97 mg, 0.084 mmol). Degassed toluene (20 mL) and DMF (7 mL) were subsequently transferred via a cannula into the reaction flask. The reaction system was set at 100 °C and stirred overnight. After cooling down to room temperature, the resulting mixture was poured into water (100 mL) and extracted with ethyl acetate (150 mL). The organic phase was collected and concentrated under vacuum to give a brown residue, which was further subjected to silica gel column chromatography with toluene/hexanes (1/2, v/v), yielding 0.56 g of 11 as yellow solid (560 mg, yield 58%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.40 (s, 1H), 7.25 (s, 1H), 3.60 (t, \(J = 8\) Hz, 2H), 1.64 (m, 2H), 1.32-1.25 (m, 14H), 0.87 (t, \(J = 4\) Hz, 3H), 0.43 (d, \(J = 4\) Hz, 18H). \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 163.62, 162.49, 153.70, 150.59, 146.17, 144.83, 140.36, 137.98, 135.24, 130.02, 117.15, 115.81, 38.47, 31.91, 29.56, 29.54, 29.33, 29.20, 28.80, 26.84, 22.72, 14.17, 0.23, −0.62.

\(5\text{-Decyl-2-(4,6-dibromothieno[3,4-b]thiophen-2-yl)-4H-thieno}[2,3-c]pyrrole-4,6(5H)-dione\) (12) 2-(4,6-Bis(trimethylsilyl)thieno[3,4-b]thiophen-2-yl)-5-decyl-4-H-thieno[2,3-c]pyrrole-4,6(5-H)-dione (0.424 g, 0.736 mmol) was dissolved in 5 mL of CHCl\(_3\). Bromine (0.083 mL, 1.62 mmol) was then added via a syringe. The mixture was stirred at room temperature for 30 min, after which the solution was poured into water (100 mL) and extracted with CHCl\(_3\) (150 mL). The organic phase was collected
and concentrated under vacuum to yield a yellow solid (0.434 g, 95% yield). No further purification was processed. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37 (s, 1H), 7.04 (s, 1H), 3.60 (t, $J$ = 8 Hz, 2H), 1.64 (t, $J$ = 8 Hz, 2H), 1.32–1.25 (m, 14H), 0.87 (t, $J$ = 8 Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 163.35, 162.24, 148.77, 146.08, 144.78, 141.57, 139.31, 138.23, 118.25, 114.76, 38.73, 31.89, 29.55, 29.31, 29.21, 28.81, 28.75, 26.86, 22.71, 14.17.

2-(4,6-Bis(3-(2,5,8,11-tetraoxadodecyl)thiophen-2-yl)thieno[3,4-b]thiophen-2-yl)-5-decyl-4H-thieno[2,3-c]pyrrole-4,6(5H)-dione (13) Compound 10 (0.323 g, 0.76 mmol) and 12 (0.15 g, 0.25 mmol) were charged into a dry, 25 mL, three-neck flask, followed by the addition of Pd$_2$(dba)$_3$·CHCl$_3$ (12 mg, 0.011 mmol) and P(o-tol)$_3$ (16 mg, 0.05 mmol). Degassed toluene and DMF (v/v = 3/1, 8 mL) were then added via syringe. The reaction was then set at 80 °C and stirred overnight. After cooling down to room temperature, the reaction mixture was poured into water (100 mL) and extracted with ethyl acetate (150 mL). The organic phase was collected and concentrated to give a brown oil, which was then purified on a silica gel column with an eluent of ethyl acetate/isopropyl alcohol (v/v = 10/1). Compound 13 was obtained as a red oil (0.13 g, 65%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.40 (s, 1H), 7.39 (s, 1H), 7.37 (d, $J$ = 4 Hz, 1H), 7.36 (d, $J$ = 4 Hz, 1H), 7.23 (d, $J$ = 4 Hz, 1H), 7.21 (d, $J$ = 4 Hz, 1H), 4.69 (s, 2H), 4.62 (s, 2H), 3.67–3.58 (m, 24H), 3.49 (m, 2H), 3.33 (s, 6H), 1.61 (t, $J$ = 8 Hz, 2H), 1.29–1.23 (m, 14H), 0.85 (t, $J$ = 8 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 165.93, 164.83, 152.22, 147.42, 146.61, 143.22, 141.09, 139.21, 138.78, 138.23, 133.96, 132.82, 131.37, 128.84, 128.39, 127.51, 126.89, 124.66, 120.39, 118.47, 74.50, 73.21, 73.07, 72.37, 69.78, 69.48, 61.51, 34.44, 32.10, 31.86, 31.76, 31.37, 29.40, 25.26, 16.74.

2-(4,6-Bis(5-bromo-3-(2,5,8,11-tetraoxadodecyl)thiophen-2-yl)thieno[3,4-b]thiophen-2-yl)-5-decyl-4H-thieno[2,3-c]pyrrole-4,6(5H)-dione (14) Compound 13 (58 mg, 0.061 mmol) was dissolved in 10 mL of CHCl$_3$, followed by the addition of ca. 20 g of dry silica gel. NBS (32 mg, 0.18 mmol) was then added. After stirring at room temperature for 30 min, the mixture was filtered on a glass filter. The filtrated silica gel was thoroughly washed with ethyl acetate/methanol (50 mL, v/v=20/1). The filtrate was collected and concentrated to give a red oil, which was then purified on silica gel column with a eluent of ethyl acetate/isopropyl alcohol (v/v = 10/1) to afford the monomeric compound 14 as a viscous red oil (45 mg, 70% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42 (s, 1H), 7.36 (s, 1H), 7.22 (s, 1H), 7.19 (s, 1H), 4.61 (s, 2H), 4.56 (s, 2H), 3.68–3.62 (m, 24H), 3.53 (m, 2H), 3.36 (s, 3H), 3.36 (s, 3H), 1.63 (t, $J$ = 8 Hz, 2H), 1.31–1.25 (m, 14H), 0.87 (t, $J$ = 8 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 163.45, 162.35, 149.31, 144.93, 144.56, 141.31, 138.99, 137.55, 137.27, 136.48, 132.88, 132.71, 132.44, 132.08, 123.13, 121.12, 118.15, 115.45, 112.86, 112.41, 71.88, 70.64, 70.58, 70.56, 70.51, 70.50, 69.89, 66.83, 66.54, 59.00, 38.65, 31.85, 29.51, 29.27, 28.77, 26.80, 22.66, 14.12.

