ORGANIC SEMICONDUCTING MOLECULES AND POLYMERS FOR SOLUTION PROCESSED ORGANIC ELECTRONICS

By

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To my parents
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<tr>
<td>ACN</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>BHJ</td>
<td>Bulk heterojunction</td>
</tr>
<tr>
<td>BTD</td>
<td>2,1,3-benzothiazole</td>
</tr>
<tr>
<td>CT</td>
<td>Charge transfer</td>
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<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>DIO</td>
<td>Diiodooctane</td>
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<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
</tr>
<tr>
<td>DPP</td>
<td>Diketopyrrolopyrrole</td>
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<tr>
<td>D-A-D</td>
<td>Donor-Acceptor-Donor</td>
</tr>
<tr>
<td>dppf</td>
<td>1,1'-diphenylphosphino-ferrocene</td>
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<tr>
<td>DPV</td>
<td>Differential pulse voltammetry</td>
</tr>
<tr>
<td>Fc/Fc⁺</td>
<td>Ferrocene/Ferrocenium</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel permeation chromatography</td>
</tr>
<tr>
<td>J_{sc}</td>
<td>Short current density</td>
</tr>
<tr>
<td>BTI</td>
<td>Bis(trifluoromethylsulfonyl)imide</td>
</tr>
<tr>
<td>NBS</td>
<td>N-bromosuccinimide</td>
</tr>
<tr>
<td>OPVs</td>
<td>Organic photovoltaics</td>
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<td>OFETs</td>
<td>Organic field-effect transistors</td>
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<td>Pd_{2}(dba)_{3}</td>
<td>Tris(dibenzylideneacetone)dipalladium(0)</td>
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<td>PC</td>
<td>Propylene carbonate</td>
</tr>
<tr>
<td>PCE</td>
<td>Power conversion efficiency</td>
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<td>Full Name</td>
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<td>[6,6]-phenyl-C71-butyric acid methyl ester fullerene</td>
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<tr>
<td>PDI</td>
<td>Polydispersity index</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>POM</td>
<td>Polarized optical microscopy</td>
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<td>P3HT</td>
<td>Poly(3-hexylthiophene)</td>
</tr>
<tr>
<td>TBAPF&lt;sub&gt;6&lt;/sub&gt;</td>
<td>Tetrabutylammonium hexafluorophosphate</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>THP</td>
<td>Tetrahydropyran</td>
</tr>
<tr>
<td>TLC</td>
<td>Thin layer chromatography</td>
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<tr>
<td>V&lt;sub&gt;oc&lt;/sub&gt;</td>
<td>Open circuit voltage</td>
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</table>
In the field of organic electronics, each material differs in its ability to balance hole (p-type) and electron (n-type) carrier creation and transport in devices, which depends on the energy level of its frontier molecular orbitals and its ability to adopt a suitable morphology for charge carrier transport. In this dissertation, both aspects of organic semiconductor design are presented. The first portion of the dissertation focuses on monodisperse conjugated oligomers, while the second portion describes a new electron-deficient moiety and its use in fully conjugated polymers.

Three approaches to active layer morphology control are presented in the first portion. First, the synthesis of a symmetrical oligothiophene which can further react via two terminal alcohol groups is presented, followed by its polymerization. Despite the inherent conjugation break along the polymer main chain, the resulting polycarbonate remains electroactive, and liquid-crystalline behavior is identified by polarized optical microscopy and thermal analyses. Second, monofunctional oligomers bearing phosphonic acid groups are synthesized as reactive molecules for hybrid organic/inorganic photovoltaic applications, as they are designed to bind to inorganic nanocrystals. Third, the synthesis of symmetrical and unsymmetrical oligomers is
presented, and the influence of the blend of unsymmetrical/symmetrical oligomers in the active layer is studied.

In the second portion of this dissertation, the electron-deficient molecule isoindigo is presented as a valuable building block for conjugated materials applied to organic photovoltaics. First, the synthesis of model compounds is described. Fully conjugated donor-acceptor polymers are then synthesized using electron-donor co-monomers of various donating strengths. These materials are of low band gaps thus absorb towards the near-IR, and they have low HOMO and LUMO energy levels. This makes isoindigo-based conjugated polymers good candidates as n-type materials. The synthesis of fully conjugated polymers composed exclusively of electron-deficient units was thus targeted. In particular, the homopolymer of isoindigo is used in all-polymer solar cells. The last part of this dissertation presents the synthesis of the copolymer of isoindigo and dithienosilole, targeted as p-type material for polymer/fullerene solar cell applications. The photovoltaic characteristics of the blends are described, both in conventional and inverted solar cell architectures.
CHAPTER 1
INTRODUCTION

1.1 Semiconducting Materials

Technologies based on electronic processes rely, in one way or another, on the conduction of electrons. Depending on the nature of the atoms which constitute the electronically active material, the extent of electrical conductivity varies greatly. The electrons involved in conductivity are found in the outermost shell of the atoms of the active material, or valence electrons, since these are the least tightly bound to the ionic core of the atoms. Metals have the highest conductivity, as they constitute the class of materials for which valence electrons are not localized around a particular atom, but rather can move freely about the lattice. Metals tend to crystallize in close packed structures, and the bonds formed by the valence electrons are relatively weak, such that the latter can become conduction electrons. The model of a metal crystal is sometimes described as a sea of free electrons in which the positively charged ions are arranged, according to the particular crystal lattice the atoms pack in.¹

In the quantum theory formalism, an electron is described by a wavefunction which is a solution to the Schrödinger equation. The energy of an electron is then quantized, hence a distribution of energy levels which the electrons can occupy. In the simple free electron model, the distribution of energy levels is continuous from zero to infinity. A less approximate model takes into account the effect of the crystal lattice on the distribution of states. A key feature of crystal lattices is that the propagation of waves within is influenced by Bragg reflections. This disturbs the continuous distribution of states, as Bragg reflections of electron waves in the crystal result in regions of energy in which the wavelike solutions of the Schrödinger equation do not exist. This removes
some energy levels from the allowed distribution, resulting in allowed energy bands separated by forbidden energy gaps, or band gaps. In a crystal according to this model, the position of the band gaps relative to the highest populated energy level determines the electrical conduction.

![Figure 1-1](image)

Figure 1-1. Schematic electron population of allowed energy bands for a metal (left), a semiconductor (center) and an insulator (right). The dark grey regions represent filled states within the allowed bands.

Solid state physics segregates materials—typically inorganic for historical reasons—in several classes depending on the population of electronic energy levels with respect to the band gaps, as depicted in Figure 1-1. A metal has high conductivity because an allowed energy band is partially filled, and so electrons respond readily to an applied electric field. In the contrary, for an insulator the highest occupied energy level corresponds with the beginning of a band gap of too high energy for electrons to access the conduction band. The concept of semiconductor appear in materials which are insulators but for which the bang gaps is small enough so that external excitation may promote electrons from the valence band to the conduction band, turning the electrical conductivity on.¹

Regardless of the material employed, the conductivity of semiconductors will not surpass that of the highly conducting metals. Rather, the strength of semiconductors
resides in the actual event of electron excitation from valence to conduction bands. Its advent upon various external stimuli at temperatures around 298 K has enabled a breadth of specific applications, some of which are treated in this dissertation as presented in Section 1.3 of this Chapter. In contrast with the inorganic materials for which the formalism of semiconductors was developed historically and briefly presented above, the active material herein is organic. There are significant differences between the charge transport characteristic of organic and inorganic materials, and thus the next section points out the key differences of organic semiconductors. This will lead into describing the important characteristics of the devices used in the applications relevant to this dissertation. Finally the key parameters that the organic chemist can tune in order to improve device performance are highlighted.

1.2 Organic Semiconductors in the Solid State.

1.2.1 Band Analogy in Organic Semiconductors.

Organic semiconductors are essentially carbon-based compounds. Carbon has the possibility of hybridizing its 2s and 2p orbitals in three different ways, resulting in sp, sp² and sp³ hybridization. The four hybrid orbitals in a sp³ hybridized C will bind covalently to other atoms into a molecular structure in which electrons are so tightly bound in the highly overlapping σ bonds that they cannot move freely outside of their respective hybrid orbital. When a carbon is sp² hybridized, one pₓ orbital remains unchanged, while the rest hybridize. If two sp² carbons are brought together as in ethylene, the electrons in the bonding orbitals still form highly overlapping covalent bonds with other atoms, while the pₓ orbitals produce less strongly overlapping π bonds, as illustrated in Figure 1-2. For ethylene (left), the highest occupied molecular orbital
(HOMO) and the lowest unoccupied molecular orbital (LUMO) correspond to the bonding and antibonding \( \pi \) orbitals.

![Molecular orbital diagram](image)

**Figure 1-2.** Simplified molecular orbital (MO) diagram of a sp\(^2\) hybridized ethylene-type single unit (left) and representation of an MO diagram (center) for an ethylene-type unit conjugated with several other ones: the unhybridized \( p_z \) can overlap with a significant number of conjugated units, leading a buildup of energy band of conjugate polymer chain.

As more and more sp\(^2\) carbons are covalently bound together, and provided there is sufficient overlap of each \( p_z \) orbital with its neighbors, then the \( \pi \) bonds become delocalized. In other words, and as illustrated in Figure 1-2 (center), in a fully conjugated chain of sp\(^2\) carbons, the electrons in the hybridized orbitals overlap with a finite number of electrons, essentially only with their direct neighbor in the \( \sigma \) bond they form, whereas the electrons in the \( p_z \) orbitals can delocalize over a succession of other \( p_z \) orbitals in the extended \( \pi \) system. As the conjugation length increases, the energy gap between the HOMO and LUMO thus reduces as a result of electron delocalization. This leads to one-dimensional bands with significant bandwidths, and a band gap still set between the HOMO and the LUMO (Figure 1-2, right). If the bandgap is small enough, then the fully conjugated system presents the electronic characteristic of a semiconductor.\(^2\)
1.2.2. Degree of Homogeneity in Solid State Organic Systems.

By analogy with inorganic crystals, covalent bonding of sp\(^2\) hybridized carbons via \(\sigma\) bonds results in an arrangement of tightly bound atoms, which constitutes a scaffold for the \(\pi\) electrons to delocalize. Unlike inorganic crystals though, organic molecules are of finite sizes at the nanometer scale. Then, orbital overlap between successive molecules determines the extent of charge transport at the macroscopic scale.\(^2\) This is a critical difference between the organic semiconductors studied in this dissertation and their inorganic counterparts. This means that for organic materials, the analogy with inorganic semiconductors suffers a decreased level of order in the bulk. The different models accounting for charge motion in organic solids underline a more difficult charge transport than in inorganic crystals. In organic thin films, it is generally thought to take place through a hopping mechanism: the charge hops from one conjugated unit to the next.\(^3\) Depending on the nature, the purity and the morphology of the organic material, the hopping process can occur between adjacent molecules, adjacent polymer chains or parts of a same polymer chain, as illustrated schematically in Figure 1-3.

Figure 1-3. Schematic description (a) of polymer chains, illustration (b) of the distribution of conjugation units in the bulk, and schematic depiction of how transport is distributed both in space (c) and in energy (d). [Adapted from Tessler, N. and coworkers Adv. Mater. 2009, 21, 2741-2761]

Hopping is favored between states of the material that are close in energy, which entails better charge transport in more uniform and ordered materials. Organic
semiconductors are considered as disordered media relative to inorganic crystals, thus
not as electronically homogeneous (Figure 1-3.d) as their inorganic counterparts, which
results in a broad distribution of energy states at the macroscopic level.\(^3\) Energy states
far away from the band gap edges can be considered as trap states, which have a
negative impact on the charge transport properties of organic semiconductors.

1.2.3 Nature of the Charge Carriers in Organic Solids.

The characteristics of the charge carriers in organic semiconductors also differ
from that found in inorganic semiconductors. Charged species (electron or hole) are
created in the organic semiconductor if enough energy is provided so that \(\pi\) electrons
may acquire this energy thereby transiting from the HOMO to the LUMO. But because
the dielectric constant of organic semiconductors is low,\(^4\) the generated electron and
hole remain bound together into an electrically neutral pair under electrostatic attraction,
the exciton. In conjugated organics, the exciton is of the Frenkel type, with binding
energies on the order of 0.5 eV.\(^4\) It is localized on the molecule or segment of polymer
chain where it was formed, and because it is susceptible to recombination, small
diffusion lengths of 5 to 10 nm are typical in organic materials.\(^5\) For charge motion to
occur under an electric field, the electrically neutral exciton needs to be further
separated into the positive and negative charge carriers.

In the rigid inorganic crystal lattice, the generation of a charged species does not
influence its surroundings. In “softer” organic solids, polarization of the \(\pi\) electron clouds
surrounding the generated charge is responsible for a local distortion of the charge’s
electronic environment.\(^6\) The term polaron is used to designate a charged species
accompanied by the local distortion it created. The electronic polarization, also
designated as electron-electron correlation, is complimentary to a distortion involving nuclei, known as the electron-lattice correlation of lattice distortion.\(^7\) The coupling between electronic and lattice evolution was illustrated simply on butadiene, by comparing the \(\pi\) electron density distribution to the evolution in the length of butadiene’s three bonds.\(^8\) Similarly, polyaromatic conjugated chains will deviate from their twisted benzenoid-like structure in the ground state to a more planar quinoid structure upon generation of charge species in the \(\pi\) system. At high charge concentrations, two polarons combine to form a bipolaron, which is defined as a pair of same charges associated with one (increased) local distortion.\(^7\) Chemically, polarons (spin of one half) and bipolarons (spinless) can be assimilated to radical cations and dications, respectively, although the concept of local lattice distortion then is lost. The polaronic nature of charged carriers in organic solids implies that their motion has more inertia since the localized distortion has to travel along with the charge. Qualitatively, this impedes efficient charge transport in organic semiconductors as compared to inorganic equivalents.

This drawback is well balanced with the many advantages that organic materials can offer to the field of electronic technologies, for which industrial applications are envisioned.\(^9\) An immediate yet critical one resides in their light weight and mechanical durability as compared to inorganic semiconductors. The production of low-cost electronic devices is also envisioned thanks to (1) the low amount of energy required to synthesize the organic semiconductors, and (2) their room temperature solvent processing using readily available industrial techniques such as slot-dye coating,\(^{10,11}\) spray casting,\(^{11,12}\) screen printing,\(^{10}\) or inkjet printing.\(^{13}\) More importantly in the frame of
the present dissertation, powerful synthetic tools are available to the chemist in order to tune the properties of organic compounds.

1.2.4 Valuable Charged Species.

In the work presented in this dissertation, the targeted applications take advantage of the organic semiconductors ability to promote an electron from HOMO to LUMO upon (1) application of a potential across a dielectric, (2) application of a potential in an electrochemical cell, or (3) absorption of photons.\textsuperscript{14} The general device structures are shown in Figure 1-4, and each is detailed in the following section.

Figure 1-4. Schematic representations of typical OFET (a), organic solar cell (b) and electrochromic (c) devices architectures.

When an electric field is applied to an organic semiconductor film across a dielectric layer, charged species can be formed in the film. In a device architecture where a second, orthogonal electric field can be applied, then these charges can flow in the direction of the second field, resulting in field effect mobility of charge carriers.\textsuperscript{2,15,16}

A typical bottom-gate top-contact organic field effect transistor architecture is shown in Figure 1-4.a. This will be developed is Section 1.3.1.

When a potential is applied to an organic semiconductor film adhered to an electrically conducting surface plunged in a proper electrolyte solution, charges are generated in the film, which are balanced and stabilized by the electrolytic counter-ions.
The formation of these charges is accompanied by changes in the absorption spectrum of the material, which can be appreciated by the naked eye as the film changes color.\textsuperscript{17} This is the concept behind electrochromic devices based on conjugated organic materials, for which a basic electrochemical setup is shown in Figure 1-4.c. This will be developed in Section 1.3.2.

When the energy of photons is sufficient to be absorbed and form charged species in an organic semiconductor film, then provided the film is in contact with electrodes of proper work function (one of which should be transparent to the incident photons), then the charged species can migrate to the two electrodes and result in photovoltaic current.\textsuperscript{18} A classic architecture for an organic solar cell is depicted in Figure 1-4.b, and will be detailed in Section 1.3.3.

1.3 Organic Electronics: Which Parameters Can the Synthetic Chemist Optimize?

All three organic electronics applications described above can be optimized by influencing two parameters, which will be identified in the following as the applications are described in further details.

