Towards conjugated polymers with low exciton binding energy
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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 $\varepsilon_r$:\(^3,4\)

$$E_b = \frac{e^2}{4\pi\varepsilon_r\varepsilon_0 r}$$

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](image)

**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. 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). A popular strategy to design two-dimensional conjugated polymers has incorporated triphenylamine into the polymer backbone, 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, 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 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.

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 π-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 π-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 π-conjugation:

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

BTT with larger π-conjugation area may lead to stronger intermolecular π-π stacking and thus to improved charge carrier mobility. Also, its enhanced π-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 it 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. Prototypical polymer structures (1 and 2) based on the above discussion.](image)

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 π-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\textsuperscript{24}/6-31G**) with the program GAMESS-UK.\textsuperscript{25} Polarizabilities of all structures were calculated using DFT (B3LYPg/aug-cc-pVTZ) with the program DALTON.\textsuperscript{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)

*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.

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>
<thead>
<tr>
<th>Conjugation type</th>
<th>( E(\text{D}^+) )</th>
<th>( E(\text{D}^-) )</th>
<th>( E(\text{D}^*) )</th>
<th>( E(\text{D}) )</th>
<th>( (E_{\text{exc}}^{\text{vert}}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cross conjugation</td>
<td>-6133.0972</td>
<td>-6133.4003</td>
<td>-6133.2608</td>
<td>-6133.3109</td>
<td>2.1</td>
</tr>
<tr>
<td>Linear conjugation</td>
<td>-6133.0949</td>
<td>-6133.4007</td>
<td>-6133.2547</td>
<td>-6133.3103</td>
<td>1.8</td>
</tr>
</tbody>
</table>

The calculated \( E_{\text{exc}}^{\text{vert}} \) 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-acceptor 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