2-(4,6-bis(3-decylthiophen-2-yl)thieno[3,4-b]thiophen-2-yl)-5-decyl-4H-thieno[2,3-c]pyrrole-4,6(5H)-dione (19) Compounds 18 (380 mg, 0.98 mmol) and 12 (176 mg, 0.3 mmol) were charged into a dry,
25-mL, three-neck flask, followed by the addition of Pd$_2$(dba)$_3$-CHCl$_3$ (12 mg, 0.011 mmol) and P(o-tol)$_3$ (16 mg, 0.05 mmol). Degassed toluene (10 mL) was then added via syringe. The reaction was then set at 80 °C and stirred overnight. After cooling down to room temperature, the reaction mixture was poured into water (100 mL) and extracted with ethyl acetate (150 mL). The organic phase was collected and concentrated to give a brown oil, which was then purified on a silica gel column with an eluent of ethyl acetate/toluene (v/v = 1/5). Compound 19 was obtained as a reddish oil (0.16 g, 60%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.41 (s, 1H), 7.39 (s, 1H), 7.37 (d, $J = 4$ Hz, 1H), 7.36 (d, $J = 4$ Hz, 1H), 7.21 (d, $J = 4$ Hz, 1H), 7.19 (d, $J = 4$ Hz, 1H), 3.48 (m, 2H), 1.58 (m, 4H), 1.29–1.23 (m, 51H), 0.84 (m, 9H).

2-(4,6-bis(5-bromo-3-decythiophen-2-yl)thieno[3,4-b]thiophen-2-yl)-5-decyl-4H-thieno[2,3-c]pyrrole-4,6(5H)-dione (20) Compound 19 (160 mg, 0.18 mmol) was dissolved in 10 mL of CHCl$_3$, followed by the addition of ca. 5 g of dry silica gel. NBS (64 mg, 0.36 mmol) was then added. After stirring at room temperature for 30 min, the mixture was filtered on a glass filter. The filtrated silica gel was thoroughly washed with ethyl acetate/toluene (v/v = 1/7, 50 mL). The filtrated was collected and concentrated to give a red oil, which was then purified on silica gel column, with an eluent of ethyl acetate/toluene (v/v = 1/6), to afford the monomeric compound 20 as a viscous reddish oil (140 mg, 70% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44 (s, 1H), 7.37 (s, 1H), 7.24 (s, 1H), 7.21 (s, 1H), 3.49 (m, 2H), 1.58 (m, 4H), 1.29–1.23 (m, 51H), 0.84 (m, 9H).

General procedure of bis(pinacolato)diboron-mediated homopolymerization (P1 and P2). A 25 mL, flame-dried two neck flask, filled with dry N$_2$, was charged with the dibrominated macromonomer (0.05 mmol), Pd(dppf)Cl$_2$ (CH$_2$Cl$_2$ adduct) (3 mg), K$_3$PO$_4$ (50 mg) and bis(pinacolato)diboron (26 mg). Degassed toluene/DMF (v/v = 4/1) (6 mL) was introduced into the reaction flask via a syringe. The reaction was set at 110 °C overnight. Afterwards, the reaction mixture was cooled to room temperature, and added dropwise into 500 mL of methanol. The precipitate was collected with a cellulose thimble, which was subjected to Soxhlet extraction with methanol for 24 h, acetone for 8 h, hexane for 5 h, and CHCl$_3$ for 5 h, respectively. The chloroform fraction was obtained as a purple solid. P1 (30 mg, ~60% yield) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.72–6.64 (4 H, br), 4.61–4.19 (4 H, br), 4.18–2.98 (17 H, br), 1.83–0.71 (br). P2 (20 mg, ~40% yield) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.72–6.64 (4 H, br), 4.2–3.2 (2 H, br), 1.83–0.71 (br).

Synthesis of CC1. A 25 mL, flame-dried two neck flask, filled with dry N$_2$, was charged with 14 (100 mg, 0.09 mmol) and bis(trimethylstannyl)thiophene (38 mg, 0.09 mmol), followed by the addition of Pd$_2$(dba)$_3$ (CHCl$_3$ adduct, recrystallized from acetone) (3 mg) and P(o-tol)$_3$ (12 mg). Degassed dry toluene (5 mL) was then introduced into the reaction flask via a cannula. The reaction was then set at 100 °C for 24 h. Afterwards, the reaction mixture was allowed to cool to room temperature, and added dropwise into 500 mL of methanol. The precipitate was collected with a cellulose thimble, which was then subjected to Soxhlet extraction with methanol for 24 h, acetone for 7 h, hexane for 5 h, and CHCl$_3$.
for 3 h, respectively. The chloroform fraction was obtained as a purple-blue solid after precipitation in methanol (80 mg, ~85%). $^1$H NMR (400 MHz, CDCl$_3$). $\delta$ 7.72–6.7 (6 H, br), 4.61–4.19 (4 H, br), 4.18–2.98 (17 H, br), 1.83–0.71 (br).
4.6 References

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Chapter 5

On the influence of donor-acceptor cross conjugation of conjugated polymers upon charge generation in polymer photovoltaics*

ABSTRACT Two-dimensional donor-acceptor (D-A) conjugated polymers, where the acceptor segments are configured as pendant groups on the polymer backbone consisting solely of donor moieties, naturally exhibit a character of donor-acceptor cross conjugation. In contrast, in standard alternating donor-acceptor copolymers, there is linear conjugation between the donor and acceptor moieties throughout the backbone. Inherent to such a 2-D configuration is the weak electronic communication between the cross-conjugated donor and acceptor moieties. This promotes a unique possibility where upon photoexcitation, the nature of cross conjugation might enable the formation of weakly-bound excitons, which may further lead to enhanced charge generation. This chapter describes the specific deployment of a 2-D polymer featuring a distinct cross conjugation between the thieno[2,3-c]pyrrole-4,6-dione acceptor and the thieno[3,4-b]thiophene donor moieties, with thiophene spacers in the backbone. Preliminary evaluation of the external quantum efficiency of the single-component device based on this polymer suggested, to our surprise, that the exciton binding energy is unambiguously higher than that of the typical linearly-conjugated polymers. The experimental observation is supported by extensive quantum chemical calculations on a series of cross- and linear-conjugated dimers. Furthermore, quantum chemical calculations suggest that the higher exciton binding energy of cross-conjugated polymers is most likely related to strong electron localization in their excited state, leading to a shorter hole-electron distance.