1.3.1 Organic Field Effect Transistors.

Figure 1-5 shows two different architectures for bottom-gate organic thin film transistors. The active part of the device is constituted of an organic semiconductor film equipped with two electrodes, called the source (S) and the drain (D). In Figure 1-5.a, these are set above the semiconductor film (bottom-gate, top-contact FET), usually by thermal evaporation of the metal on top of the spin-coated film. In Figure 1-5.b, the source and drain are set under the semiconductor film directly onto the dielectric. The distance between the source and the drain is the channel length L, and the transverse dimension of the device is the channel width W. A third electrode, the gate (set at the
bottom of the device is this case), is electrically isolated from the semiconductor film by a dielectric layer. The gate overlaps the whole channel length and width, such that when a potential $V_G$ is applied between source and gate across the dielectric, charges are generated in the semiconductor layer. The accumulation of charges in the active layer forms a conducting channel between the source and the drain. These charges are then driven across the channel from source to drain by applying an orthogonal potential between the latter two electrodes. OFETs act essentially as electronic valves, as the gate field tunes the amount of charge carriers in the channel while the source and the drain determine the flow of these charges.

![Figure 1-5](image_url)

Figure 1-5. Schematic representations of a bottom gate/top contact OFET (a), and bottom gate/bottom contact OFET (b). L is the channel length, W is the channel width, $V_D$ is the potential bias between source (S) and drain (D) electrodes and $V_G$ is the potential bias between gate and source.

The response of the devices is measured as current-voltage characteristics. These can be done by either varying the drain voltage while keeping the gate voltage constant, or by varying the gate voltage at a fixed drain voltage. A linear regime and a saturation regime exist in the I-V characteristic of FETs, for which the currents are given by Equation 1-1 and Equation 1-2, respectively.²
\[ I_{D,\text{lin}} = \frac{W}{L} \mu C \left( V_G - V_T \right) V_D - \frac{V_D^2}{2} \]  
\[ I_{D,\text{sat}} = \frac{W}{2L} \mu C \left( V_G - V_T \right)^2 \]  

(1-1) 

(1-2) 

C is the capacitance of the dielectric, \( \mu \) the charge mobility in the semiconductor and \( V_T \) is the threshold voltage. The latter parameter can be understood as the lower-limit for \( V_G \) beyond which the channel becomes conducting.

The latter two equations clearly show the dependence of the current output on the value of the charge carrier mobility \( \mu \). As explained in the previous section, charge transport in organic semiconductors is strongly dependent on the degree of uniformity and ordering in the bulk. An important technological measure of device performance related to mobility is the ratio of the current intensity when the current is flowing to that of when the channel is off, also called on/off ratio. Obviously, the morphology of the semiconductor thin film in the channel between S and D is thus a key parameter for high performance OFETs.

The nature of the charge carriers accumulated in the channel upon application of \( V_G \) depends on the sign of the applied voltage. As illustrated in Figure 1-6, the application of a negative \( V_G \) generates positive charges in the organic semiconductors adjacent to the gate dielectric. With proper alignment of the source and drain electrodes’ work functions to the HOMO level of the organic semiconductor, applying a potential between S and D leads to extraction of positive charges, or holes. A semiconductor able to stabilize and carry such charges is designated as p-type. Under positive gate bias, the opposite situation occurs, and provided the work functions of the electrodes is well chosen, then electrons can be extracted at the electrodes. Electron-transporting
semiconductors are designated as n-type. A material able to conduct both hole and electrons with comparable significant mobilities is considered to be ambipolar.

![Diagram showing energy levels for different gate voltages](image)

**Figure 1-6.** Schematic energy diagram illustrating the working principle of an OFET with respect to applied $V_G$. Depending on the work function of the metal used, once hole (b) or electrons (c) are created depending on the sign of $V_G$, then a flow of holes (electrons) can take place between the two metal electrodes.

The position of the HOMO and LUMO energy levels of the semiconductor thus determines the propensity of the material for p- or n-type character, which will influence the nature of the charge carriers in an OFET. The accessibility of the HOMO (LUMO) also determines the extent of the potential to be applied at the gate to generate holes (electrons). The lower $V_G$ is likely to be at significant current output, the lower $V_T$ will be also. Lastly, the ambient stability of the device requires that it operates at potentials at which exposure to oxygen or water does not lead to chemical degradation of the active layer. For the reasons stated above, the position of the HOMO and LUMO levels of the organic semiconductor is another key parameter in high performance OFETs.

### 1.3.2 Electrochromics.

An electrochromic material by definition will change color upon doping (addition or removal of electrons) of the material. For the electrochromism to be of interest in display-type applications, the material should be of a particular color in one electrical state and transmissive in an electrically different state. For conjugated organic
materials, this has been best achieved with conjugated polymers spray cast onto transparent conducting electrodes based on indium tin oxide (ITO).\textsuperscript{12,20}

![Figure 1-7. Repeat unit structures and photographs of spray-cast dioxythiophene-based polymer films in the neutral colored, and oxidized transmissive states and their corresponding normalized absorption spectra. [Adapted from Dyer, A. L. and coworkers ACS Appl. Mater. Interfaces 2011, 3, 1787-1795]](image)

This has been extensively reviewed by Beaujuge and Reynolds\textsuperscript{17} and is a main aspect of the research conducted in the Reynolds group, although not the primary focus of this dissertation. In short, the color depends on how far in the visible region (400 to 750 nm) of the spectrum the polymer absorbs, and what the relative intensity of the absorption profile is at each wavelength.\textsuperscript{21} The best electrochromic polymers so far incorporate the dioxythiophene unit in their backbones, which has led to the full palette of primary colors available as soluble conjugated polymers, as displayed in Figure 1-7.

Since absorption profile and energy gap are closely related, controlling color entails controlling the energy of the HOMO and LUMO levels. The polymers displayed in Figure 1-7 switch from colored to transmissive upon oxidation in an electrochemical
cell. In general, in a properly prepared electrochemical setup, the lower the potential at which the electrochemical process takes place, the more reversible, fast and durable the switching will be, since low potentials mean less energy stressing the polymer film. Hence, in the case of cathodically coloring polymers such as the poly(dioxythiophene)s family, a readily accessible HOMO (low ionization potential) is an important parameter for high performance polymer electrochromic display applications based on oxidative processes. The influence of the nanoscale morphology of the material has not yet been fully understood in the context of electrochromic applications, as the operation of electrochromic devices rely on the contribution of external parameters such as electrolytes and counterions.

1.3.3 Organic Solar Cells.

Solar cells are designed to absorb photons. Immediately, as described for electrochromics, the absorption profile of the material is important for solar cells. Specifically, the more extended the absorption towards the near-IR, the more photons are susceptible to be absorbed, and this is achieved by organic semiconductors with small HOMO-LUMO gaps.\textsuperscript{22,23} The influence of the frontier molecular orbitals energy cannot be limited to extended absorption when it comes to organic solar cell performance. The following briefly describes the mechanisms at play for solar energy conversion to identify the parameters relevant to the work presented in this dissertation.

Through absorption of light, excitons are created in the active layer. The electrically neutral electron hole pair has to be split in order to generate a photocurrent. Because the binding energy of the exciton, on the order of 0.5 eV, is too high for a spontaneous thermal separation and because the exciton diffusion length, on the order of 10 nm, is too small for a pair, on average, to be able to migrate though the film to the
electrodes where it might be separated, another component has to be added into the active layer. The concept of active layer heterojunction, where two semiconductors with different HOMO and LUMO energies are in contact, was first applied in solid state organic photovoltaics in bilayer devices. The goal of the heterojunction as schematically illustrated in Figure 1-8 is to create a local energy offset which can drive the exciton dissociation to the separated charged species.

Figure 1-8. Schematic representation of the electronic processes involved in a bilayer heterojunction cell: (a) formation of the exciton, (b) diffusion of the exciton to the heterojunction, (c) dissociation of the exciton into positive and negative charge carriers, and (d) migration of the charge carriers to their respective electrodes. Illustration of the energy offset between the HOMOs and LUMOs of the two components in the heterojunction.

The heterojunction component with the higher HOMO and LUMO levels (lower ionization potential and electron affinities) is designated as the donor (p-type) and the other component is the acceptor (n-type). Briefly, as illustrated in Figure 1-8, absorption of light creates an exciton (a) in a semiconductor (here the donor), the exciton diffuses (b) to the donor-acceptor interface, undergoes charge (c) separation, and the charges...
are then allowed to migrate (d) to their respective electrodes for charge collection and photocurrent. Whether the dissociation at the interface occurs by direct charge separation, through a charge transfer state or via an energy transfer followed by charge separation in the opposite direction is beyond the scope of this Chapter.\textsuperscript{25-29} As the exciton is created, it acquires a certain energy related to that of its parent photon. As the exciton then undergoes the different energetic steps described above, some energy loss has occurred from the initial generation of the exciton to the final extraction of the separated charges. For instance, a minimum of 0.3 eV is a commonly accepted value for the LUMO (HOMO) offset required to drive electron (hole) transfer at the D-A interface.\textsuperscript{30} At the end of the process the energy difference between the charges collected at the electrodes determines the amplitude of the device’s photovoltage. The photocurrent, on the other hand, is linked to the number of electrons and holes collected.

The electrical power generated by the solar cell is the photovoltage times the photocurrent. A typical solar cell characteristic, or I-V curve, is displayed in Figure 1-9. The most important parameters describing the performance of a solar cell are the open circuit voltage ($V_{oc}$), the short circuit current ($J_{sc}$), the fill factor (FF) and the power conversion efficiency (PCE). At any point on the I-V curve, the power is given by the product of the current and the voltage. The point of maximum power ($P_{out}$) is the point on the curve where the latter product is maximum. The power conversion efficiency, then, is the ratio of the maximum power output to the total power input in terms of incident photons, as described in Equation 1-3. For the latter value, 1000 W/m\textsuperscript{2} is usually selected as solar simulator intensity.
Figure 1-9. Example I-V curves for a solar cell under illumination and in the dark, along with the two equations relating the fill factor (FF) and the power conversion efficiency (PCE) to the solar cell parameters.

\[
PCE = \frac{P_{\text{out}}}{P_{\text{in}}} = \frac{J_{\text{max}} V_{\text{max}}}{P_{\text{in}}} = \frac{J_{\text{SC}} V_{\text{OC}} \cdot FF}{P_{\text{in}}} \tag{1-3}
\]

\[
FF = \frac{J_{\text{max}} V_{\text{max}}}{J_{\text{SC}} V_{\text{OC}}} \tag{1-4}
\]

The fill factor is defined in Equation 1-4 as the maximum power divided by the product of the open circuit voltage and the short circuit current, and is a measure of the deviation of the device response to the maximum power theoretically attainable.

Equation 1-3 relates the power conversion efficiency to the \( V_{\text{oc}} \), \( J_{\text{sc}} \) and FF. Over time, a more suitable approach than bilayer heterojunctions appeared: the bulk heterojunction (BHJ). It is still widely used nowadays and will be discussed in Section 1.5.1 in more details.

1.4 Energy Levels and Morphology: How to tailor these two Key Parameters?

From the description of the three applications above, control over the morphology and control of the energy of the HOMO and LUMO are the two main materials properties that influence performance, and how the synthetic chemist can contribute is described in the following.
1.4.1 Energy Levels Control.

As conjugated successions of aromatic rings (except for polyacetylene), most conjugated polymers have significant bond length alternations, which lead to non-degenerate ground states between aromatic and quinoid forms. While the band gap of a conjugated polymer depends on several structural features which can be varied synthetically, such as planarity, substitution, aromaticity and interchain interaction, bond length alternation has the greatest effect on band gap. The donor-acceptor (D-A) approach has proven to be a very powerful method to tune the energy of the HOMO and the LUMO of conjugated molecules and polymers.

The donor-acceptor (D-A) approach is based on the conjugation of an electron-rich aromatic unit (donor) and an electron-deficient aromatic (or ethylenic) unit (acceptor). The resulting push-pull driving forces favor electron delocalization and the formation of quinoid mesomeric structures (D-A to D\(^+\)=A\(^-\)) over the conjugation length, reducing the extent of bond length alternation. When spectroscopy is used to evaluate the HOMO-LUMO energy gap, intramolecular charge transfer can also account for the extended absorption, which is linked to the high-lying HOMO of the donor unit and the low-lying LUMO of the acceptor unit. A pictorial way to represent this concept is shown in Figure 1-10 (center).

The strength of the D-A approach resides in its versatility, since many aromatic variations are synthetically accessible to tune the push-pull character along the conjugated backbone while providing sites for alkylation to retain solubility. Electron-rich units are typically based on phenyl, thiophene or pyrrole rings substituted with inductive donating group such as alkyl, alkoxy or alkylamine groups. Variations of the latter have led to a library of donor moieties for D-A conjugated systems. Examples are
shown in Figure 1-10 (left). Electron-deficient units are mostly based on phenyl and thiophene rings which are substituted with electron-withdrawing groups such as carbonyls, nitrile and imine functionalities. Examples of such are also depicted in Figure 1-10 (right).

The simplest electron-rich units are benzene, thiophene and pyrrole. These have been substituted with alkoxy groups to increase their electron-donor character. In organic electronics, dioxopyrroles (DOP) are amongst the most electron-rich single aromatic units.\(^{32}\) Fused phenyls like fluorene\(^ {33-35}\) and carbazoles\(^ {36-39}\) first introduced the carbon-bridged structural advantage of planarizing a two aromatic ring moiety while providing an alkylation site away from the backbone twisting points. This carried over to the bithiophene unit with the synthesis of cyclopentadithiophene (CPDT),\(^ {40,41}\) and later to the substitution of the carbon bridge for silicon (dithienosilole, DTS)\(^ {42-45}\) and recently germanium (dithienogermole, DTG).\(^ {46-48}\) It is thought that the bigger the bridging atom (Ge>Si>C), the farther the alkyl solubilizing group can branch out from the conjugated units, improving the planarization of the whole backbone. Fused di- or tri-ring aromatics
also have spurred in the recent years, with the development of thieno[3,2-b]thiophene,\textsuperscript{49} benzodithiophenes,\textsuperscript{50,51} dithienopyrrole\textsuperscript{52,53} and more.