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5.1 Introduction

Bulk-heterojunction polymer solar cells (BHJ-PSCs)\(^1\) have undergone remarkable progress in the past two decades, with notable contribution from the research on one-dimensional linear-conjugated alternating donor-acceptor copolymers. In these polymers, the donor and acceptor moieties are configured alternatively via linear conjugation.\(^2,3,4,5\) On the other hand, performance progress has also been achieved for BHJ-PSCs based on two-dimensional conjugated polymers, where the acceptors are installed as pendant groups on the donor backbone via cross conjugation, as represented by a handful of examples.\(^6,7,8,9,10,11\) In this context, early explorations mostly employed thienylenevinylene side chains in conjunction with polythiophene backbones. In another strategy towards two-dimensional conjugated polymers, triphenylamine units were incorporated into the polymer backbone, taking advantage of the relatively low HOMO and high charge carrier mobility of triphenylamine conjugates. Such a design has endowed the polymer with a decent hole mobility and PV devices with a power conversion efficiency of 4.37% when applied in solar cells in combination with [70]PCBM.\(^6\) In recent years, concurrent with the active research on alternating donor-acceptor copolymers, new 2-D polymers have emerged with better light-harvesting capacity and improved intermolecular packing, continuously enhancing solar cell performances. For example, by systematically investigating the acceptor and side-chain effect, Peng et al. have reported an efficiency of 5.65%, which was attributed to its good light absorption, improved charge carrier mobility and well-defined phases in the photovoltaic blend with [70]PCBM.\(^11\) Note that the available structural designs of 2-D donor-acceptor conjugated polymers have commonly been based on an ethylenic linker between the donor backbone and the pendant acceptor moiety, in order to maximize the planarity of the conjugation system.

Compared to the extensive studies on D-A linear-conjugated polymers from various perspectives, the area of fundamental aspects remains virtually unexplored for two-dimensional D-A cross-conjugated donor polymers. Furthermore, in spite of the substantial optimizations on polymer structures in the past decade, the photovoltaic performance of PSCs based on 2-D polymers was still notably lower than that of linear alternating D-A conjugated counterparts, even when the same donor and acceptor moieties were employed. In this respect, deeper fundamental understanding on the photoelectronic properties of 2-D cross conjugated polymers is highly valuable.

The current chapter describes our investigations of the exciton binding energy characteristics of 2-D donor-acceptor cross-conjugated donor polymers. This work is inspired by some inherent characteristics of donor-acceptor cross-conjugated polymers. With some preliminary examinations via quantum chemical calculations on some oligomers comprising of a donor backbone and cross-conjugated pendant acceptors, we found that the HOMO of such oligomers is effectively delocalized along the entire backbone, while the LUMO is localized on the acceptor. Also note that a donor-acceptor
cross conjugation naturally features a weaker D-A electronic communication, in comparison with the linear conjugation counterpart. Based on this premise, an interesting possibility was postulated: upon photoexcitation of such a 2-D polymer, the hole-electron pair of the photo-generated exciton might be more separated, due to an enhanced hole delocalization and consequently its weaker communication with the acceptor part. A more separated hole-electron pair would lead to a lower exciton binding energy, enhancing the efficiency of charge generation. In pursuit of testing this hypothesis, we specifically designed a 2-D polymer (CC1, as shown in Scheme 1) featuring distinct cross conjugation between the polythiophene donor backbone and the pendant thieno[2,3-c]pyrrole-4,6-dione acceptor moieties, bridged with a thieno[3,4-b]thiophene moiety. In virtue of the proven concept that TEG chains increase the dielectric constant of organic materials, which may contribute to enhanced dielectric screening,\textsuperscript{12,13} we also installed TEG chains instead of alkyl chains as solubilizing side chains. The initial idea behind the design presented here was to obtain a material with reduced exciton binding energy upon photoexcitation, which should be observable when the polymer is subjected to proper photoelectronic experiments. More specifically, we employ here quantum efficiency experiments on actual single-component PV devices, to initiate a direct study of the exciton binding energy characteristics of our organic material. This protocol is motivated by a consensus, that accessing the electrical gap energy ($E_{\text{elec}}$, also referred to as transport gap) of the subject material is the key to obtain the exciton binding energy ($E_b$), given $E_b = E_{\text{elec}} - E_g$, where the optical gap $E_g$ can be readily determined from absorption spectroscopy measurements. In 1965, Castro et al. discovered that high-energy photons could generate, in anthracene crystals, mobile charges by a mechanism characteristic of an intrinsic process,\textsuperscript{14} which further enabled them to estimate the conduction band of anthracene. This specific protocol was later applied to the study of excitons in poly(para-phenylenevinylene), which yielded an exciton binding energy of 0.9±0.15 eV.\textsuperscript{20} Over the years, direct photocurrent generation with high-energy photons has been observed and studied with photoactive materials, from both experimental and theoretical perspectives.\textsuperscript{15,16} A systematic study of quantum efficiency on a series of representative conjugated polymers was conducted by Li et al. in 2016,\textsuperscript{19} where it was confirmed that with increased excitation energy, external quantum efficiency (EQE) spectra of pristine polymer films showed a transition from exciton to free-charge generation. This transition was observed as a steep increase of EQE when the excitation photon energy reached the electrical gap.

5.2 Results and discussion

**Polymer design and synthesis.** Within the present design, we utilized thieno[3,4-b]thiophene instead of an ethylenic linker as the donor-acceptor bridge. Such consideration not only furnishes the donor-acceptor fragment with good coplanarity, but also readily takes advantage of the thiophene chemistry.
Our choice of the acceptor moiety is based on a pre-evaluation of the frontier orbitals of a series of cross-conjugated monomers based on thieno[3,4-b]thiophene (for discussion details, see Chapter 3). The necessity for this pre-evaluation is brought forward by (i) the lack of systematic study on cross-conjugation systems, and (ii) our assumption that D-A cross-conjugation, due to its nature of weak donor-acceptor electronic communication, would probably have a relatively small influence when bandgap optimization is under consideration. To this end, we selected thieno[2,3-c]pyrrole-4,6-dione as the acceptor, with some extra concern on the potential synthetic challenge. The structure of the resulting polymer (CC1, for synthesis details, see Chapter 4) is shown in Figure 1.

![Figure 1](image)

**Figure 1.** Chemical structure of polymer CC1, comprising a polythiophene backbone, thieno[2,3-c]pyrrole-4,6-dione acceptor, and a thieno[3,4-b]thiophene bridge.

**Optoelectronic properties.** The UV-vis absorption of CC1 as a CHCl₃ solution is shown in Figure 1(A). Despite our different strategy of using thieno[3,4-b]thiophene as the backbone-acceptor linker, the important aspects of the absorption are similar to all previously reported 2-D cross conjugated polymers, i.e., CC1 showed a notably blue-shifted absorption maximum relative to 1-D donor-acceptor alternating conjugated polymers of similar optical bandgaps, featuring pronounced absorption of the visible photons. The absorption bands peaking at 361 nm and 536 nm are ascribed to the π-π* transition in the pure-donor backbone and the donor-to-acceptor intramolecular charge transfer, respectively. The thin-film absorption showed a remarkable ~140 nm red shift of the absorption edge relative to that of solution, benefiting from the strong π-π stacking interaction of CC1 in the solid state.
Figure 1. (A) Normalized UV-Vis absorption spectra of polymer CC1 in CHCl3 solution and as a pristine film. The external quantum efficiency of a PV device based on an active layer comprising of solely CC1 is also included (red curve). (B) A bar-chart comparison of exciton-binding energies between CC1 (red bar) and a few other polymer examples (grey bars) studied elsewhere.19 The presented exciton binding energies were extracted with the same method. (C) The chemical structures of MEHPPV, PTB7, PCDTBT, PCE10 and P3HT.
To validate the initial hypothesis that donor-acceptor cross conjugation may potentially lead to a reduced exciton binding energy upon photoexcitation, we employed the experimental evaluation proposed by Castro\textsuperscript{21} and Chandross \textit{et al.}\textsuperscript{20} and developed by Li \textit{et al.}\textsuperscript{19} where the external quantum efficiencies of pristine polymers films are directly used to extract the exciton binding energy.\textsuperscript{19,20,21} The EQE profile of a device(ITO/PEDOT:PSS:CC1/LiF/Al) with an active layer comprising solely CC1 is shown in Figure 1(A). The measured EQE starts with an onset at the low-energy side. This onset energy is equal to the optical bandgap of the thin film, confirming the excitation from ground state S\textsubscript{0} to the first singlet excited state S\textsubscript{1}. As the photon energy increases, the EQE profile shows a pseudo-plateau region where the EQE values are slightly varied, which corresponds to the excitation to S\textsubscript{1} state and its higher vibrational levels. Note that the flatness of this pseudo-plateau region seems to be related to the intermolecular packing characters of the film, based on our observation on a pseudo-plateau for an as-prepared P3HT film and an actual plateau for an annealed P3HT thin film.

Thin films of pristine CC1 responded weakly towards thermal annealing. Nevertheless, as the photon energy continues to increase, a clear ~10-fold enhancement of the EQE appeared, the onset of which corresponds to the transport gap.\textsuperscript{19} From this, the exciton binding energy was calculated as the interval between the first and second onset. We found a value of 1.07±0.06 eV for CC1, with the error based on the statistics of 12 devices. We compared in Figure 1(B) the acquired value to those of a few linearly conjugated D-A polymers and MEHPPV as well as P3HT (as listed in Figure 1(C)). It is worth noting that in spite of the different chemical structures of the presented linearly conjugated polymers, their exciton binding energies seem to be quite close to each other, taking the error bars into consideration. Interestingly, the exciton binding energy of CC1 is unambiguously higher than most of the other polymers, except MEHPPV. This observation seems to contradict our postulate and it suggests that donor-acceptor cross conjugation in a polymer adversely affects exciton delocalization and dissociation in comparison with linear conjugated polymers. Hence, it would disfavor subsequent charge generation.
Quantum chemical evaluations. The above experimental result indicates that the presented 2-D cross conjugation design does not enhance the photogeneration of free charge carriers, as would be desirable for polymer photovoltaics, caused by a relatively high exciton binding energy of CC1. In view of the contrasting observation involving CC1 and the other representative linearly conjugated polymers, we were inspired to compare and quantify the exciton binding energies of cross-conjugated oligomers and their linearly conjugated counterparts, from a quantum chemical perspective. To do this, we constructed a series of donor-acceptor cross-conjugated oligomers and their linearly conjugated counterparts, as shown in Figure 2(B). Note that the thieno[2,3-c]pyrrole-4,6-dione acceptor in CC1 needs to be transformed into thieno[3,4-b]pyrrole-4,6-dione in order to formulate a linear conjugation along the backbone. The exact structures used for the quantum chemical calculations are shown in Figure 2(B). For comparison, we take the vertical exciton binding energy \((E_{b}^{exc})_{vert}\) as the observable, defined by eq.(1) which is derived in consideration of the reaction \(D^* + D \rightarrow D^+ + D^-\), where \(D^*, D, D^+\) and \(D^-\) refer to the lowest excited-state, ground-state, cation and anion forms of molecule \(D\), respectively:

\[
(E_{b}^{exc})_{vert} = E(D^* + D^-) - E(D^*) - E(D) \tag{1}
\]

where \(E(D^*), E(D^-), E(D^*)\) and \(E(D)\) represent the total energies of the vertical cationic state, vertical anionic state, vertical first excited state and ground state of the subject molecule. The calculation results of the total energies are included in Table 1, and the exciton binding energies are shown in Figure 2(A).
Figure 2. (A) Calculated exciton binding energy comparison of four pairs of cross-conjugated versus linear-conjugated dimers. (B) The chemical structures used in the quantum chemical calculations.
Table 1. Calculated total energies of the vertical cationic and anionic states, vertical first excited state and ground state of subject molecules, and deduced exciton binding energies \( (E_b^{\text{exc}})_{\text{vert}} \). For BDT-cross and BDT-linear, total energies of ground-state, vertical cationic and anionic states, charge separated state \( (E_{\text{cs}}) \) and excited state \( (E^*) \) were calculated. Total energies in atomic units. Exciton binding energies were calculated from the total energies and converted to eV (by multiplying 27.211).

<table>
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<th>( E(D^-) ) (eV)</th>
<th>( E(D^{*}) ) (eV)</th>
<th>( E(D) ) (eV)</th>
<th>( (E_b^{\text{exc}})_{\text{vert}} ) (eV)</th>
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<tr>
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<td>−7389.5356</td>
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<tr>
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<td>−7389.6193</td>
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<td>−7389.4654</td>
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<table>
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<th>( E(D^+) ) (eV)</th>
<th>( E(D^-) ) (eV)</th>
<th>( E_{\text{cs}} ) (eV)</th>
<th>( E^* ) (eV)</th>
<th>( (E_b^{\text{exc}})_{\text{vert}} ) (eV)</th>
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<td>0.64</td>
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</table>

*Energies of BDT-cross and BDT-linear were calculated in a dielectric medium of propanoic acid (dielectric constant \( \varepsilon_r \approx 3.5 \)). Charge separated (CS) states were determined as the difference between the ionization potential of the cation and the electron affinity of the anion in the same configuration as in its respective excited state. Finally, the exciton binding energy was estimated as the difference between \( E_{\text{cs}} \) and \( E^* \).