The most widely used electron-accepting moieties were initially based on the cyanovinylene unit,\textsuperscript{54-57} and then the benzothiadiazole unit (BTD) later on.\textsuperscript{36,39,41,42,59} The development of new electron acceptors in the recent years resulted in materials with considerably deeper LUMO energy levels (higher electron affinities). Figure 1-11 shows the energetic distribution of some of the acceptors which are part of the best performing D-A materials in organic solar cells and FETs. The energies in Figure 1-11 are that reported by the different authors from the polymer thin films onsets of reduction, which I have attempted to homogenize (when needed based on the electrochemical conditions reported) by correcting the calculation from reduction onset to energy level using \(-5.1\) eV for Fc/Fc\(^+\) vs vacuum. This discrepancy is best explained in Barry Thompson’s PhD dissertation, and the \(-5.1\) eV value was recently highlighted by Bazan and coworkers.\textsuperscript{60} The LUMO levels gathered for conjugated polymers based on BTD are in the \(-3.4\) to \(-3.7\) eV range. Those of polymers based on thieno[3,4-b]thiophene (TT)\textsuperscript{51,61} are reported as slightly lower, between \(-3.5\) and \(-3.8\) eV, and so are that of thienopyrrole-dione (TPD).\textsuperscript{43,46,48,62} When BTD and TT were substituted with fluorine,\textsuperscript{50,61,63} their LUMO levels shifted downwards. Adding a nitrogen atom in the ring of BTD had a similar effect.\textsuperscript{64} Imide-based acceptors, such as diketopyrrolopyrrole (DPP),\textsuperscript{49,65-70} naphthalene diimide (NDI)\textsuperscript{71-74} and perylene diimide (PDI)\textsuperscript{74-78} have LUMO levels which are generally lower than the previous acceptors, approaching \(-4.0\) eV. The benzothiadiazole-quinoxaline\textsuperscript{58,79} and bisbenzothiadiazole\textsuperscript{53} acceptors lower the LUMO even more.
Deep LUMOs have several implications for organic solar cells and field effect transistors. First, this brings the electrons in the doped semiconductor within the range of stability against reaction with ambient atmospheric contaminants.\(^1\)\(^9\) Homo- or co-polymers of diketopyrrolopyrrole (DPP),\(^8\)\(^0\)\(^8\)\(^1\) benzobisimidazobenzophenanthroline (BBL),\(^8\)\(^2\)\(^-\)\(^8\)\(^4\) perylene diimide (PDI) or naphthalene diimide (NDI),\(^7\)\(^1\)\(^-\)\(^7\)\(^4\) bithiophene imide (BTI)\(^8\)\(^5\)\(^,\)\(^8\)\(^6\) and bisindenofluorene\(^8\)\(^7\) have been reported as high electron mobility materials, some exceeding 0.1 cm\(^2\)/Vs in air-stable OFETs. Second, the most prominently used n-type material in OPVs heterojunctions are not conjugated polymers (as discussed in Section 1.5.4 in more detail), rather they are fullerene derivatives, with LUMO levels around -4.2 eV.\(^1\)\(^8\)\(^,\)\(^8\)\(^8\)\(^-\)\(^9\)\(^0\) Because the value of the \(V_{oc}\) in organic solar cells is linked to the offset between the HOMO of the p-type material (conjugated polymer) and the LUMO of the n-type material (fullerenes), deep LUMO levels for D-A polymers combined with their low band gaps (1.2-1.6 eV) entail that they have deep HOMO levels

<table>
<thead>
<tr>
<th>Acceptor Unit</th>
<th>BTD</th>
<th>TT</th>
<th>TPD</th>
<th>PTD</th>
<th>DPP</th>
<th>NDI/PDI</th>
<th>BTDQ</th>
<th>BBT</th>
</tr>
</thead>
<tbody>
<tr>
<td>LUMO Energy (eV)</td>
<td>[−3.40, −3.70]</td>
<td>[−3.50, −3.80]</td>
<td>[−3.50, −3.80]</td>
<td>[−3.70, −4.00]</td>
<td>[−3.60, −4.00]</td>
<td>[−3.50, −3.80]</td>
<td>[−4.00, −4.30]</td>
<td>[−4.20, −4.40]</td>
</tr>
</tbody>
</table>

Figure 1-11. Structures of several acceptors from the literature, along with the LUMO energy level distribution of polymers incorporating them. LUMO energies are corrected to Fc/Fc\(^+\) at -5.1 eV vs vacuum (when needed), to homogenize the values.
as well. Hence the propensity for high $V_{oc}$ in devices using deep LUMO, low-band gap polymers. One concern to nuance the latter point is that should the LUMO be too deep, then there would not be enough LUMO(p-type)-LUMO(n-type) offset at the heterojunction to efficiently drive exciton separation at the interface.

1.4.2 Morphology control in single component active layers.

There are two levels of morphology control that relate to the field of organic electronics: 1) morphology control in a single component active layer to achieve highest degree of ordering and 2) morphology control in two-components blends to induce favorable phase segregation in the active layer. Only the first one is treated here, and the second one will be covered in Section 1.5 of this Chapter.

High mobility devices often require processing techniques such as single crystal growth or vapor deposition, which are much more demanding than solution based techniques in terms of cost and reproducibility. Table 1-1 gathers some of the best performances with classic materials reported in the literature. At satisfying on/off ratios in p-channel OFETs, devices that are solution processed only recently manage to overcome the 1 cm$^2$V$^{-1}$s$^{-1}$ threshold in hole mobility, whereas numerous devices made by vapor deposition or using single crystals have been reported with hole mobilities above unity. A comprehensive review was recently published by Zhu and coworkers. The synthetic design of oligomers to achieve liquid crystallinity is one approach to induce long range ordering in solvent processible systems, and oligothiophenes are good candidates. Liquid crystallinity has also been exploited to induce ordering in fully conjugated poly(alkylthiophenes) leading to high p-type OFET performances, as in the case of PQT-12 or PBTTT.
Table 1-1. Processing method, p-channel field effect mobility and on/off ratio for some of the classic OFET materials reported in the literature.

<table>
<thead>
<tr>
<th>Single Crystal</th>
<th>Vapor Deposited</th>
<th>Solution Processed</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mobility (cm²V²s⁻¹)</td>
<td>On/Off ratio</td>
</tr>
<tr>
<td>1</td>
<td>1.3 × 10⁶</td>
<td>1.0 × 10⁴</td>
</tr>
<tr>
<td>2</td>
<td>15.4 × 10⁶</td>
<td>6.0 × 10⁶</td>
</tr>
<tr>
<td>3</td>
<td>1.0 × 10⁴</td>
<td>0.2 × 10⁶</td>
</tr>
</tbody>
</table>

Supramolecular assemblies of conjugated systems have been reviewed extensively, and the reader is directed to the relevant literature.⁹⁵,⁹⁶

1.5 Morphology Control in Organic Solar Cells: Successful Variations.

1.5.1 Polymer/PCBM solar cells.

Probably the most efficient active layer morphology control in organic solar cells was the advent of the bulk heterojunction.¹⁸ This approach consists in intimately blending the two components (p-type and n-type) in the active layer, such that a greater interface area could be achieved. It results in an interpenetrated junction between electron-donor and electron-acceptor materials. Bulk heterojunctions can dissociate excitons efficiently over the thickness of the solar cell active layer, and thus create separated electron-hole pairs anywhere in the film. The main disadvantage is the increased disorder, as the reduced percolation pathways of the separated charges to
the contacts may result in spatially-trapped charges, leading to undesired recombination.

It is thus necessary to add a level of control over the BHJ, and considerable effort across the field was made in that direction. Because the BHJ is obtained after spin-coating a blend from solution, depending on the solvent evaporation rate, the morphology is not necessarily the most thermodynamically stable one. This means that the choice of the casting solvent will have an influence on the bulk morphology.\(^\text{97}\) For similar reasons, solvent vapor annealing treatments\(^\text{98}\) can also impact the BHJ, as the blend exposed to the solvent vapor is allowed to rearrange. Thermally annealing the devices after spin casting the active layer has also become a popular and powerful method to increase the solar cell efficiency.\(^\text{99}\)

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**Figure 1-12.** Structure of the best performing solar polymers reported to date, along with their energy levels, electrochemical band gaps, solar cell parameters and PCE.

Both annealing methods usually yield higher phase segregation between the p- and n-type materials, with bigger domains which can also feature higher degrees of crystallinity. The latest lever for BHJ morphology control consists in the use of solvent
additives. These small molecules are added in a low volume percent (up to 8 %) to blend solution. During deposition of the active layer blend, the presence of the extra solvent molecules of different boiling points and polarity result in an altered BHJ morphology. This was shown to significantly reduce the phase segregation size in some cases, using alkyl dithiols\textsuperscript{100,101} or diiodoalkanes\textsuperscript{46,65,102} leading to an increased p-/n-type interface area and increased photocurrents. The highest efficiencies reported for polymer solar cells now exceed 7%: the structures of PBDTTT-CF\textsuperscript{61}, PDTSTPD\textsuperscript{43}, DTG-TPD\textsuperscript{46}, PBnDT-DTffBT\textsuperscript{64} and PBnDT-XTAZ\textsuperscript{50} are shown in Figure 1-12.

1.5.2 Small molecule/PCBM solar cells.

Conjugated small molecules, which in the field of organic electronics are usually considered as monodisperse elongated chromophores in the 1 to 5 kg/mol range, have shown some interest in molecular BHJ solar cells. The synthesis of discrete molecules requires less stringent stoichiometry than that of conjugated polymers, and the purification is more straightforward such that from a materials science perspective, there is less batch to batch variation. The technology and the device fabrication are essentially the same, with the molecules as p-type and the fullerenes as n-type materials. But because of the low molecular weight of a conjugated small molecule compared to a polydisperse high molecular weight polymer, the morphological behavior of the molecular active layer differs from that of a polymer-based one. Specifically, both components in the blend have the ability to crystallize, which is advantageous for charge carrier mobility but can lead to excessive domain sizes. A most up-to-date review of molecular BHJ solar cells was recently published by Nguyen and coworkers\textsuperscript{103}, which also reported the first molecular devices exceeding 4% efficiency\textsuperscript{104}. From the review of all molecular solar cell systems, the team observed that
carrier extraction and recombination in these systems appear more prevalent than in polymer-based devices, which they suggest the finite size and the crystallinity of the small molecules may be responsible for.

![Figure 1-13. Structure of the two best performing solar small molecules reported to date, along with their energy levels, electrochemical band gaps, solar cell parameters and PCE.](image)

Nevertheless, there is improvement to expect from molecular systems, as the regained interest in such is recent compared to polymer based devices. More detailed studies on device processing conditions designed specifically for the more crystalline active layers can improve efficiency. New materials also can lead to improved devices, as the latest two reports of high performance molecular solar cells, based on the two new molecules shown in Figure 1-13, reached 5.4%\textsuperscript{105} and 5.8%\textsuperscript{106} in BHJ with fullerenes.

**1.5.3 Organic/inorganic hybrid solar cells.**

Early reports by Alivisatos et al. of photovoltaic devices based on hybrid systems combining a conjugated polymer and cadmium selenide nanocrystals (NCs) in thin film blends have sparked considerable research efforts on organic semiconductor / chalcogenide NC hybrids.\textsuperscript{107} Since NC do not disperse well within the unfunctionalized polymer matrix and tend to aggregate,\textsuperscript{108,109} a limiting factor to the latter type of hybrid solar cells’ efficiency is the unfavorable phase segregation in the active layers. By varying the shape of the inorganic NCs,\textsuperscript{110,111} inorganic chemists have offered solutions to this morphology issue: blends of three-dimensional branched NCs with
unfunctionalized polymers afforded power conversion efficiencies up to 2.2% with poly(3-hexylthiophene), 107,112 2.1% with poly(phenylene vinylene)113,114 and up to 3.2% with polymers taking advantage of the donor-acceptor approach.115,116 Since NCs are coated with trialkylphosphine oxide or alkylcarboxylate surfactants depending on the colloidal NC synthesis method employed, they are inherently surrounded by an insulating layer of aliphatic molecules, which was early determined to be detrimental to the electronic interaction between the organic and inorganic components of the hybrids.117 Subjecting the NCs to a solvent treatment aimed at replacing the original surfactants also contributed to increased efficiencies of hybrid solar cells.108,118-121

As a means of controlling both the morphology of the hybrid active layer and the NCs surfactants composition, conjugated polymers that bare functional groups such as amines,122,123 phosphine oxides,124-126 thiols 123,127,128 and carbodithioic acids129 were introduced. Although they provided better control of the dispersion of the NCs in the polymer matrix, little enhancement of the overall power conversion efficiencies was observed. A related approach consists in using discrete conjugated oligomers in place of polymers, allowing for a greater molecular control of the hybrids formation due to the well-defined structure of the oligomers. In most previous studies, the oligomers bare functional groups enabling their grafting onto the inorganic NPs: amongst others,130,131 oligoanilines with carbodithioic acid groups,132,133 oligo(phenylene vinylene)s with phosphine oxide groups,134,135 oligo(phenylene ethynylene)s with thiol groups136 and oligothiophenes with thiol,137 carbodithioic acid,129 carboxylic acid,138-140 phosphonate141 and phosphonic acid142-144 anchoring groups have been reported. Some report the further electropolymerization of the attached ligands, but most systems are treated as
discrete inorganic core/organic shell type entities to be characterized and processed as such into optoelectronic devices.

1.5.4 Polymer/polymer solar cells.

The majority of conjugated materials for all-organic electronics developed up to date are p-type, but low bandgap n-type conjugated polymers with high electron affinities and high ionization potentials (ambient stable) are also important in the related field of all-polymer solar cells, because the commonly used fullerene derivatives typically have limited absorption in the visible region. Fullerene derivatives, such as PC\textsubscript{60}BM and PC\textsubscript{70}BM, are constant components in the highest efficiency cells due to their advantageous electron mobility and their ability to crystallize into charge percolation networks.\textsuperscript{88-90} The main disadvantage of fullerenes for BHJ cells is the limited chemical modifications available to extend their light absorption to wavelengths longer than 600 nm,\textsuperscript{145-147} explaining the extensive synthetic effort focusing rather on broadening the spectral absorption of their donor–acceptor (D–A) p-type polymeric counterparts.\textsuperscript{22,23} Soluble n-type polymers are attractive because of their versatile processability: their macromolecular nature yields high-quality thin films as active layers, while variations in the side-chain can control the material’s solubility and phase separation in the bulk. Except for BBL-based devices,\textsuperscript{148,149} palladium-catalyzed cross-couplings are used to synthesize n-type D–A polymers for most all–polymer solar cells incorporating cyanovinylenes,\textsuperscript{150-152} PDIs\textsuperscript{76-78,153} or BTD\textsuperscript{154,155} acceptors in conjugation with various donors, yielding maximum efficiencies between 1.8 % and 2.3 % at AM 1.5.

In all–polymer solar cells, the n-type material is a polymer which should fulfill specific energy levels requirements with respect to the p-type polymer in the active layer.\textsuperscript{154,156} The most common p-type material used in all–polymer OPVs are
derivatives of alkylated poly(thiophenes) and poly(phenylene-vinylenes), which have HOMO and LUMO levels in the -5.2 to -5.4 eV and -3.1 to -3.2 eV ranges respectively.\(^{30}\) The n-type polymer used in heterojunction with such p-type polymers should thus be designed with HOMO and LUMO levels lower than -5.5 to -5.7 eV and -3.4 to -3.5 eV, respectively, to achieve energy levels offsets greater than 0.3 eV and drive the excitons to the charge-separated state at the p-/n-type interface. To be able to compete with the current fullerene derivatives, the energy offsets for the n-type polymer should be balanced with a bandgap below 1.8 eV to extend its absorption into the near-IR.

1.6 Thesis of This Dissertation.

As the field of organic electronics learns the mechanisms at work behind successful device operation, two parameters stand out as key to high performance: control over the morphology of the active layer, and control over the energy of the frontier molecular orbitals (HOMO and LUMO) of the conjugated organic semiconductors in the active layer.

The synthetic chemist’s approach to morphology control in this field is to embed the material’s ability to adopt a particular morphology in the structure of the compound itself, through synthetic design. Depending on the application, the active layer can be composed of a single component or of (at least) two components. There are thus two levels of morphology control relevant to organic electronics. Regarding specific applications in this dissertation, single component active layers relate to both organic FETs and solar cells, while the latter level pertains mostly to heterojunction organic solar cells. Well-defined oligomers have the advantage of being monodisperse and can often readily crystallize into ordered domains. Therefore, they are ideal candidates to probe the efficacy of a new approach to morphology control. The third chapter of this
dissertation presents the use of synthetic chemistry to tailor well-defined oligomers towards both levels of morphology. In a first part, telechelic oligomers are polymerized into higher molecular weight compounds with the goal of accessing the mechanical properties of polymeric materials while retaining some morphological freedom characteristic to the single oligomer, as desired for solution-processed OFETS. The second part of Chapter 3 describes how unsymmetrical oligomers with variable energy gaps can be functionalized such that they may graft onto inorganic nanocrystals (NC) for hybrid solar cell applications. Such hybrid systems could become useful tools to control the phase segregation domain size in the active layer of hybrid solar cells, particularly since the NC can be of various shapes with controlled aspect ratios, an could eventually be anisotropically distributed within the active layer. The last part of Chapter 3 presents a synthetic strategy affording symmetrical and unsymmetrical oligomers, which can be mixed as part of the active layer in a molecular solar cell with an improved effect on its morphology and thus its efficiency.

With the development of donor-acceptor chemistry in the past decade, a wide variety of electron-deficient moieties were incorporated in the backbones of conjugated molecules and polymers, resulting in organic semiconductors with reduced bandgaps and tailored energy levels. In particular for heterojunction OPVs, researchers seek to adjust the position of the energy levels of a p-type compound with respect to that of the n-type component. Isoindigo is an electron-deficient molecule introduced in 2010 by us as a new acceptor for organic electronics. A common property of isoindigo-based conjugated molecules and polymers is their low-lying LUMO (high electron affinity) between -3.8 and -4.0 eV, which is close to that of fullerene derivatives. The electron-
accepting strength of isoindigo reduces the bandgap of the materials to 1.55 eV, extending their absorption to 800nm. This results in deep HOMO levels (high ionization potential) compared to other small bandgap systems, which is also an attractive feature of isoindigo-based systems. The fourth chapter of this dissertation demonstrates the use of isoindigo as a new acceptor in solution-processible donor-acceptor conjugated polymers. The first two parts of Chapter 4 introduce the isoindigo molecule and some model oligomers with properties relevant to organic electronics. The third part of Chapter 4 illustrates the breadth of the absorption profiles depending on the design of the polymer repeat unit, which is related to the position of the FMO energies. Taking advantage of the deep HOMO and LUMO energy levels, and yet extended absorption, the fourth part of Chapter 4 sheds a different light on isoindigo-based conjugated polymers, now synthetically designed as all-acceptor for n-type applications. Reductive electrochromics and all-polymer solar cell results are presented to illustrate the use of all-acceptor poly(isoindigos) as n-type materials. The last part of Chapter 4 focuses on conjugated polymers designed specifically as p-type for polymer solar cells in bulk heterojunctions with fullerene derivatives.
2.1 Structural and Polymer Characterization.