In spite of the structure-to-structure difference, and of the qualitative nature of the in-vacuum calculations on dimers, these results tend to suggest that regardless of the donor/acceptor choice and D-A bridging strategies, donor-acceptor cross conjugation results in an increased exciton binding energy compared to the linear conjugation counterpart. While directly correlating the exciton binding energy of organic materials with specific photoelectronic properties remains challenging experimentally, quantum chemical studies can help in understanding the relationship between structure and exciton binding energy in unique perspectives. For example, exciton binding energies of cross- and linear-conjugated molecular systems will be strongly correlated to some of their excited state properties, such as the electron density displacements upon excitation and the subsequent charge separation. To this end, we quantified the charge densities of the ground state and first excited state of a dimer segment from CC1 (Figure 3(a)) and its linear conjugated counterpart (LC1), constructed with the same thiophenic and thienothiophenic units. Herein the construction of a reasonable linear conjugated counterpart is only possible when the thieno[2,3-c]pyrrole-4,6-dione moiety in CC1 is transformed into thieno[3,4-b]pyrrole-4,6-dione (Figure 3(c)). We regarded such a transformation viable in consideration of the same
atomic constitution and almost identical electron deficiencies of thieno[2,3-\textit{c}]pyrrole-4,6-dione and thieno[3,4-\textit{b}]pyrrole-4,6-dione.

Figure 3. (a) Dimer structure of the building blocks from \textbf{CC1}, where the conjugation moieties are numbered from 1 to 10. (b) The electron density shift on each conjugation moiety from ground state to excited state of \textbf{CC1}. The numbers in (b) correspond to those in (a). (c) The linear-conjugated counterpart of structure (a), based on the same electron donor and acceptor, named as \textbf{LC1} herein. (d) The electron density shift on each conjugation moiety from ground state to excited state of structure (c). The numbers in (d) correspond to those in (c). Note that for both (b)
and (d), a positive value means a gain of electron density and a negative value means a loss of electron density during the excitation process.

The result is visualized by grouping the atoms per conjugation moieties, as shown Figure 3(a) and 3(c), such that each conjugation unit is observed as a contributor to charge displacement upon excitation. For both the cross-conjugated dimer and its linear-conjugated counterpart, there is a noticeable electron transfer from some of the electron-donating moieties to the thienopyrrole-4,6-dione moieties, as clearly indicated by the electron density gains of segments 3 and 8 in Figure 3(b) and segments 1 and 6 in Figure 3(b). A closer look discloses quite different scenarios. In the case of the CC1 dimer, the electron donation predominantly stems from thiophenic units 4-6, with some extra contribution from unit 1. Probably due to the weak electronic communication nature of cross conjugation, there is no observable delocalization of electrons, which are almost ubiquitously localized on the small acceptor units. On the other hand, the thienopyrrole-4,6-dione units in the linear conjugated dimer accept electrons from the thiophenic units at the end, suggesting an apparent donor-acceptor character enabled by linear conjugation. A contrasting feature between Figures 3(b) and 3(d) is the notable delocalization of electrons along the conjugation length from segments 1 to 6 in the linear conjugated dimer, arising from efficient electronic coupling involving the thienopyrrole-4,6-dione and thiophenic units. It is noteworthy that our findings are in line with the work by Heeger et al.,\textsuperscript{22} on a specific linear conjugated donor-acceptor system. There, it was pointed out that despite the strong electron withdrawing capability of the acceptor unit, it does not act solely as an acceptor, but behaves collectively with the neighboring electron-rich moieties as one delocalized segment which might favor photoexciton splitting. Overall, the above analysis implies that good charge delocalization tends to contribute to a lower exciton binding energy, likely benefitting from a spatially more separated hole-electron pair, which is qualitatively shown in Figures 3(b) and 3(d).
5.3 Conclusions

The influence of cross conjugation on the charge generation properties of 2-D conjugated polymers was evaluated experimentally and through quantum chemical calculations. The investigation was conducted by specifically designing a 2-D cross-conjugated thieno[3,4-b]thiophene donor/thieno[2,3-c]pyrrole-4,6-dione acceptor structure, and further comparing to its linear conjugated counterpart. A few other cross-conjugation/linear-conjugation structures were also compared with the help of quantum chemical calculations. Preliminary evaluation of the external quantum efficiencies of single-component devices suggests that such a 2-D configuration resulted in a relatively high exciton binding energy compared to a series of representative polymers based on linear conjugation throughout the π system. The present study is supported by a quantum chemical comparison of the exciton binding energies of the dimer fragment of the 2-D polymer and a linear conjugated dimer based on the same donor and acceptor moieties. The calculations showed that the 2-D configuration exhibited a higher exciton binding energy relative to the linear configuration. This clearly echoes the above extensive experimental results. The present study does not conclusively indicate a relatively high exciton binding energy for 2-D cross-conjugated polymers, in a universal sense. For that, systematic studies on various structures are necessary to obtain a deeper understanding of this special type of conjugated polymers. In virtue of the currently limited understanding on the fundamental perspectives of 2-D cross conjugated polymers, our study will hopefully contribute to the rational design of conjugated polymers in the future.
5.4 Experimental

**Materials and devices.** All reagents were purchased from commercial sources and were used without further purification unless indicated otherwise. UV/Vis measurements were conducted on a Perkin Elmer Lambda 9000 spectrometer in 1-cm quartz cuvettes with concentrations of 0.03–0.1 mg/mL in CHCl₃. The devices for EQE measurements were fabricated based on indium tin oxide (ITO) coated glass substrates. These substrates were precleaned with deionized water, CMOS grade acetone, and then isopropanol, respectively, each for 15 min. Possible organic residues were removed by UV-ozone cleaning for 20 min. A layer of PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate), VP Al4083, H. C. Stark) (thickness ~ 60 nm) was spin-cast on top at 1500 rpm for 50 s. After being baked at 140 °C for ~10 min, the substrates were transferred into a nitrogen-filled glovebox (<0.1 ppm of O₂ and H₂O). Atop that polymer solutions were spin-coated in a N₂-filled glovebox from o-DCB solution (600 rpm for 5 s and 400 rpm for 120 s). The thickness of the photoactive layers was about 100 nm. Finally, LiF/Al (1 nm and 100 nm, respectively) were thermally evaporated at a pressure of < 10⁻⁶ Torr on top of the organic layer to make the sandwiched structure ITO/PEDOT:PSS/active layer/LiF/Al.