2.1.1 General Structural Characterizations.

All $^1$H NMR (300 MHz) and $^{13}$C NMR (75 MHz) spectra were recorded on a Varian Mercury 300 spectrometer. Chemical shifts for $^1$H and $^{13}$C NMR were referenced to residual signals from CDCl$_3$ ($^1$H NMR $\delta = 7.26$ ppm and $^{13}$C NMR $\delta = 77.23$ ppm). Mass spectrograms were recorded on a Finnigan MAT95Q Hybrid Sector mass spectrometer. Elemental analyses were carried out by Atlantic Microlab, Inc, or by the CHN elemental analysis service in the Chemistry Department of the University of Florida.

2.1.2 X-Ray Spectroscopy.

Crystals of T6-dibenzoate (3-9) were grown by slow evaporation from a 50:50 dichloromethane:pentane solution.

Crystal growth was attempted for compounds P-il-P and T-il-T (Section 4-2) using several methods which are summarized in Table 2-1. Chloroform, THF and toluene are good solvents, while acetonitrile is a poor solvent for the present compounds.

<table>
<thead>
<tr>
<th>Table 2-1. Crystal growth methods employed for P-il-P and T-il-T.</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-il-P</td>
</tr>
<tr>
<td>T-il-T</td>
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</table>
The best crystals were obtained for both compounds by dissolving 10 mg of the material in 1 mL of chloroform in a small glass vial (12 x 35 mm) with a plastic cap. The solutions were gently heated to ensure full dissolution. The plastic cap was perforated with a needle (five holes) and tightened to the vial containing the solution. This was then inserted in a bigger glass vial (27.5 x 7.0 mm, screw cap) containing acetonitrile (3 mL), and the cap was tightened onto the big vial. This setup was allowed to stand for 4 days without disruption, affording mm-scale single crystals.

X-ray data was obtained by the Center for X-ray Crystallography, supervised by Dr. Khalil A. Abboud, at the University of Florida, Department of Chemistry. For T6-dibenzoate (3-9), data were collected at 173 K on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing MoKα radiation (λ = 0.71073 Å). Cell parameters were refined using up to 8192 reflections. A full sphere of data (1850 frames) was collected using the ω-scan method (0.3° frame width). The first 50 frames were re-measured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was < 1 %). Absorption corrections by integration were applied based on measured indexed crystal faces. The structure was solved by the Direct Methods in SHELXTL6, and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. The asymmetric unit consists of four half molecules with no solvent molecules. One of the half molecules in the asymmetric unit has a significant disorder from O9 till the aryl ring. The disorder is refined in two parts with the minor part constrained to maintain a geometry similar to the major part. A total of 1280 parameters were refined in
the final cycle of refinement using 6973 reflections with I > 2σ(I) to yield R₁ and wR₂ of 9.03% and 15.78%, respectively. Refinement was done using F².

For **P-il-P** and **T-il-T**, X-Ray Intensity data were collected at 100 K on a Bruker SMART diffractometer using MoKα radiation (λ = 0.71073 Å) and an APEXII CCD area detector. Raw data frames were read by program SAINT and integrated using 3D profiling algorithms. The resulting data were reduced to produce hkl reflections and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects and numerical absorption corrections were applied based on indexed and measured faces. The structure was solved and refined in *SHELXTL6.1*, using full-matrix least-squares refinement. The non-H atoms were refined with anisotropic thermal parameters and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms. The molecules are located on inversion centers thus a half molecule exists in the asymmetric unit.

For **P-il-P**, in the final cycle of refinement, 3457 reflections (of which 3099 are observed with I > 2σ(I)) were used to refine 200 parameters and the resulting R₁, wR₂ and S (goodness of fit) were 3.48%, 9.15% and 1.063, respectively. The refinement was carried out by minimizing the wR₂ function using F² rather than F values. R₁ is calculated to provide a reference to the conventional R value but its function is not minimized.

For **T-il-T**, the thiophene ring is disordered along a 180 rotation along the C4-C5 bond but the disorder is very small; in the order of 5%. Thus only the S (S1’) atom of the minor part was possible to locate and refine isotropically. In the final cycle of refinement, 3400 reflections (of which 2694 are observed with I > 2σ(I)) were used to refine 195
parameters and the resulting $R_1$, $wR_2$ and $S$ (goodness of fit) were 3.53%, 9.28% and 1.077, respectively. The refinement was carried out by minimizing the $wR_2$ function using $F^2$ rather than $F$ values. $R_1$ is calculated to provide a reference to the conventional $R$ value but its function is not minimized.

2.1.2 Molecular Weight Characterizations.

Gel permeation chromatography (GPC) was performed at 40°C using a Waters Associates GPCV2000 liquid chromatography system with an internal differential refractive index detector and two Waters Styragel HR-5E columns (10 μm PD, 7.8 mm ID, 300 mm length) using HPLC grade THF as the mobile phase at a flow rate of 1.0 mL/min. Injections were made at 0.05-0.07 % w/v sample concentration using a 220.5 μL injection volume. Retention times were calibrated against narrow molecular weight polystyrene standards (Polymer Laboratories; Amherst, MA).

2.1.3 Thermal Characterizations.

Thermogravimetric analysis (TGA) was performed on TA Instruments TGA Q5000 Series using dynamic scans under nitrogen. The heating rate for all samples used (on the 3 to 5 mg scale) was 10°C/min, starting from 25°C up to 700°C. Pt pans were used as sample holders. Differential scanning calorimetry (DSC) analysis was performed using a TA Instruments Q1000 series equipped with a controlled liquid nitrogen cooling system. The samples were prepared by loading 1-3 mg of sample in an aluminum pan, and enclosing it with a hermetic aluminum lid. All DSC experiments consisted in an initial heating scan from 40°C to 200°C-250°C to erase inconsistencies because of the thermal history of the sample preparation, and then cooled at 10°C/min to a temperature between -50 and -100°C/min.
2.1.4 Polymer Free-Standing Film Preparation.

Two different methods were used to created free standing films of T6PC. First, 20 mg of the polymer was dissolved in THF and cast it in a 7 x 1.5 cm Teflon mold. After the solvent evaporated, the film was peeled off of the mold easily. Alternatively, the polymer can be dissolved in toluene and the solution cast on top of a water layer in a vial. Toluene is less dense than water so the polymer solution stays above the water layer and as toluene evaporates, a nice film forms on top of the water layer, easy to pick up and dry. To prepare the free standing film of P(iI-F), the polymer (400 mg) was dissolved in 20 mL of toluene and cast in a 20 cm diameter glass Petri dish. An argon flow was set over the dish using a wide funnel.

2.2 Electrochemical Methods.

Electrochemistry was employed to evaluate the electroactivity of the materials synthesized as presented in this dissertation. In the case of small molecules, the material was dissolved in a 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAPF₆) in dichloromethane solution. The background was current was recorded from -2.0 V to +1.5 V vs Fc/Fc⁺ prior to any experiment to evaluate the electrochemical purity of the electrolyte. In the case of polymeric samples, thin films were used instead. For general electrochemical behavior and energy levels determination, the polymer films were dropcast from toluene or chloroform solution (0.2 g/mL) onto platinum disk electrodes (0.02 cm²) and switched 10 times at a scan rate of 50 mV s⁻¹ in the corresponding range of potentials prior to characterization until a complete stabilization of the current responses was reached.

For reduction spectroelectrochemical measurements, the polymer thin films were spray coated onto ITO coated glass slides (Delta Technologies, Ltd. (7 x 50 x 0.7 mm,
sheet resistance, Rs 8-12 Ω/sq). The films were sprayed from 2 mg/mL toluene solutions of the polymers, and contacts were made using copper tape. The coated ITO slides were transferred to an argon filled glovebox, in which the electrochemical cells were assembled. The cells consisted of a quartz cuvette, a Ag/Ag\(^+\) reference electrode and platinum wire as a counter electrode, fit together through a Teflon cap with proper holes. Each cell was filled with the proper electrolyte, sealed with Teflon tape and taken out of the glovebox to perform the initial electrochemical reduction break-in cycles and the subsequent spectroelectrochemical experiments.

The TBAPF\(_6\) salt was purchased (98%, Acros) and recrystallized from ethanol. Tetraethylammonium tetrafluoroborate was purchased (Aldrich) and thoroughly dried under vacuum prior to utilization. The salts were transferred to an argon-filled drybox (OmniLab model, Vacuum Atmospheres). Acetonitrile was distilled over calcium hydride, freeze-pump-thawed, and kept under inert atmosphere (Ar) before being transferred to the drybox in which the electrolyte solutions were made. Dichloromethane was collected at the solvent drying system, freeze-pump-thawed, and used in the same way as acetonitrile. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) studies were performed using an EG&G Princeton Applied Research model 273A potentiostat/galvanostat in the argon-filled drybox. Experiments were carried out in a one compartment electrochemical cell using Ag/Ag\(^+\) reference electrode and platinum foil as a counter electrode; all potentials were reported vs Fc/Fc\(^+\) redox couple. The following setup parameters were applied for the DPV studies: a step size of 1.4 mV, a step time of 0.035 s, and amplitude of 55 mV.
2.3 Optical and Spectroscopic Characterizations.

2.3.1. UV-vis Spectroscopy.
Absorption spectra were obtained using a Varian Cary 500 Scan UV-vis/NIR spectrophotometer and quartz crystal cells (1 cm x 1 cm x 5.5 cm, Starna Cells, Inc.). The oligomer films were spin coated on 1 x 1” glass slides from 10 mg/mL chloroform solutions. The polymer films in the solid state UV-vis absorption experiments, including spectroelectrochemistry, were sprayed from toluene solutions unless solubility was an issue in which case chloroform was used.

2.3.2. Photoluminescence Quenching Experiments.
The ground state absorption measurements were recorded on a Cary100 UV-vis absorption spectrometer and corrected for background due to solvent (HPLC grade) absorption. Fluorescence emission spectra and PL quenching data were collected on a Photon Technology International (PTI) photon counting fluorescence spectrometer. Fluorescence lifetime measurement was conducted on a PicoQuant Picoharp-300 TCSPC instrument.

The concentration of the CdSe NCs stock solution was determined to be 27 μM by a reported method, and diluted to 20 μM for experiment A or 1 μM for experiment B.

Experiment A (Figure 2-1) describes the PL quenching experiment of oligomer emission by addition of incremental amounts NC solution. To a solution of 2 mL oligomer in CHCl₃ (5 μM) in 1 cm quartz FL cuvette, CdSe NCs in CHCl₃ with known concentration were titrated so that the ratio of oligomer/ CdSe was controlled. More than 90% of photoluminescence of the oligomers were quenched when 100 nM of CdSe NPs were added (Oligomer: CdSe 50:1).
Experiment B describes the reverse experiment, where the evolution of the emission of the NCs in solution is monitored at various ratios of CdSe NC/oligomer. As depicted in Figure 2-1 (right), this was achieved by mixing 0.5 mL of a 1 μM CdSe solution with 1.5 mL of oligomer solution of the following concentrations: 16.7 μM (for 50:1 oligomer:CdSe); 33.4 μM (for 100:1 oligomer:CdSe) and 66.8 μM (for 200:1 oligomer:CdSe). The solutions were stirred and irradiated with light at the CdSe peak absorption wavelength (which does not overlap with the absorption of the all-thiophene organic oligomer). The resulting emission was recorded and plotted against that of other oligomer:CdSe ratio mixtures.

2.3.3 Polarized Optical Microscopy

In combination with DSC thermograms, polarized light microscopy (POM) was used to identify possible crystalline phase transition and liquid-crystallinity. The sample would be deposited (small amount, < 0.1 mg) on a clean 1” x 3” microscope glass slide, covered with a microscope glass cover slide and fitted in the hot stage. The temperature
would then be increased (180°C max) to reach that of sample flow and the cover slide would be pressed to spread the sample between the two slides and obtain a thin layer. In the isotropic melt, no light was observed at crossed polarizer and analyzer. As the sample was cooled down, crystallization would be observed as structural patterns appeared close to the crystallization temperature identified by DSC. In the case of the polycarbonate in Section 3-3, T6PC, the structural features would be observed at room temperature but no higher than 65°C.

The images of the stretched free standing films were captured on a film which was held in between two clips, and set in an oven, in which the temperature was increased from 40°C to 70°C. When the temperature was high enough (60-65°C), the film was stretched automatically from the spring of the paper clip. Figure 2-2 depicts the setup.

![Image](image.png)

Figure 2-2. Free standing film stretching setup (left) and the stretched film set under the polarized light microscope objective.

The POM was performed on a Leica DMRXP polarizing microscope equipped with a Wild Leitz MPS46 camera. Samples were heated in a Linkam Scientific LTS350 hot stage controlled by a Linkam TP92 central processor.

### 2.4 Device Fabrication.

#### 2.4.1 OFETs Fabrication.

For the devices fabricated and studied, highly doped silicon was used as the gate electrode, while the dielectric was a 200 nm thick SiO₂ film. The bottom contact FET
(channel widths 5 to 100 μm and lengths 0.35 to 7.0 mm) was prepared by spin-coating (2000 rpm, 60 s) a 10 mg/mL T6PC-trichloromethane solution. According to the DSC results annealing steps (RT to 200°C to RT at 20°C/min) were performed leading to no transistor characteristics.

Initial attempts to mechanically orient drop-cast films of T6PC onto a silicon substrate by rolling, using a 5 mm-diameter rubber roll, a 15 mm-diameter polypropylene roll and a 2 mm-diameter steel roll were unsuccessful. Successful orientation (observed by POM) was achieved by stretching free standing films prior to deposition on the SiO₂ dielectric. Top contact FETs (channel widths 25 to 70 μm and lengths 0.5 to 1.5 mm) were prepared by manually stretching a film (1 mg/mL T6PC-THF solution) onto untreated, hexamethyldisilazane (HMDS) treated, and octadecytrichlorosilane (OTS) treated dielectrics. Solution processing and electrical measurements by using a Keithley 4200 machine were performed inside a nitrogen filled glovebox at room temperature. The film stretching was performed under ambient conditions.

2.4.2. All-Polymer Solar Cells.

Polymer solar cells were processed on pre-patterned indium tin oxide (ITO) coated glass substrates with a sheet resistance of 20 Ω per square. First a thin layer (30 nm) of poly(3,4 ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS; Baytron Al 4083 from HC Starck) was spin-coated on ultrasonically cleaned ITO substrates, followed by backing on a hot plate at 180°C for 10 min. An active layer of the device consisting of the blend of polymer (P3HT) and Poly(II) was then spin coated from chlorobenzene solvent with a thickness 95 nm. The device was subsequently heated on a hotplate at 150°C for 10 min. LiF (1 nm) and aluminum (100 nm) were thermally
evaporated at a vacuum of \( \sim 0.10 \) nbar on top of active layer as a cathode. The area of the devices was 0.04 \( \text{cm}^2 \). The current density-voltage measurements of the devices were carried out using a semiconductor parameter analyzer system. The photocurrents were measured under AM 1.5G illumination at 1000 W/m\(^2\) from a solar simulator. Device fabrication was done under nitrogen atmosphere and characterizations were performed in an ambient environment without any encapsulation.