**External quantum efficiency measurements.** EQE measurements were performed with a home-built setup equipped with 1000 W Xenon Arc Lamp (Newport) as light source, monochromator (Zolix), optical chopper (ThorLabs), lock-in amplifier (Standard Research SR830), current amplifier (Standard Research SR570), and calibrated Silicon and Germanium detectors (ThorLabs). The beam spot used for EQE measurement was focused and collimated with a set of optical lenses. The EQE spectra were measured at zero bias.

**Quantum chemical calculations.** Geometries of all structures except BDT-cross/linear were optimized using DFT (B3LYP/6-31G**) with the program GAMESS-UK. Vertical excitation energies were calculated using time-dependent DFT (TD-DFT). The lowest 10 vertical excitation energies were calculated using TD-DFT (B3LYP/aug-cc-pVDZ) with DALTON. Geometry optimizations and electron densities of BDT-cross/linear were calculated at Density Functional Theory (DFT) level by using the B3LYP exchange correlation functional in combination with the cc-pVDZ basis set as implemented in the Gaussian 09 software package. Lowest singlet excited states were calculated using TD-DFT by using the long-range corrected functional CAM-B3LYP with the cc-pVDZ basis set (also as implemented in Gaussian 09). In the modelling of BDT-cross/linear structures, a polarisable continuum model was used with propanoic acid as the solvent. For a given structure/configuration, local excited states of the dimers were computed and characterized using TD-DFT. The charge density shifts upon excitation were estimated using a Mulliken population analysis of the ground state and excited state densities.
5.5 References


6.1 On the search for the exciton binding energy-structure relationship of conjugated polymers

By and large, the study presented in this thesis has made two establishments: (1) In a donor-acceptor cross-conjugated polymer with thieno[2,3-c]pyrrole-4,6-dione as the acceptor, the hole-electron distance is probably not increased relative to the linear-conjugated case. Hence, a decreased exciton binding energy was not observed (contrary to intuition). (2) Theoretically, electronically effective and spatially small acceptor moieties as the pendant groups do not decrease exciton binding energies relative to their respective linear-conjugated counterparts. These observations contribute to the principles of designing low \( E_b \) polymers. They have inspired us to derive reasonable hints to the proper design of the next-phase polymers with low exciton binding energies. Below, we briefly discuss these inspirations with two perspectives.

(i) We learn forthwith from Chapter 5 that to attain a reduced \( E_b \), the conjugated system should be sufficiently capable to delocalize the charge (the electron, in our case), rather than to localize it. In spite of the extremely limited number of reports on the relationship between \( E_b \) and chemical structures, it is worth noting that a few reports have highlighted the contribution of extensive charge delocalization to efficient charge generation in polymer:fullerene blends.\(^1\)\(^2\)\(^3\)\(^4\) In this context, we propose that simply considering the influence of conjugation length of donor moieties (i.e. the delocalization of the excitonic hole) in conjugated polymers on their exciton binding energy characteristics may be interesting. To do this, we constructed three linear-conjugated dimer structures in series and subjected them to quantum chemical calculations. The structures are shown in Figure 1.
These calculations were conducted in a dielectric medium of propanoic acid. Details of the quantum chemical calculations are the same as those of BDT-cross/linear (see Table 1, Chapter 5).

The calculation results indicate that when the number of conjugated thiophene units increased from 2 to 4 (corresponding to structures T2, T3 and T4, respectively), the exciton binding energy sequentially decreased from 0.71 eV for T2, to 0.65 eV for T3, and finally to 0.59 eV for T4. These results nicely point to the possibility to decrease the intrinsic exciton binding energies of conjugated polymers, simply by optimizing the length of continuously conjugated donor (or acceptor) moieties. Certainly, in designing actual polymers, it is paramount to seek a balance between the conjugation length of donor moieties and other molecular/material properties, such as the optical bandgap, regio-regularity, steric hindrance, solubility, etc.

(ii) Another potentially interesting angle to look at the exciton binding energy-structure relationship, regards the physical size of the electron-withdrawing moieties. This perspective, by nature, is precisely the same as discussed in (i), since a spatially bigger conjugated moiety would allow the electron to be delocalized to a larger extent. In this context, the cross-conjugation strategy does not necessarily become void, given the utilization of a properly sized acceptor moiety.

Ubiquitously, preceding investigations on polymer structures had explicit goals of tuning energy levels and morphologies. This has led to a significant understanding on the property dependence on structure. Due to the feasibility of effectively tuning these properties with various small acceptor moieties, spatially sizable acceptors rarely received dedicated attention, with only a couple of examples. With the appreciation for the unique possibility where donor-acceptor cross conjugation reduces the intrinsic exciton binding energy of conjugated polymers, we have conducted a proof-of-concept \( E_b \) evaluation with the help of quantum chemical calculations on the structures shown in Figure 2.
Figure 2. Structures of two calculated dimer structures, featuring differently sized acceptor moieties. **CC-sa** means cross-conjugation-small-acceptor, and **CC-ba** means cross-conjugation-big-acceptor. These calculations were conducted in a dielectric medium of propanoic acid. Details of the quantum chemical calculations are the same as those of BDT-cross/linear (see Table 1, Chapter 5).

Despite the difference in the electron-withdrawing capabilities, we focused on the size effect of the acceptors in cross-conjugated systems. When positioned in a dielectric medium of propanoic acid, **CC-sa** was calculated to have an exciton binding energy of 0.73 eV. When a spatially more sizable acceptor was employed, the exciton binding energy of such a dimer structure drastically reduced to 0.45 eV.\(^5\)

Although we do not provide a detailed analysis on the electronic structures of these molecular structures, as we did in Chapter 5, this contrasting result seems to indicate that there is spacious room to play in for the exploration of the potential of cross-conjugated donor-acceptor systems.