### 2.4.3. Polymer/PCBM Solar Cells.

Conventional architecture bulk-heterojunction (BHJ) solar cells were fabricated by the spin coating of 30-nm-thick layers of poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS; Baytron Al 4083 from HC Starck) on a ultrasonically cleaned, indium tin oxide (ITO) coated, patterned glass substrates, followed by backing on a hot plate at 180\(^\circ\)C for 10 min. An active layer of the device consisting of the blend of polymer \( \text{P}(\text{iDTS}) \) and \( \text{PC}_{70}\text{BM} \) (99% pure, Solenne BV) with a ratio of 1:4 (with and without 4% DIO) was then spin coated from chlorobenzene solvent with a thickness of 105 nm. The device was subsequently heated on a hotplate at 150\(^\circ\)C for 10 min. LiF (1 nm) and aluminum (100 nm) were thermally evaporated at a vacuum of \( \sim 10^{-7} \) mbar on top of active layer as a cathode.

For the inverted geometry, a thin layer of sol-gel ZnO (35 nm) was spin coated onto ITO-coated glass. The ZnO sol-gel films were then annealed in air for 30 min at 200\(^\circ\)C. The same process for the active layer in the conventional architecture was used for the inverted devices. After annealing the active layer, a thin layer of MoO\(_3\) (10 nm) was thermally evaporated and then Ag electrode was deposited to complete the inverted device structure. The area of the devices was 0.04 \( \text{cm}^2 \). The current density-voltage measurements of the devices were carried out using a 150 W Newport ozone
free xenon arc lamp as the light source in conjunction with a Keithley 4200 semiconductor parameter analyzer system. Solar measurements were carried out under 1000 W/m² AM 1.5G illumination conditions. Device fabrication was done under nitrogen atmosphere and characterizations were performed in an ambient environment without any encapsulation.
**CHAPTER 3**

**CONJUGATED SMALL MOLECULES FOR ACTIVE LAYER MORPHOLOGY CONTROL IN TRANSISTORS AND SOLAR CELLS APPLICATIONS**

### 3.1 Design of Symmetrical and Unsymmetrical Oligomers for Three Different Approaches to Morphology Control

Driven by their ability to $\pi$-stack, discrete conjugated small molecules can arrange into very ordered crystalline phases. Solution processing requires non-conjugated aliphatic chains to be covalently introduced onto the chromophore, disrupting the crystalline order otherwise adopted by unalkylated molecules. Still, solution processability is considered as one of the great advantages of organic electronics: solubilizing groups are often employed to the detriment of higher degrees of ordering.

**Figure 3-1.** Three synthetic approaches to control the active layer morphology of organic electronic devices.

In some instances, suitable aliphatic/aromatic phase separation as well as ordering of the solubilizing groups themselves yield improved ordering in the solid state. In this Chapter, conjugated small molecules bearing some commonly used solubilizing
groups are also functionalized with different chemical functionalities tailored to enable specific control of the material’s morphology in thin films. Three approaches to morphology control are presented, as depicted in Figure 3-1. First, a symmetrical all-thiophene oligomer bearing two reactive terminal alcohol groups (one on each end, Figure 3-1.a) is synthesized. This telechelic coil-rod-coil oligomer is designed to further polymerize with an appropriate co-monomer (“linker”) into its macromolecular equivalent. The ability of the afforded polymer to demonstrate electroactivity while retaining some of the ordering capabilities of the monomer suitable to OFETs is studied. Second, unsymmetrical oligomers bearing a reactive phosphonic acid (PA) group (one PA on one end, Figure 3-1.b) are synthesized based on either all-donor or donor-acceptor-donor (D-A-D) aromatic patterns. These unsymmetrical reactive molecules are designed to bind onto inorganic CdSe nanocrystals (NCs) as a means to control the active layer morphology of organic/inorganic hybrid solar cells. Third, symmetrical and unsymmetrical D-A-D oligomers bearing either common n-hexyl or specific triisobutylsilyl end groups are synthesized (Figure 3-1.c). As part of Jianguo Mei’s PhD dissertation, initial results on the symmetrical n-hexyl derivative showed propensity for the conjugated molecule to crystallize, and this was developed extensively for molecular BHJ solar cells in Ken Graham’s PhD work. In particular in this Chapter, the influence of an unsymmetrical triisobutylsilyl-end-capped derivative on the crystallization of the symmetrical derivative is presented. The unsymmetrical molecule was treated as an additive to the composition of molecular BHJ solar cells based on the symmetrical derivative main component, influencing the morphology of the active layer.
3.2 Synthesis of Functionalized Oligomers

The first part of this Chapter describes the synthesis of the small molecules described above, while each following sections focus on the approach each type of molecules was designed for.

3.2.1 Symmetrical Sexithiophene Bearing Two Terminal Alcohol Groups

The synthesis of a telechelic sexithiophene bearing two terminal alcohol groups requires the preparation of a proper end-capping unit, as shown is Scheme 3-1.

Scheme 3-1. Synthesis of the thiophene end-capping moiety bearing a protected terminal alcohol. a) thiophene, n-BuLi, THF, -78°C, 63% b) 1. n-BuLi, THF, -78°C; 2. trimethyltin chloride, >90%.

The alcohol functionality is attached as a THP-protected alcohol to a thiophene ring via displacement by 2-lithiated thiophene of the bromine on 2-((5 bromopentyl)oxy)-tetrahydro-2H-pyran starting material 3-1, affording compound 3-2 which is subsequently stannylated at the 5 position. This yields the end-capping moiety 3-3 to be used in a subsequent palladium catalyzed coupling reaction.

The core of the sexithiophene is prepared as shown in Scheme 3-2, starting with the bromination of 2,2'-bithiophene at the 5 and 5' positions in high yields to afford 3-4. Bromination of 3-hexylthiophene at the 2 position using NBS in cold DMF yields 2-bromo-3-hexylthiophene 3-5, which is subsequently converted to the corresponding Grignard reagent. Two equivalents of the latter reagent are reacted with compound 3-4 in a nickel-catalyzed Kumada cross-coupling to afford the dihexylquaterthiophene 3-6 in good yields. This is dibrominated into 3-7 with little purification as the insoluble product.
can be filtered and recrystallized from a hexanes/ethanol mixture; it is subsequently reacted with two equivalents of the end-capping moiety 3-3 described in Scheme 3-1, under Stille coupling conditions.

Scheme 3-2. Synthesis of T6-diol and T6-dibenzoate (3-9) for crystal growth. a) NBS, DMF, r.t., 89%. b) NBS, DMF, 0°C, 93%. c) 1. Mg, ether; 2. 3-4, Ni(dppp)Cl₂, toluene:ether, 60°C, 86%. d) NBS, DMF, 0°C, 78%. e) 3-3, PdCl₂(P(Ph)₃)₂, THF, reflux, 92%. f) HCl (conc.), DCM:MeOH, r.t., 95%. g) pyridine, THF, benzoyl chloride, r.t., 80%.

This affords the sexithiophene 3-8, a precursor to the telechelic T6-diol. In order to recover the reactivity of the terminal alcohols, the THP protecting groups on 3-8 are cleaved off in dilute acidic conditions in a dichloromethane:methanol mixture at room temperature. Upon deprotection of the hydroxyl groups, an orange solid precipitates out of the reaction mixture. The filtered solids were identified by NMR as T6-diol with good purity. Because the purity of monomers is key in achieving high molecular weight polymers, further purification of T6-diol was carried out. Several attempts to crystallize T6-diol, either by solution slow evaporation or vapor diffusion between good and bad solvents were unsuccessful. Column chromatography using a mixture of hexanes and ethyl acetate proved to be the best purification method. Since attempts to crystallize the T6 oligomer failed for the diol form, one more synthetic step was carried out where T6-diol was end-capped with phenyl rings into its dibenzoate derivative 3-9 using benzoyl chloride as a reagent. Crystals of compound 3-9 were successfully grown by slow
evaporation from a 50:50 dichloromethane:pentane solution. The crystal structure is displayed in Figure 3-2.

Figure 3-2. Crystal structure of T6-dibenzoate 3-9

The inner bithiophene core is completely planar in the anti conformation, and it has a 34.9° dihedral angle with respect to the neighboring 3-hexylthiophene moieties. The twisting of thiophene rings in conjugated backbones can have a significant effect on the band gap of the material. The hexyl side-chains are opposite to one another in this crystal structure and exhibit an all-trans conformation, which is consistent with the generally accepted structure of 3',4''-dialkyl-quaterthiophenes.94,160,161

With T6-diol synthesized and of suitable purity for polymerization, this telechelic oligomer can be further reacted with a proper linker to afford macromolecules with tertiary structures potentially offering advantageous morphology in the context of organic electronic applications. The polymerization of T6-diol, the opto-electronic characteristics of the afforded polymer and its morphological properties are described in Section 3-3 of this Chapter.

3.2.2 Unsymmetrical Oligomers Bearing one Phosphonic Acid Group

The synthesis of rod-like unsymmetrical oligothiophenes bearing a phosphonic acid group at one end requires the functional group to be attached to a thiophene ring
during the synthesis of the chromophore, as depicted in Scheme 3-3. The synthetic strategy employed here relies on the conversion of 2-bromothiophene into diethyl thiophen-2-ylphosphonate 3-11, under nickel-mediated Arbuzov-type conditions. This was followed by stannylation of 3-11 at the 5-position of the thiophene ring to afford the phosphonate-bearing end-capping moiety 3-12, to be used in subsequent palladium catalyzed coupling reactions.

Scheme 3-3. Synthesis of the thiophene end-capping moiety bearing a phosphonate group. a) NiCl$_2$ (anhydrous), P(OEt)$_3$, 145°C, 55%. b) 1. LDA, THF, -78°C; 2. trimethyltin chloride, >85%.

Head-to-tail (HT) fully regio-regular oligomers based on 3-alkylthiophene offer the benefit of a controlled degree of regio-regularity compared to polymers that always exhibit some degree of region-irregularity. Each step of the oligomer synthesis needs to be completely regio-selective, since the separation of regio-isomers is tedious. The oligomers are once again assembled by metal catalyzed cross-couplings between substituted aromatic rings. Regio-regularity allows for more uniform secondary and tertiary structures in the bulk.$^{162}$ A similar regio-regular oligomer has been previously reported by Fréchet et al. where five 3-hexylthiophene rings were connected in a head-to-tail fashion.$^{143}$ The synthetic approach was different though, as the oligomers were build in a centro-symmetric fashion around a silyl core and separated in half after the last coupling. The approach described in the following reduces the number of steps while giving access to a longer oligomer.
The regio-selectivity is achieved by taking advantage of both the electronic and steric effects of the alkyl side chain on the 3-position of the thiophene ring. Bromination with NBS at low temperatures in the absence of light affords the 2-brominated species alone (compound 3-5). Deprotonation using LDA accesses the 5-position of the ring selectively, where the anion can react with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane to afford the borylated thiophene 3-13 for subsequent Suzuki coupling.

The synthesis of the regio-regular heptathiophene phosphonate ester rrT7-PE is described in Scheme 3-4.

Scheme 3-4. Synthesis of the regio-regular T7-phosphonate rrT7-PE. a) 1. LDA, THF, -78°C; 2. 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 86%. b) 3-5, Pd2(dba)3, P(o-tolyl)3, Et4NOH, toluene, 85°C, 72%. c) NBS, DMF, 0°C, 55%. d) 3-13, Pd2(dba)3, P(o-tolyl)3, Et4NOH, toluene, 85°C, 80%. e) NBS, THF, 0°C, 71%. f) 1. LDA, THF, -78°C; 2. 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 52%. g) Pd2(dba)3, P(o-tolyl)3, Et4NOH, toluene, 85°C, 39%. h) NBS, THF, 0°C, 83%. i) 3-12, Pd2(dba)3, P(o-tolyl)3, toluene, 85°C, 28%.

The first Suzuki coupling reacting 3-5 and 3-13 to yield pure 3-14 was low yielding (~30%) mostly because of the troublesome separation of the dimer from its starting materials and a small amount of undesired head-to-head (HH) and tail-to-tail (TT) coupling by-products (less than 5% by proton NMR). One way to overcome the tedious separation of the HT product from the HH and TT by-products was to limit the extent of purification on 3-14 and carry out the next bromination step on the mixture of isomers.
The bromination being regio-selective to the heterocyclic carbon between the alkyl-side chain and the sulfur atom, the desired HT isomer is mono-brominated and the TT by-product is dibrominated. The increased polarity of the three products then allowed the purification of 3-15 by column chromatography. This afforded pure 3-15 in 40% yield over 2 steps from 3-13. A second Suzuki coupling between 3-13 and 3-15 afforded the regio-regular terthiophene 3-16 in decent yield. Since by-products in this step have different numbers of rings, the purification of 3-16 by column chromatography is possible. Subsequent bromination and borylation steps to afford 3-17 and 3-18 respectively and their Suzuki cross-coupling eventually yields the regio-regular sexithiophene 3-19, which is again brominated to 3-20. The last coupling reaction is the Stille coupling of the stannylated thiophene 3-12 bearing the phosphonate to the sexithiophene 3-20 to afford rrT7-PE.

Although this synthetic route enabled the synthesis of an extended strictly regio-regular heptathiophene functionalized with a phosphonate group, the number of steps involved was still high and the overall yield rather low: to extend the oligomer to six conjugated thiophene rings, seven steps were necessary from the 3-hexylthiophene starting material with an overall yield of 5%. This is especially critical in the field of organic electronics as low cost is a pursued advantage of organic-based materials. A second route was designed to still enable the synthesis of functionalized unsymmetrical thiophene-based oligomers. Symmetrical aromatic cores are first extended though high-yielding symmetrical cross-couplings, and then subjected to reaction with commercially available 2-(5-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3-10) in a
stoichiometry such that the monocoupled product is isolated for further extension to the target asymmetric functional oligomer. The synthesis is described in Scheme 3-5.

Scheme 3-5. Synthesis of the phosphonic acid-functionalized T6-PA and T4BTD-PA. a) Pd\(_2\)(dba)\(_3\), P(o-tolyl)\(_3\), Et\(_4\)NOH, toluene, 85°C, 31%. b) 3-12, Pd\(_2\)(dba)\(_3\), P(o-tolyl)\(_3\), toluene, 85°C, 30%. c) 1. TMS-Br, DCM, r.t. 2. MeOH, r.t, 85%. d) 3-13, Pd\(_2\)(dba)\(_3\), P(o-tolyl)\(_3\), Et\(_4\)NOH, toluene, 85°C, 92%. e) NBS, AcOH, CHCl\(_3\), 0°C, 97%. f) 3-10, Pd\(_2\)(dba)\(_3\), P(o-tolyl)\(_3\), Et\(_4\)NOH, toluene, 85°C, 26%. g) 3-12, Pd\(_2\)(dba)\(_3\), P(o-tolyl)\(_3\), toluene, 85°C, 64%. h) 1. TMS-Br, DCM, r.t. 2. MeOH, r.t, 94%.

In the synthesis of the first thiophene-based oligomer—a sexithiophene (T6) bearing one phosphonic acid group (T6-PA)—the oligothiophene core is extended to the 5,5'':-dibromo-3,3'':-bis(hexyl)-2,2':5',2''-terthiophene core (3-7) as described previously in Scheme 3-2. In the following step targeting a monocoupled product, 3-7 is reacted with 1.5 equivalents of 3-10, in a Suzuki cross-coupling reaction in toluene. We selected Pd\(_2\)(dba)\(_3\) and tri(o-tolyl)phosphine as palladium and phosphine ligand respectively, and tetraethylammonium hydroxide as boron-activating base. Under
such conditions and after purification by column chromatography, yields of 31% for the
targeted monocoupled product 3-21 and 23% for the dicoupled symmetrical
sexithiophene by-product were obtained. Moderate yields are expected in this
unsymmetrical synthesis step because of the necessary stoichiometry and the
purification process. Monobrominated pentathiophene 3-21 was reacted with the
stannylated thiophene 3-12 under Stille coupling conditions, which yielded the
phosphonate-monofunctionalized sexithiophene T6-PE. The increased polarity of the
oligomer induced by the presence of the phosphonate group facilitated purification by
column chromatography. The last step to the phosphonic acid T6-PA involves treatment
of the phosphonate T6-PE using trimethylsilyl bromide in DCM followed by hydrolysis
with methanol.

The second thienylene oligomer—a five-ring oligomer consisting of one central
benzothiadiazole (BTD) unit flanked by two thiophene rings on each side and bearing
one phosphonic acid (T4BTD-PA)—was synthesized by reacting 4,7-dibromo-
benzothiadiazole with two equivalents of 3-13 under the same Suzuki cross-coupling
conditions than that used for the synthesis of the pentathiophene 3-21, to afford
compound 3-22 in high yields. The latter is then dibrominated using NBS in chloroform
to afford the symmetrical precursor 3-23. Similarly to the conversion of 3-7 into 3-21
during the synthesis of the T6-PA oligomer, the stoichiometry of the reaction of 3-23
with borylated thiophene 3-10 needed to be adjusted in order to optimize the ratio of
targeted monocoupled compound 3-24 to the unreacted and dicoupled by-products.
Unlike for the synthesis of the sexithiophene, for which 1.5 equivalents of the borolane
were used, in this case 3-23 was reacted with 0.80 equivalents of 3-10. Such a
stoichiometry was expected to still afford the targeted monocoupled product in acceptable yields while being able to recover the valuable starting material 3-23 rather than the unreactive dicoupled by-product. After purification of the reaction by flash chromatography, the unsymmetrical product 3-24 was obtained in 26% yield while the recovered starting compound 3-22 accounted for 53% of the material. Although slightly lower, the yield for the latter unsymmetrical coupling was comparable to the one when 1.5 equivalents of the borolane were used in the synthesis of T6-PA. Therefore, the stoichiometry for this kind of unsymmetrical cross-coupling can be chosen depending on interest for specific by-products. Compound 3-24 was then coupled to the stannylated thiophene 3-12 to install the phosphonate group onto the oligomer, affording T4BTD-PE in 64% yield. The phosphonate was hydrolyzed as previously using trimethylsilyl bromide to yield the phosphonic acid monofunctionalized T4BTD-PA.

Once the two phosphonic acid-functionalized oligomers T6-PA and T4BTD-PA were synthesized, their interaction with CdSe nanocrystals was studied. Section 3-4 of this Chapter describes the evolution of the photoluminescence in mixtures of the oligomers and their inorganic counterparts in solution, as well as the synthesis of the hybrid systems and their opto-electronic properties.

3.2.3 Symmetrical and Unsymmetrical Functionality-Free Donor-Acceptor-Donor Oligomers

In the previous section, unsymmetrical oligomers with one reactive functional group were synthesized in a step-by-step procedure, particularly involving the isolation of the unsymmetrical monobrominated precursor to the full oligomer. The following section describes the one-pot synthesis of an unsymmetrical oligomer by sequential addition of two different thienyl borolanes to a symmetrical dibrominated core under
Suzuki cross-coupling conditions. This is an adaptation of a procedure which we first reported in 2010, to accommodate the synthesis of unsymmetrical compounds. The first thienyl borolane is the commercially available 2-(5'-hexyl-[2,2'-bithiophen]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3-25). The second thienyl borolane differs from 3-25 in that the n-hexyl chain (referred to as C6) is replaced by a triisobutylsilyl group (referred to as Si). As shown in Scheme 3-6, 3-27 is synthesized in two steps by first lithiating 5,5'-dibromo-2,2'-bithiophene with an equivalent of n-BuLi followed by quenching with the addition of triisobutylsilyl chloride. Separation of the monosilylated product 3-26 from starting material and disilylated by-product by column chromatography was facilitated by the polarity and solubility difference conferred by the halogen atoms. This was then lithiated again under the same conditions and quenched with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane to afford the borolane 3-27.

Scheme 3-6. Synthesis of the bithiophene end-capping moiety bearing a triisobutylsilyl group. a) 1. n-BuLi, THF, -78°C; 2. chlorotriisobutylsilane, 35%. b) n-BuLi, THF, -78°C; 2. 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, >70%.

Because the unsymmetrical oligomer differs from the parent symmetrical derivative by the bulkiness of one side chain, it is designed as a molecular additive to the main symmetrical component of the active layer. A convenient one-pot synthetic procedure affording both the main symmetrical component and the unsymmetrical additive alleviates concerns over the synthetic cost of such an approach to active layer
morphology control. As shown in Scheme 3-7.a, the dibromoisoindigo starting material is first reacted with 1.75 equivalents of 3-25 under Suzuki coupling conditions.

Scheme 3-7. One-pot synthesis (a) of iIT₂-C₆Si and iIT₂-C₆₂ and synthesis (b) of iIT₂-Si₂. a) Pd₂(dba)₃, P(o-tyl)₃, Et₄NOH, toluene, 85°C, 29%, 40%, 64% for iIT₂-C₆Si, iIT₂-C₆₂, and iIT₂-Si₂, respectively.

The stoichiometry was chosen so that ca. 65% of the starting material undergoing cross-coupling with 3-25 would do so twice in the reaction mixture to yield the symmetrical iIT₂-C₆₂, leaving 35% of the starting material coupled only on one side, thus still able to undergo further cross-coupling. The reaction was monitored by TLC using 2:1 hexanes:dichloromethane as eluent. After heating and stirring the reaction mixture for 3 hours, the red starting material spot for the dibromoisoindigo with a retention factor of 0.5 disappeared while two spots developed at lower retention factors (0.25, blue and 0.35, purple) corresponding to the dicoupled iIT₂C₆₂ and the monocoupled intermediate species, respectively. TLC showing almost complete conversion of the dibrominated starting material, the second borolane 3-27 was added to the reaction mixture, which was allowed to stir while heated for an additional 12 hours. TLC of the crude showed two main blue spots with retention factors of 0.25 and 0.33 corresponding to the symmetrical iIT₂-C₆₂ and unsymmetrical iIT₂-SiC₆ products as confirmed by co-spoting with the pure compounds. A very faint spot corresponding to the symmetrical disilyl iIT₂Si₂ by-product was observed, suggesting that a little amount of dibromoisoindigo
starting material remained in the mixture upon the addition of 3-27, despite the lack of evidence by TLC. After workup, the two targeted compounds $\text{iIT}_2\text{-SiC}_6$ and $\text{iIT}_2\text{-C}_6_2$ were successfully isolated by column chromatography in 29% and 40% yields respectively. Scheme 3-7.b shows the synthesis of the symmetrical disilyl oligomer $\text{iIT}_2\text{Si}_2$, which was designed as main active layer component in control devices.

In summary, this first Section described the synthesis of three different types of oligomers designed to provide morphology control over the active layer of optoelectronic devices, each in their particular way. In the following, the ability of each oligomer to do so is described, the experiments carried out in each case being specific to the system studied.

### 3.3 Morphology Control via Telechelic Oligomer Polycondensation

Half way between discrete oligomers and fully conjugated polymers is a class of polymers consisting of a non-conjugated backbone where aliphatic segments either bear pendant oligothiophenes or are alternated with oligothiophenes in the main chain, most frequently as polyesters. In the following, the polymerization of T6-diol into T6PC is described. The electrochemical and spectroscopic properties of T6PC were investigated. Wide angle X-ray diffraction gave insight on the morphological features suggested by thermal analysis and polarized optical microscopy of thin films and free standing films. The performance of mechanically oriented polymer samples in OFETs was evaluated.

#### 3.3.1 Synthesis of T6PC from T6diol

With T6-diol in hand, a linker molecule had to be selected, with which the terminal diols of the telechelic oligomer would react to form a macromolecule. The nature of the linkages would determine the nature of the alternating copolymer, and the polymer
repeat unit would be composed of 1) two hexyl aliphatic chains, 2) one sexithiophene conjugated rod and 3) the molecular structure of the chosen linker. The linker itself should not impair the electronic properties of the sexithiophene. It should also be of low molecular weight and size to avoid “diluting” the electroactive sexithiophene in an electro-optically inactive matrix. Phosgene was a good candidate because of its reactivity and its short length. Phosgene is essentially the smallest linker possible leading to a polycarbonate (PC) when reacted with diols. The only but major drawback is its toxicity, especially as phosgene is a gas at atmospheric conditions. In its trimeric form though, triphosgene is a solid which makes its handling much safer and better suited for the precise stoichiometric balance required in polymerization reactions. Scheme 3-8 shows the polymerization of T6-diol using triphosgene, resulting in the polycarbonate T6PC. The best polymerization conditions were a modification of that reported in the literature for the synthesis of polycarbonates from bisphenol A and triphosgene.\textsuperscript{170}

\[ \begin{align*}
\text{T6-diol} & \quad \xrightarrow{\text{a}} \quad \text{T6PC} \\
\text{HOOC} & \quad \text{C} & \quad \text{H}_{12} & \quad \text{C} & \quad \text{H}_{12} & \quad \text{OH} & \quad \xrightarrow{\text{a}} \\
\text{C}_6 & \quad \text{H}_{12} & \quad \text{C}_6 & \quad \text{H}_{12} & \quad \text{C} & \quad \text{H}_{12} & \quad \text{O} & \quad \text{C}_6 & \quad \text{H}_{12} & \quad \text{C} & \quad \text{H}_{12} & \quad \text{O} & \quad \text{C}_6 & \quad \text{H}_{12} & \quad \text{C} & \quad \text{H}_{12} & \quad \text{O} & \quad \text{C}_6 \\
\end{align*} \]

Scheme 3-8. Polymerization of T6-diol into T6PC using triphosgene. a) triphosgene, pyridine, THF, 79%.

The polymerization occurred smoothly in either anhydrous DCM or anhydrous THF, the choice of the solvent depending mostly on the initial solubility of the diol oligomer, which was not an issue for T6-diol. Stoichiometric amounts of the diol and triphosgene were dissolved in the appropriate solvent at room temperature under inert atmosphere, and stirred until complete dissolution of the reagents. Approximately 4 equivalents of anhydrous pyridine were added dropwise at room temperature. The
reaction mixture started gelling after an hour and half of stirring, and was allowed to stir at room temperature for an additional 12 hours.

The extent of polymerization could easily be monitored by $^1$H-NMR as the triplet at 3.65 ppm corresponding to the two $H_h$ of the methylene next to the hydroxyl group moves downfield to 4.14 ppm after polymerization as a result of the withdrawing effect of the newly formed carbonate functionality. As can be seen on Figure 3-3.a, a small peak remains at 3.65ppm that could correspond to methylenes next to unreacted end-groups (red arrow). The IR spectrum of T6PC, displayed in Figure 3-3.b, shows the appearance of the carbonate carbon-oxygen single and double bonds peaks, centered at 1260 cm$^{-1}$ and 1742 cm$^{-1}$ respectively (blue spectrum), compared to that of T6-diol (black spectrum).

Figure 3-3. $^1$H-NMR (a) of the polycarbonate T6PC and IR spectra (b) of T6-diol and T6PC. The red arrow at 3.65 ppm indicates the protons on the carbon alpha to unreacted terminal alcohols.

The reaction mixture was then diluted with chloroform, washed with water and finally the organic extracts were precipitated in methanol and purified by Soxhlet extraction using methanol, hexanes and chloroform. The remainder of this study is performed on the polymer sample from the chloroform Soxhlet fraction. A number
average molecular weight ($M_n$) and polydispersity index (PDI) of 22,700 kDa (PDI = 2.07) for T6PC from the latter fraction was measured by gel permeation chromatography (GPC) against polystyrene standards. The polymer is soluble in THF, toluene and chlorinated solvents such as dichloromethane, chloroform and chlorobenzene.

### 3.3.2 Spectroscopy, Electrochemistry and Spectroelectrochemistry of T6PC

The UV-vis absorption spectra of T6PC and T6-diol in THF solution are identical, as shown in Figure 3-4.a (black plain and dashed lines, respectively). The polymer was then sprayed onto ITO-coated glass slides from THF solution (2 mg/mL) and the thin film absorption was recorded (blue line).

![Figure 3-4](image)

**Figure 3-4.** UV-vis spectra (a) of T6-diol and T6PC in solution (black lines) and T6PC thin film sprayed onto ITO-coated glass slide (blue line), and UV-vis spectra (b) of the chemical doping process of T6PC with EPR signals of the neutral and oxidized species (inset). Orange lines are neutral and blue lines are oxidized species.

In solution, one symmetrical absorption band centered at $\lambda_{\text{max}} = 424$ nm is observed for T6PC with an absorption onset at 500 nm. In the solid state, the absorption of T6PC is red-shifted with the appearance of local maxima: the peak absorption is shifted to 479 nm, with a higher energy shoulder at 455 nm and a lower energy shoulder
at 515 nm. The transition from solution to thin film is thus characterized by a higher vibronic resolution, which could be accounted for by a better ordering of the material in the solid state. With a solid state absorption onset at 556 nm, the optical energy gap of \textbf{T6PC} is calculated to be 2.23 eV, which is about 0.2 eV higher than the bandgap typically reported for the fully conjugated polythiophene P3HT.\textsuperscript{30}

In order to test the electroactivity of the polymer in solution, chemical oxidation experiments were carried out. The chemical oxidation of a dichloromethane solution of \textbf{T6PC} by the addition of silver hexafluorophosphate as oxidant was monitored in parallel by UV-vis absorption spectroscopy and EPR spectroscopy, as shown in Figure 3-4.b. As the concentration of oxidant in solution is increased, the neutral state absorption band centered at 424 nm gradually decreases while two new bands centered at 630 and 1090 nm emerge. This translates into the yellow neutral solution switching to a blue color as the oxidant concentration is increased (inset). While the neutral solution is EPR silent (orange line in the inset, Figure 3-4.b) as expected for a diamagnetic sample, the addition of silver hexafluorophosphate oxidant resulted in a broad EPR signal (blue line, inset) centered at $g = 2.005$ with a peak to peak width of 2.8 G. The emergence of the two absorption bands upon chemical doping coupled with the appearance of an EPR signal supports the formation of radical cations in solution, and the results are consistent with previous reports of oligothienylene doping.\textsuperscript{161} No additional band was observed when excess oxidant was added in solution.

To investigate the redox properties of \textbf{T6PC} in the solid state, electrochemical measurements were conducted on thin films of the polymer dropcast from THF solution onto Pt button electrodes. Figure 3-5.a shows the cyclic voltammograms of \textbf{T6PC} films
recorded in 0.1M lithium bis(trifluoromethylsulfonyl)imide (LiBTI) in acetonitrile (ACN) under inert atmosphere. All potentials are calibrated versus Fc/Fc⁺.

![Diagram](image)

Figure 3-5. Tenth (solid lines) and 150th (dashed lines) cyclic voltammograms (a) from 0 to 0.4 V (black lines) and from 0 to 0.95 V (blue lines) of T6PC drop-cast onto Pt-button electrodes in 0.1 M LiBTI/ACN under inert atmosphere. Differential pulse voltammogram (b) of T6PC drop-cast onto Pt-button electrodes under the same conditions.

Initial scans up to 1.0 V revealed two oxidation processes which were not stable to repeated scans. A first oxidation wave, displayed in black in Figure 3-5.a, was isolated by confining the CV potential window from 0 V to 0.40 V. With an anodic peak potential at 0.34 V and a cathodic peak potential at 0.21V, this first oxidation process centered at a half-wave potential of 0.27 V was quasi-reversible and stable to at least 150 scans from 0 to 0.40 V (black voltammograms, Figure 3-5.a). When the potential window was increased to from 0 to 0.95 V, a second oxidation process with anodic and cathodic peak potentials at 0.82 V and 0.52 V was observed, but the current intensity decreased over repeated cycles, as shown in blue in Figure 3-5.a. The first oxidation process likely corresponds to the formation of the radical cation in the film of T6PC, while the second recorded oxidation would correspond to the formation of the dication species. This suggests that the electrochemically generated radical cation is a readily accessible and
stable species, while accessing the dication is only possible at potentials at which film degradation occurs. Figure 3-5.b shows the DPV of the **T6PC** film on Pt button electrode, recorded in the same conditions as for the CV measurements. From the onset of oxidation at 0.20 V, a HOMO energy level of 5.30 eV is calculated, which is within 0.1 eV of that reported in the literature for P3HT. With an optical energy gap of 2.23 eV, the LUMO is calculated to be at 3.07 eV.

The spectroelectrochemistry of **T6PC** thin films was conducted on films sprayed onto ITO-coated glass slides. The electrolyte was switched to 0.1M LiBTI in PC. The CV and DPV of the polymer were first recorded to break in the films and identify the required potential window, as displayed in Figure 3-6.a.

![Figure 3-6](image)

Figure 3-6. Cyclic voltammograms (a) from -0.1 to 0.45 V (black line) and from -0.1 to 1.05 V (dashed line) and DPV (dash-dot line) of **T6PC** sprayed onto ITO-coated glass slides in 0.1 M LiBTI/PC under inert atmosphere. Spectroelectrochemistry (b) for a spray-cast film of **T6PC** on ITO-coated glass, from 0.2V to 1.05V versus Fc//Fc²⁺, 0.1 V potential increments, recorded in LiBTI/PC solution.