Looking back upon the path we have been on, we have confirmed, based on several evidences, that charge delocalization, rather than localization, most likely constitutes one of the fundamental principles for the design of conjugated polymers with intrinsically low exciton binding energies. Finally, we hope for a proper utilization of the donor-acceptor cross-conjugation principle in more rational, systematic, and productive future studies.
6.2 References

5 Unpublished data.
Summary

Organic materials with intrinsically low exciton binding energy are not only important for conventional bulk-heterojunction polymer photovoltaics, they hold great promise for the development of organic solar cells based on a single-component photoactive layer, where bound hole-electron pairs must spontaneously dissociate to form free and mobile charges at environment temperatures. This has motivated us to look into, particularly, how the nature of conjugation can affect the exciton binding energy characteristics of conjugated polymers. In a non-trivial way, the chemical purity of conjugated polymers also has a strong effect on the nature (the quality) of the conjugated system. Thus, the chemical quality and the (photo)physical properties of all conjugated polymers benefit from synthetic procedures that lead to structurally pure products. To this end, we have investigated one-pot Suzuki-Miyaura homopolymerization that involves in-situ borylation/cross coupling of dibrominated donor-acceptor conjugated macromonomers, in contrast to the standard Stille copolymerization of organostannanes and aryl halides. Especially, we show how this synthetic strategy behaves when the polymer has incorporated 2,5,8,11-tetraoxadodecyl (TEG) chains, which is commonly employed in order to increase the dielectric constant of organic semiconductor materials.

Chapter 2 aims at obtaining high-quality donor-acceptor conjugated polymers via a one-pot Suzuki-Miyaura homopolymerization that involves in-situ borylation/cross coupling of dibrominated donor-acceptor conjugated macromonomers. This polymerization strategy is in contrast to the standard Stille copolymerization of, specifically, dithienosilole and isoindigo monomers. Reaction kinetics investigation revealed that bis(pinacolato)diboron promotes an efficient polymerization. The homopolymer showed a blue-shifted light absorption compared to the Stille copolymer, which was rationalized by quantum chemical calculations of a series of oligomers containing various donor-acceptor configurations. The calculations suggested that the homopolymerization of asymmetrical macromonomers likely introduced both acceptor-acceptor and donor-donor segments into the backbone. The acceptor-acceptor segment is found to contribute mostly to the blue-shift of the maximum absorption wavelength. Furthermore, detailed analysis of MALDI-TOF (matrix-assisted laser-desorption ionization-time of flight) mass spectra of these two polymers indicated that while the homopolymer is well defined, the Stille copolymer is end-capped mostly with the dithienosilole moieties and/or methyl groups, implicating that destannylation and methyl transfer are the most-likely chain-termination pathways that limit high molecular weight. This is in sharp contrast to the homopolymerization, where chain-terminators are required to control the molecular weight for obtaining soluble material.
In Chapter 3, we have systematically studied the electronic properties of donor-acceptor cross-conjugation systems. This is done by subjecting a series of specially designed D-A cross-conjugated monomers/dimers to quantum chemical calculations. More specifically, in these conjugated polymers, the acceptor moieties are configured as pendant groups of the donor backbone, \textit{via} a distinct cross conjugation. We conceived that a conjugated backbone consisting of pure donor moieties introduces an enhanced delocalization of the highest occupied molecular orbital (HOMO) of the polymer, while cross-conjugated acceptors lead to a well localized lowest unoccupied molecular orbital (LUMO). Furthermore, these features might synergistically yield an increased hole-electron distance, which could result in a relatively low exciton binding energy when compared to a conjugated analogue with linear donor-acceptor (D-A) conjugation. This chapter first discusses structural optimization based on theoretical calculations on a series of monomers. In the end, we also directly compared the exciton-binding energy characteristics of a prototypical donor-acceptor cross-conjugation dimer and its linear-conjugation counterpart.

The work in Chapter 3 enabled us to rationally design a prototypical D-A cross-conjugated polymer, of which the synthesis is described in Chapter 4. Note that TEG side-chains were employed in the designed polymer. This polymer featured a distinct cross conjugation between the thieno[2,3-c]pyrrole-4,6-dione acceptor and the thieno[3,4-b]thiophene donor moieties, with thiophene spacers in the backbone. It was found that in spite of efficient chain growth, the as-presented one-pot Suzuki-Miyaura homopolymerization (see Chapter 2) persistently introduced unassignable impurities to the polymer (P1). Although an exact explanation was not found yet, it was hypothesized that the oxygen atoms in the TEG chains may chelate the boron atoms in the system of Suzuki-Miyaura homopolymerization. This hypothesis was supported by an experiment with a control polymer (P2) where alkyl chains were employed as solubilizing side chains, where the problem with P1 was well eliminated, as evidenced by our mass spectra analysis. Stille copolymerization was used to generate the desired 2-D conjugated polymer (CC1). This work hints to previously unexpected, but important and negative aspects of bis(pinacolato) diboron-promoted homopolymerization leading to structural imperfections, which might limit its application scope.

The successful syntheses have subsequently allowed us to actually study the influence of donor-acceptor cross-conjugation on the exciton-binding energy characteristics of conjugated polymers. A combined device physics and quantum chemical study of such a 2-D polymer (CC1), with a special focus on exciton binding energy, is described in Chapter 5. Preliminary evaluation of the external quantum efficiency of this polymer suggested, to our surprise, that the exciton binding energy is unambiguously higher in cross-conjugated donor-acceptor systems than that of the typical linearly-conjugated polymer analogues. The experimental observation is supported by extensive quantum chemical calculations on a series of cross-conjugated and linear-conjugated dimers. Furthermore, quantum chemical calculations
suggest that the higher exciton binding energy of cross-conjugated donor-acceptor polymers is most likely related to strong electron localization in their excited state, leading to a shorter hole-electron distance. Further, these results have inspired us with some potentially interesting perspectives, from which we see the possibility to actually reduce the exciting binding energy of conjugated polymers. These inspirations are briefly discussed in Chapter 6.
Samenvatting