Consistent with the Pt button electrochemistry, two oxidation waves are observed when the potential window was scanned from 0 to 1.05 V (CV2, dashed line). The current intensities decreased significantly, by half over thirty cycles (not shown), confirming the poor stability of the polymer film at such high potentials. Nevertheless,
spectroelectrochemical measurements were performed on the T6PC films, stepping the potential from 0.20 V to 1.05 V at 0.1 V increments, as shown in Figure 3-6.b.

Initial oxidation leads to the decrease of the neutral absorption band centered at 480 nm, while two new bands emerge around 630 nm and 1050 nm, which then merge into a single absorption band peaking at 730 nm, at potentials higher than 0.8 V. The overall absorption intensity at potentials higher than 0.5 V starts decreasing, which is another indication of thin film degradation. The appearance of the two bands at lower potentials corresponds with the formation of radical cation species in the film, as identified from the solution chemical doping experiments. Although it leads to film degradation, the progressive fusion at higher potentials of these two bands into a single one at intermediate wavelengths corresponds to the formation of dication species in the film, which was previously documented for similar oligothienylene systems.171

Since the first oxidation process was significantly more stable to repeated cycles than the second one, spectroelectrochemical measurements focusing on a shorter potential window were conducted. A film of T6PC on ITO already subjected to at least 10 CV scans from -0.1 to 0.45 V was inserted in the spectrophotometer with the spectroscopy cuvette as electrochemical cell, and step potentials were applied from 0.23 V to 0.54 V in 10 mV increments, resulting in the spectra displayed in Figure 3-7.a. The neutral spectrum (yellow line) featuring the peak absorption around 480 nm and some vibronic resolution as described previously gradually decreases as two new bands centered a 621 and 1036 nm appear. They eventually stabilize to ca. 40% of the neutral film peak absorption intensity. This is accompanied by a reversible color change from orange to blue as displayed in the inset of Figure 3-7.a. Consistent with the
solution chemical doping spectra and the CV experiments, this dual-color electrochromism can be attributed to the generation of radical cations within the thin film of T6PC.

Figure 3-7. (a) Spectroelectrochemistry for a spray-cast film of T6PC on ITO-coated glass, from 0.23V to 0.54V versus Fc/Fc+, 10mV potential increments, recorded in LiBTI/PC solution (switching film pictures in inset) and (b) Square-wave potential step absorptometry, from 10s to 0.5s switching times.

The contrast can be visually appreciated on the oxidized film in the inset as both neutral and oxidized areas coexist on either side of the electrolyte solution meniscus. A well-defined isosbestic point can be seen at 533 nm. This is consistent with the polymer repeat unit structure, as the chromophore content in the backbone is monodisperse: spectral change arises from the removal of an electron from π-systems which are all of the same conjugation length. In the switching speed experiment (Figure 3-7.b), the contrast (defined as the difference in % transmittance at 454 nm) was recorded as a function of the potential step time ν. The contrast decreases from 27% at ν = 10s to 16% at ν = 0.5s. Although the maximum contrast does not compare to that of the best electrochromic polymers because the design of T6PC does not allow it to become fully
transmissive in the first oxidation process, still it appears that the electrochromic switching is fast with little loss of contrast even at potential step times of 1s.

The polycondensation of T6-diol into its polycarbonate affords a polymer which by design contains conjugation breaks, yet the previous set of experiments shows that electroactivity, at least in an electrochemical sense, is maintained in thin films. The nature of the charged species was identified and correlated to the observed electrochromism in the films. The next section focuses on the morphological characteristics induced by the covalent linking of the telechelic oligomers into macromolecules.

3.3.3 Liquid-Crystallinity and Bulk Morphology

Upon polymerization, T6PC acquired film-forming characteristics with sufficient mechanical strength that free standing films were easily obtained by simple evaporation of a THF solution. A 7.0cm x 1.5cm free standing film of T6PC was easily peeled off of a rectangular Teflon mold, as displayed in Figure 3-8.a. At room temperature, the film does not stretch, but once heated at 65°C, the film can be stretched up to 300% of its initial length prior to mechanical failure. The thermal behavior of conjugated systems is an important property to investigate, as thermal treatments can have a significant impact on the material’s morphology. The TGA thermograms of T6-diol and T6PC in Figure 3-8.b show that both compounds are thermally stable up to 422°C and 370°C respectively, setting a 5% weight loss as thermal stability threshold. The DSC thermogram of T6-diol (Figure 3-8.c, dashed line) shows a sharp melting transition that occurs at 104°C during the second heating scan. Upon cooling, a crystallization peak appears at 64°C. Compared to T6-diol, the DSC thermogram of T6PC shows
broadened peaks which are shifted to lower temperatures at 84°C. In particular, a second peak at 52°C appears in the heating scan of T6PC.

Figure 3-8. Picture (a) of a 7.0cm x 1.5cm freestanding film of T6PC, TGA thermograms (b) of T6-diol (solid line) and T6PC (dashed line) under nitrogen, DSC thermograms (c) of T6diol (dashed line) and T6PC (solid line), and evolution of the DSC thermogram (d) of T6PC with annealing time at a room temperature.

A glass transition temperature ($T_g$) is observed at 18°C, but no crystallization peak was recorded in the cooling scan. Annealing experiments were performed at various temperatures to identify possible phase transitions, yet the only effective procedure took place at room temperature, as detailed in Figure 3-8, and described in the following. The polymer was subjected to one heating and cooling cycle (10°C/min) to erase its
thermal history. A second heating scan was recorded immediately afterwards (annealing time $t = 0$), then cooled in similar conditions. The polymer was then allowed to rest in the DSC pan for one hour in the instrument sampler (which is kept a room temperature) and then heated again ($t = 1h$). This was repeated three more times with increasing annealing times of 3, 24 and 48 hours. This led to identify one reproducible trend: as the polymer was left at room temperature ($23^\circ C$), the two endothermic transition peaks intensify with time. These results suggest that room temperature (which is close to the $T_g$) offers enough energy for T6PC to undergo some phase transition, in an overall relatively slow process. This behavior was observed previously on samples of poly(3-decylthiophene) (P3DT) of 14.1 kDa weight-average molecular weight (PDI = 1.64). In the reported DSC thermograms of P3DT, after initial heating and cooling, reheating the sample immediately only displayed broad features; but after a day at room temperature, samples crystallized (either from the melt or from the mesophase) recovering a thermal behavior closely similar to that of the pristine samples. In the case of T6PC, no noticeable change was observed after 2 days of annealing at room temperature.

Polarized optical microscopy coupled to a heating stage to monitor microscopic morphology changes upon thermal treatment was used to identify possible phase transitions. Figure 3-9 shows the POM images of T6-diol and T6PC. When a sample of T6-diol is heated above its melting point, and then allowed to cool back to its crystallization temperature, a well ordered phase with strong birefringence under polarized light emerges (Figure 3-9, left).
Figure 3-9. Polarized light optical microscope images of T6-diol (left) and T6PC (center and right), at crossed polarizer/analyzer.

The observed Maltese cross patterns are typical of a spherulitic arrangement of the crystallized domains. Specifically, the spherulites could be a result of needle-shaped crystals that emerge from a common center and are radially-oriented, which would explain the Maltese cross pattern. Spherulites were also observed under similar conditions in reports by Pisula et al. of the self-assembly of phenylene-thienylene oligomers bearing linear alkyl and alcohol terminated chains, like T6-diol. The molecular arrangement could be explained in terms of amphiphilicity, as a result of competition between hydrogen bonding of the terminal hydroxyl groups and mutual exclusion of the alkyl and alcohol groups; with the added propensity of the conjugated cores to \( \pi \)-stack.

Upon polymerization of the diol into T6PC, the oligomers lose some degree of freedom as a consequence of the covalently formed carbonate functionalities. The polarized-light pattern changes accordingly to a less ordered structure, as shown in Figure 3-9. POM images of a T6PC film on ITO-coated glass reveal a microstructure similar to a Schlieren-type nematic texture but on a small scale. Schlieren textures characteristic of nematic phases typically display features on the 100 microns scale. In the case of T6PC, as detailed in the right-hand side of Figure 3-9, the birefringence
features are on the 1 to 5 microns scale. Optical micrographs showing a fine nematic texture identical to that in Figure 3-9 have been described previously by Windle et al. on POM captions of random copolyesters of ethylene terephthalate and hydrobenzoic acid. Another example of such fine texture can be found in a report of liquid crystalline poly(phenylene ethynylene) by Bunz et al. In the case of T6PC, it was observed at room temperature after the sample was held at 140°C for one hour and allowed to cool down. When reheated, the texture holds up to the second melting temperature in the 50 to 55°C range, after which the sample becomes optically isotropic. Therefore, the T6PC thin film shows local optical anisotropy on a scale of a few microns at room temperature. This could be explained by phase separation between the aromatic cores and the aliphatic segments as well as π-stacking between neighboring chromophores, which can lead to some degree of order in the polymer.

Quantitative insight on how well T6PC organizes when the polymer chains are aligned is provided by two-dimensional wide angle X-ray spectroscopy measurements performed on extruded filaments of the polymer. The sample was prepared as a thin filament of 0.7 mm diameter by heating it up for extrusion to 65°C at which it becomes plastically deformable. The diffractogram in Figure 3-10.a was obtained at 30°C. The distance for the outer reflections is 3.7 Å. This peak position corresponds to the intermolecular distance between two π-stacked chains. Being located on the equatorial axis in the wide-angle region, this reflection indicates that the lamellae of π-stacked chains are aligned along the extrusion direction as depicted in Figure 3-10.b. Additionally, several pronounced reflections on the equatorial axis appeared related to the d-spacings of 1.70 nm, 0.76 nm, 0.50 nm, which are attributed to the interlamellae
distance. Some of the best polymeric OFETs reported in the literature so far are based on materials for which the π-stacking distance lies in the range of 3.9-3.6 Å.42

Figure 3-10. 2D-WAXS pattern (a) of T6PC as an extruded filament at 30°C (above) and scattering intensity distribution as a function of the scattering vector (below). (b) Model for the aligned polymer chains.

OFETs were fabricated at the MPI with T6PC as active layer. Highly doped silicon was used as the gate electrode, while the dielectric was a 200 nm thick SiO$_2$ film. A bottom contact FET (channel widths 5-100 μm and lengths 0.35 to 7.0 mm) was prepared by spin-coating a 10 mg/mL T6PC-chloroform solution. The solution processing and electrical measurements were performed inside a nitrogen filled glovebox at room temperature. Unfortunately, little transistor behavior was obtained under such conditions, as hole mobilities of 10$^{-7}$ cm$^2$V$^{-1}$s$^{-1}$ with an on/off ration of 10$^2$ were recorded. Annealing studies on the solution processed device did not improve the
performance. Since T6PC has mechanical properties such that it can be stretched up to 300% of its length without mechanical failure once heated to 65°C, it was proposed that polymer chains could be mechanically oriented by stretching a sample prior to device fabrication. Figure 3-11.a shows the evolution of the birefringence of a T6PC free standing film with film orientation with respect to the crossed polarizer/analyzer direction (0 and 45 degrees) before (top) and after (bottom) stretching.

![Figure 3-11](image.png)

Figure 3-11. POM capture of the free standing film (a) before (top) and after (bottom) stretching at 0° (left) and 45° (right) with respect to the analyzer at crossed polarizer/analyzer. POM capture of the stretched film transistor (b) at 0° (left) and 45° (right) with respect to the analyzer at crossed polarizer/analyzer.

While there is no preferred orientation before stretching, the film becomes clearly anisotropic after it is stretched; suggesting that such a mechanical treatment efficiently aligns the polymer chains. This observation made in our labs was communicated to our collaborators at the MPI, who applied it in OFET device fabrication. In this setup, top contact FETs (channel widths 25-70 μm and lengths 0.5 to 1.5 mm) were prepared by manually stretching a film of T6PC onto the dielectric surface. Figure 3-11.b shows the POM images of the stretched film transistor at 0 (left) and 45 (right) degrees with respect to the crossed polarizer/analyzer. Unfortunately, no transistor characteristics were obtained likely due to a poor interface between the film and the dielectric, most probably caused by the clamping of the film.
In summary, the secondary structure designed through polycondensation of the terminal diols (a process likely applicable to many other electroactive oligomers) allows the material to acquire physical properties of macromolecules, while retaining electroactivity and displaying micron-scale ordering in thin films. Extruded polymer samples show that chromophores π-stack with a distance of 3.7 Å, which is within the range of high-mobility materials reported in the literature. Unfortunately, the material did not perform well in OFETs, even after attempts to mechanically align the polymer chains by taking advantage of the good mechanical properties of T6PC.

### 3.4 Morphology Control via Monofunctional Oligomer/Inorganic Nanoparticle Hybrids

With the phosphonic acid-functionalized sexithiophene and bithiophene-BTD-bithiophene oligomers synthesized (Scheme 3-9), their design as electroactive ligands for inorganic CdSe nanocrystals was tested. First their optical and electrochemical properties were studied, and then their interaction with the nanocrystals was probed by solution photoluminescence evolution in mixtures. Finally, hybrids were obtained and their composition was analyzed.

![Scheme 3-9. Structure of T6-PA and T4BTD-PA oligomers.](image)

The UV-vis absorption and fluorescence spectra were obtained for T6-PA and T4BTD-PA, as shown in Figure 3-12. T6-PA has one absorption band centered at 426 nm, while the spectrum of T4BTD-PA features two absorption bands peaking at 360 nm.
and 505 nm. Molar absorptivities of 20,000 – 50,000 M$^{-1}$cm$^{-1}$ were recorded in CHCl$_3$ solutions, as summarized in Table 3-1. From the absorption onset in solution, a relatively high energy gap of 2.4 eV is calculated for T6-PA, as expected of an oligomers with homogeneous $\pi$ system. The BTD-based oligomer, on the other hand, features a longer wavelength absorption onset corresponding to a lower HOMO-LUMO gap of 2.0 eV. This is due to the DA interaction attributable to the mixing of the BTD acceptor unit with the flanking bithiophene donors. The CdSe NCs have a long wavelength absorption peak at 624 nm characteristic of the quantum confinement effect and the absorption increases steadily towards the UV region of the spectrum.

![UV-vis absorption and fluorescence spectra](image)

Figure 3-12. UV-vis absorption (a) and fluorescence (b) spectra of the two oligomers and the CdSe NPs in chloroform solution.

This is in accordance with the size of the NCs, and an optical energy gap of 1.9 eV is calculated. We measured the photoluminescence of each oligomer, in ester and acid form, in dilute chloroform solution. The oligomer solutions exhibit intense fluorescence with quantum efficiency near or above 50%, as summarized in Table 3-1. The peak emission wavelength of T4BTD-PA is red-shifted compared to T6-PA: the peak
fluorescence is at 565 nm for **T6-PA** and 676 nm for **T4BTD-PA**, which is consistent with the absorption results. Solution fluorescence lifetimes were determined for both acids and esters, and there is little difference between the acid and the ester form for each oligomer, as expected for the dilute solutions used where little aggregation is expected. While the T6 oligomer shows short lifetimes of ca. 0.9 – 1.0 ns, the BTD oligomers exhibits significantly longer lifetimes of ca. 5 ns. The longer the exciton lifetime is, the better chance it has to reach a heterojunction at which it can be separated into a hole and an electron before recombination occurs.

Table 3.1. Absorption and fluorescence $\lambda_{\text{max}}$, optical HOMO-LUMO gaps, extinction coefficients, FL quantum yields and FL lifetimes for each oligomer.