Organische materialen met intrinsieke lage excitonbindingsenergie zijn niet alleen belangrijk voor conventionele bulk-heterojunctie polymere fotovoltaïsche cellen, ze zijn veelbelovend voor het ontwikkelen van een nieuwe soort organische zonnecel. Dat is een organische zonnecel die een fotoactieve laag heeft die uit slechts één halfgeleider bestaat, die bij omgevingstemperatuur in staat is direct na absorptie van licht vrijwel ongebonden elektron-gatparen te vormen, vrije en mobiele ladingen. Dit motiveerde ons om nauwkeurig naar de aard van conjugatie en het effect van conjugatie op excitonbindingsenergie in geconjugeerde polymeren te kijken. Op een meer triviale manier heeft de chemische zuiverheid van geconjugeerde polymeren ook een sterk effect op de aard (en de kwaliteit) van het geconjugeerde systeem. De chemische kwaliteit en de fotofysische eigenschappen van alle geconjugeerde polymeren worden in hoge mate bepaald door de synthetische procedures door middel waarvan ze gemaakt worden. Structureel schonere producten hebben betere eigenschappen. Daartoe hebben we onderzoek gedaan naar één-pot Suzuki-Miyaura homopolymerisaties waarbij in-situ borylering/kruiskoppeling van gedibromeerde donor-acceptor geconjugeerde macromonomeren plaatsvindt. De resultaten werden vergeleken met die van de standaard Stille co-polymerisaties van organostannananen en aryl halides. In het bijzonder laten we zien hoe de deze synthesestrategie beïnvloed wordt door ingebouwde 2,5,8,11-tetraoxadodecyl (TEG) ketens, welke doorgaans toegepast worden om de dieëlektrische constante van een organische halfgeleidend materiaal te vergroten.

aanemelijke ketenafsluitroutes zijn en dat deze afsluitroutes het bereiken van een hoog moleculair gewicht in de weg staan. Dit in tegenstelling tot homopolymerisaties, waar ketenafsluiters juist een vereiste zijn voor het beheersen van het molecuulgewicht en zo het verkrijgen van een oplosbaar materiaal.

In hoofdstuk 3 wordt een systematische studie beschreven naar de elektronische eigenschappen van donor-acceptor kruis-geconjugeerde systemen. Dit is uitgevoerd door een serie speciaal ontworpen D-A kruis-geconjugeerde dimeren bloot te stellen aan kwantumchemische berekeningen. Anders dan gewoonlijk zijn bij deze geconjugeerde polymeren de acceptorfunktionaliteiten geconfigureerd als aanhangende groepen van de donor hoofdketen, en wel specifiek via kruis-conjugatie. We vonden dat wanneer een geconjugeerde hoofdketen uit enkel donorfunktionaliteiten bestaat, het polymer een verbeterde delocalisatie van de hoogste bezette moleculaire orbitaal (HOMO) vertoonde. Deze kenmerken zouden kunnen leiden tot een vergrote elektron-gatafstand. Dat kan op zijn beurt weer leiden tot een relatief lage excitonbindingsenergie in vergelijking met een geconjugeerd analoog met lineaire donor-acceptor (D-A) conjugatie. Allereerst behandelt dit hoofdstuk de discussie over structurele optimalisatie gebaseerd op theoretische berekeningen van een serie van verschillende monomeren. Afsluitend maken we een directe vergelijking van de exciton-bindingsenergiekarakteristieken van een prototypisch donor-acceptor kruis-geconjugeerd dimer en zijn linear-geconjugeerde tegenhanger.

Het werk in hoofdstuk 3 stelt ons in staat om een logisch ontwerp te maken van een prototypisch D-A kruis-geconjugeerd polymer, waarvan de synthese beschreven staat in hoofdstuk 4. Een kanttekening hierbij is dat TEG zijketten werden toegevoegd aan het ontwerp van het polymer. Dit polymer wordt gekenmerkt door een duidelijke kruis-conjugatie tussen de thieno[2,3-c]pyrrooldion acceptor- en de thieno[3,4-b]thiofeen donorfunktionaliteiten, met thiofeen koppelstukken in de hoofdketen. Er werd gevonden dat ondanks de efficiënte ketengroei, de één-pots Suzuki-Miyaura homopolymerisatie (zie hoofdstuk 2) toch aanhoudend onverklaarbare onzuiverheden in het polymer (P1) opleverde. Alhoewel een duidelijke verklaring nog niet gevonden is, wordt verondersteld dat de zuurstofatomen in de TEG ketens mogelijk complexeren met de booratomen in het reactiemengsel van de Suzuki-Miyaura homopolymerisatie. Deze hypothese werd ondersteund door een experiment met een controlepolymer (P2), waarbij de TEG zijketten werden vervangen door standaard alkyl ketens. Het probleem van P1 werd hierbij geëlimineerd, getuige een massaspectroscope analyse. De Stille co-polymerisatie werd gebruikt om het gewenste 2-D geconjugeerde polymer (CC1) te verkrijgen. Dit werk wijst op mogelijke, voorheen onverwachte maar belangrijke en negatieve aspecten van bis(pinacolato)diboorgepromote homopolymerisatie. Deze methode leidt tot structurele imperfecties die mogelijk een beperking van de toepasbaarheid veroorzaken.

De succesvolle syntheses hebben ertoe geleid dat wij in staat zijn om de invloed van de donor-acceptor kruis-conjugatie van de excitonbindingsenergiekarakteristieken van geconjugeerde polymeren te
bepalen. In hoofdstuk 5 beschrijven we een gecombineerde materiaalstudie, op zowel het gebied van natuurkunde als kwantumchemie, van een dergelijk 2-D polymeer, met hierbij een bijzondere focus op de excitonbindingsenergie. Een eerste evaluatie van de externe kwantumefficiëntie van dit polymeer suggereerde, tot onze verrassing, dat de excitonbindingsenergie eenduidig hoger is in kruis-geconjugeerde donor-acceptorsystemen in vergelijking tot de gebruikelijke lineair-geconjugeerde polymeeranalogen. Deze experimentele observatie wordt ondersteund door een set extensieve kwantumchemische berekeningen op een serie van kruis-geconjugeerde en lineair-geconjugeerde dimeren. De kwantumchemische berekeningen suggereren dat de hoogste bindingsenergie van de kruis-geconjugeerde donor-acceptorpolymeren naar waarschijnlijkheid sterk gerelateerd is aan de sterke elektronlocalisatie in hun aangeslagen toestand, wat leidt tot een kortere electron-gatafstand. Deze resultaten inspireren ons met betrekking tot de mogelijkheden om de excitonbindingsenergie van geconjugeerde polymeren te reduceren. Deze ingevingen staan kort beschreven in hoofdstuk 6.
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Eindelijk, hier ben ik.

Memory is weird and lovely at the same time. We can sense a lot of things like they’re from yesterday, though they’re obviously years ago, or millions of seconds to count. For example, I remember vividly my first travel to the Netherlands. I already had a light cold, and the unexpected low temperatures in the plane made it a bit worse. But happily then, the magic weather of Groningen cured me! (Thank you, Groningen~) From there, I had a feeling that the following years in Groningen would be unforgettable. And now, I know it will be unforgettable.

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