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\text{max}}$ abs (nm)</th>
<th>Optical $\Delta E$ (eV)</th>
<th>$\varepsilon_{\text{abs}}$ (M cm$^{-1}$)</th>
<th>$\lambda_{\text{max}}$ Fl (nm)</th>
<th>$\Phi_{\text{Fl}}$</th>
<th>$\tau_{\text{Fl}}$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T6-PE</td>
<td>424</td>
<td>2.4</td>
<td>55600</td>
<td>537/564</td>
<td>0.54</td>
<td>0.86</td>
</tr>
<tr>
<td>T6-PA</td>
<td>426</td>
<td>2.4</td>
<td>48700</td>
<td>539/565</td>
<td>0.49</td>
<td>0.85</td>
</tr>
<tr>
<td>T4BTD-PE</td>
<td>504</td>
<td>2.1</td>
<td>30000</td>
<td>675</td>
<td>0.79</td>
<td>5.60</td>
</tr>
<tr>
<td>T4BTD-PA</td>
<td>508</td>
<td>2.0</td>
<td>21000</td>
<td>676</td>
<td>0.79</td>
<td>5.55</td>
</tr>
<tr>
<td>CdSe</td>
<td>624</td>
<td>1.9</td>
<td>632000</td>
<td>650</td>
<td>0.001</td>
<td>1.26</td>
</tr>
</tbody>
</table>

The redox properties of each oligomer were investigated using cyclic and differential pulse voltammetry in solution. For each oligomer, a small amount of material was dissolved in a dry and degassed dichloromethane-based electrolyte containing 0.1M tetrabutylammonium hexafluorophosphate (TBAPF$_6$), so as to achieve a concentration of 1 mM in oligomer. All measurements were performed in an argon-filled glovebox. All potentials are reported against the Fc/Fc$^+$ standard. For the **T6-PA** oligomer in solution, the oxidative CV (Figure 3-13.a) shows two quasi-reversible processes centered at half-wave potentials of 0.33 V and 0.56 V. No reduction was
observed when the potentials were scanned cathodically of 0 V up to -2.0 V. The absence of reduction process for T6-PA is not surprising since it is an electron-rich chromophore which would require even more negative potentials to accommodate the addition of an electron in its π-system. For T4BTD-PA, the oxidative CV shows one reversible oxidation process centered at a half-wave potential of 0.50 V. In contrast to T6-PA, the reductive CV of T4BTD-PA recorded one reversible reduction process centered at a half-wave potential of -1.66 V. This is consistent with the D-A nature of the chromophore, which results in a lowered LUMO energy level (higher electron affinity).

Figure 3-13. CV and DPV of (a) T6-PA and (b) T4BTD-PA in 0.1 M TBAPF$_6$ in dichloromethane, at 50 mV/s scan rate.

From the oxidative DPV, oxidation onsets for T6-PA and T4BTD-PA were measured at 0.22 V and 0.40 V respectively. As accounted for above, only T4BTD-PA showed a reduction process in reductive DPV experiments, with an onset of reduction at -1.55 V (see Figure 3-13, dashed lines). Converting the voltage values calibrated against the Fc/Fc$^+$ standard into energy values against vacuum, using a Fc/Fc$^+$ redox standard set at -5.1 eV, HOMO energy levels were calculated at -5.32 eV for T6-PA and at -5.50 eV for T4BTD-PA. We could calculate the LUMO energy of T4BTD-PA from the reductive DPV onset to be at -3.55 eV, giving an electrochemical energy gap of 1.95 eV.
which is close to its optical energy gap value of 2.0 eV measured spectroscopically. The absence of a voltammogram wave attributable to the reduction of the all-thiophene oligomer prevented the electrochemical estimation of LUMO energy for the latter. Since the optical energy gap of the BTD-based oligomer is only within 0.05 eV of its electrochemical energy gap, the corresponding optical energy gap listed in Table 3-1 was used to deduce the energy of the LUMO for T6-PA, which was -2.92 eV vs vacuum. Figure 3-14 depicts the position of the HOMO and LUMO energy levels with respect to the positions of the conduction and valence bands of the CdSe NCs used in this study, between -4.3 and -4.5 eV, and between -6.2 and -6.3 eV respectively.\(^{177}\)

![Energy levels diagram](image)

**Figure 3-14.** Energy levels diagram (absolute values) for the HOMO and LUMO levels of T6-PA, T4BTD-PA and NCs.

The LUMO levels of the oligomers are more than 1 eV higher than the CB of the NCs and likewise the HOMO levels are more than 0.5 eV higher than the VB of the NCs. Such energetic offsets result in staggered energy gaps for each organic oligomer / CdSe NCs complex, which is analogous to that described as type II heterojunctions in solid state semiconductor physics.\(^1\) In terms of the expected photoelectrochemical behavior, this type of heterojunctions suggests that photoexcitation of either the
oligomers or the NCs should lead to electron transfer from the oligomer (as an electron-donor) to the CdSe NCs (as an electron-acceptor).

The two phosphonic acid-functionalized oligomers in this study are designed to undergo ligand exchange with native surfactants. In the following, we monitored the evolution of the photoluminescence (PL) intensity of each oligomer upon addition of incremental amounts of CdSe NCs in solution, and compared the evolution for the phosphonate derivatives versus the phosphonic acid ones.

3.4.2 Oligomer/CdSe NC PL Quenching Experiments

Photoluminescence quenching is a powerful tool to probe the electronic interaction between two different electroactive species. This technique was used in particular by Frechet et al to decipher between charge and electron transfer processes in a system composed of 4 nm CdSe NCs and phosphonic acid functionalized pentathiophenes.\textsuperscript{143} They observed significant PL quenching of the pentamers’ fluorescence in solution upon addition of CdSe NCs, and likewise significant quenching of NCs’ emission upon addition of the pentamer. The PL quenching of shorter thiophene trimers was also quenched by CdSe NCs, but the emission of the NC in the reverse experiment increased. This was accounted for by the difference in staggered energy gaps between the NCs and the pentamer (type II heterojunction) compared to straddling energy gaps (type I heterojunctions) between the NCs and the wider-energy gap trimer. Ruling out the possibility of energetic surface defect passivation by the phosphonic acid anchoring group itself, the dual luminescence quenching was explained by an electron-transfer mechanism from the thiophene pentamers to the NCs. Similar observations were reported by Advincula et al. for phosphonic acid functionalized thiophene dendrons, and this type of experiments was used by others as well. In the dilute solutions typically
used for fluorescence experiments, photoluminescence evolution upon the interaction of two different species requires them to be in close proximity of one another, regardless of the quenching mechanism.\textsuperscript{109} The inorganic synthesis of CdSe NCs involves the use of surfactants usually composed of long alkyl chains and a polar functional group, such as oleic acid or trioctylphosphine oxide (TOPO), with which the NC surface is coated after the reaction is over. There is thus an inherent insulating layer of aliphatic surfactants coating each NC, which has been shown to be detrimental to their electronic interaction with conjugated polymers.\textsuperscript{178} The exact nature of the aliphatic surfactants coating the NCs is not straightforward, as it depends on the nature and purity of that used during NC synthesis, and the purification process that followed. Nevertheless, the use of functional groups such as phosphonic acids or carboxylates, which bind strongly to the NCs surface, have been shown to displace some of the aliphatic native surfactants, during a ligand exchange process which results in new molecules anchored to the NC surface.\textsuperscript{179}

The two phosphonic acid-functionalized oligomers in this study are designed to undergo ligand exchange with native surfactants. We monitored the evolution of the PL intensity of each oligomer upon addition of incremental amounts of CdSe NCs in solution (Experiment A, Figure 3-15), and compared the evolution for the phosphonate derivatives versus the phosphonic acid ones. Figure 3-15.a shows the PL evolution for the T6 phosphonate (\textbf{T6-PE}, left) and the T6 phosphonic acid (\textbf{T6-PA}, right) in dilute chloroform solution (5 \(\mu\)M) as 20 \(\mu\)M CdSe in chloroform was added, in increments. The relative concentrations were such that only microliters of CdSe solution were added to the fixed volume of 2 mL of oligomer solution, thereby negating the effect of dilution on
the PL intensity. For the phosphonate T6-PE, the addition of the CdSe leads to little quenching of the oligomer luminescence. This suggests that the ester form of T6 has, at best, a weak interaction and thus there is little binding of the oligomers to the NCs. The opposite is true for the acid form T6-PA, where very strong luminescence quenching was observed at substantially low CdSe concentration (nanomolar range). The fluorescence is essentially fully quenched at a concentration ratio of T6-PA:CdSe equals 50:1 in solution.

Figure 3-15. Evolution of the fluorescence in chloroform of (a) T6-PE (left) and T6-PA (right) upon addition of CdSe NPs into the solution, (b) CdSe NPs upon addition of T6-PE (left) and T6-PA (right) solutions, (c) T4BTD-PE (left) and T4BTD-PA (right) upon addition of CdSe NPs into the solution, and figurative description of the two types of experiments (top right).

When carefully monitoring the 610 to 630 nm range for any enhancement of the emission from the CdSe in the oligomer/CdSe mixture, no luminescence increase was
observed. This was not surprising considering the low concentration of CdSe NCs in solution, and was not sufficient to decipher between electron or energy transfer mechanisms. This was further tackled by studying the PL quenching of CdSe by T6 oligomers. When solutions of CdSe NCs were selectively excited at 630 nm, their emission intensities were recorded when various amounts of T6 oligomers were mixed in. This was done according to the experimental procedure B described in Figure 3-15, keeping the concentration of CdSe constant in each measurement. It is observed that the photoluminescence of CdSe decreased upon addition of T6-PA, while by comparison, the same amount of T6-PE had no influence on the CdSe emission. As the mechanism of photo-induced charge transfer process is concerned, either of the following scenario are to be considered: 1) direct excitation of the organic ligands (CdSe NCs) followed by the electron injection (hole migration) from the ligands (CdSe NCs) to the CdSe NCs (the ligands), or 2) Energy transfer happens from the excited state of the ligands to the CdSe NCs generating excitons in the NCs before the hole migration from NCs back to the ligands. In all events, charge separation between the components of the hybrid materials is involved.

Figure 3-15.c shows the same PL quenching experiment of oligomer emission by addition of CdSe conducted with the BTD-based oligomers (phosphonate T4BTD-PE, left and phosphonic acid T4BTD-PA, right). The quenching intensity difference between the phosphonate and the phosphonic acid was similar to that observed for the T6 oligomers: the luminescence of the acid form was very sensitive to the addition of CdSe, while the ester form remained fluorescent when the same amount of CdSe was added. This led to the same conclusion that the phosphonic acid functionalized oligomers have
a strong binding ability to the CdSe NCs. Unfortunately, the reverse experiment type B for the BTD-based oligomers was not possible since the absorption of both organic and inorganic species overlap significantly.

In summary, the intensity of the PL quenching suggests that the phosphonic acid group allows the oligomers to be in close contact with the CdSe NCs, to an extent where a 50:1 oligomer:NC ratio is sufficient to achieve complete transfer of the excited state from the oligomer to the NP. Because of the low concentrations employed, any evolution in the PL intensity should be due to an oligomer/NC complex formation, i.e. direct interaction between the two. This seems to occur by a charge transfer process rather than energy transfer as the emission of both species is quenched in the case of T6-PA.

3.4.3 Hybrids Synthesis and Characterization

From the PL quenching experiments, a 50:1 ratio of T6-PA:CdSe or T4BTD-PA:CdSe was found to be sufficient to completely quench the luminescence of the organic chromophore. We thus stipulated that such a ratio or higher would be suitable for the synthesis of the hybrids themselves. The hybrid preparation consists in the exchange of the superficial native ligands of the NCs with T6-PA or T4BTD-PA by mixing in chloroform, followed by precipitation of the NC/oligomer hybrid in an appropriate solvent and centrifugation to remove the supernatant containing any unbound species. Experimentally, 10 mg of the oligomer was dissolved in 5 mL of degassed chloroform, to which was added a solution of the NCs in chloroform at the appropriate concentration for an excess of 200:1 ratio in oligomer:NCs. The mixture was stirred vigorously in the absence of light at room temperature for 30 minutes, after which it was precipitated in a poor solvent for the NCs/oligomer hybrid, but good solvent for
the unbound surfactants and excess oligomer. For the T6-PA/CdSe NC system, ethyl acetate was used to precipitate the hybrids, while methanol was suitable to precipitate the T4-BTD-PA/CdSe NC system. After centrifugation of the suspension and removal of the supernatant containing unbound species, the precipitates were redissolved in chloroform and precipitated once again in the proper solvent. This was repeated several times, while recording the UV-vis absorption spectrum of the chloroform solutions in each step. As unbound oligomers remained in the supernatant which was removed after each precipitation, the overall absorption profile of the redissolved precipitates featured less absorption contribution from the oligomers. Once the relative absorption intensities of the NCs versus that of the oligomer stabilized, the chloroform solution containing the redissolved oligomer/NC hybrid was considered free of unbound oligomers. The UV-vis absorption spectra of such washed hybrids solutions are shown in Figure 3-16.a.

Figure 3-16. Absorption spectra (a) of the T6-based hybrid (blue line) and the T4BTD-based hybrid (red line) along with the spectrum of free CdSe NCs in solution. TGA thermograms (b) of the pristine CdSe NCs (dashed line) and the two hybrids, under nitrogen flow.

Compared to the pure NCs solution absorption displayed as a dashed line, the absorption profile of the T6 hybrid (blue line) has a broad absorption band centered at
426 nm from the contribution of the bound **T6-PA** oligomers. Likewise the absorption profile of the BTD-based hybrid shows the contribution of the NCs-bound **T4BTD-PA** peaking at 360 nm and 508 nm, as well as that of the NCs themselves as a shoulder around 625 nm in the red curve. Only weak fluorescence was observed in dilute solutions of the hybrids in chloroform, with quantum yields below 0.1% at 564 nm for the **T6** hybrid solution and at 676 nm for the **T4BTD** hybrid solution. This along with the absorption profiles of the hybrids supports the strong binding and interaction between the oligomers and the NCs.

With the hybrids synthesized, and the presence of surface-bound oligomers established, a more quantitative estimation of the average number of oligomers at the NCs surface was attempted. Thermogravimetric analysis can be employed to determine a total weight loss difference between the pristine NCs and the ones functionalized with the electroactive oligomers. In principle, during the ligand exchange process, if a native surfactant such as TOPO (MW = 415 g/mol) is replaced by **T6-PA** (MW = 827 g/mol) or **T4BTD-PA** (MW = 797 g/mol), then a NC/**T6-PA** or NC/**T4BTD-PA** hybrid should have a higher organic content by weight than the pristine NC. One obvious limitation to this method is that it is in fact very difficult to determine the exact number of native surfactants before ligand exchange. The results from a TGA experiment on hybrids are thus at best qualitative. Figure 3-16.b shows the TGA thermograms for a CdSe sample before ligand exchange (dashed line) and after ligand exchange with **T6-PA** (blue line) or **T4BTD-PA** (red line). A 6% weight loss difference at 500°C was observed for the BTD-based hybrid compared to the pristine CdSe sample, and an 8% difference for the T6-based one. This confirms that the ligand exchange process did increase the organic
content in the hybrid, supporting the presence of higher molecular weight species bound to the surface of the NCs.

A more quantitative way to estimate the number of surface-bound oligomers consists in a careful comparison of the hybrid’s absorption with that of the pristine NCs and the free oligomer. The absorption spectra of the latter three species in the case of T6 is shown in Figure 3-16.a.

The relative absorption intensities of the free oligomers (dashed blue line) and the free NCs (dashed black line) was adjusted such that the sum of their absorption spectra (black solid line) resulted in a profile for which the intensities at the respective absorption maxima (at 426 nm and 624 nm) matched that of the hybrid’s (solid blue line). This was achieved for an absorbance of 0.912 at 426 nm for T6-PA and 0.087 at 624 nm for the NCs. From Beer’s law, concentrations of 18.7 μM and 136 nM were calculated respectively, using the extinction coefficients listed in Table 3-1, resulting in an oligomer to NC ratio of 137. The same spectral analysis and calculations were
applied to the BTD-based system (Figure 3-17.b), yielding concentrations of 185 nM and 25.9 μM in NC and oligomer respectively, and a ratio of 140 oligomers per NC. These ratios are of course average values and remain an approximation of the number of oligomers bound to the NCs, but they suggest that a significant coverage of the NCs was achieved using T6-PA and T4BTD-PA.

3.5 Morphology Control via BHJ Crystallinity Disruption.

Contrary to the first two oligomeric systems studied in this chapter, the three molecules that are shown in Scheme 3-10 and are the focus of this section do not bear any reactive functional group. This is a set of molecules which are all based on the same bis-bithiophene (T₂) isoindigo (ii) aromatic core, but differ by the nature of their aliphatic end chains. As described in the synthesis part in Section 3.2.3, iIT₂-C₆₂ is symmetrical and has two n-hexyl end chains. Its unsymmetrical counterpart, iIT₂-C₆Si, has one n-hexyl chain on one side and a triisobutylsilyl group on the other side. The third molecule is the symmetrical triisobutylsilyl-substituted derivative.

Scheme 3-10. Structure of iIT₂-C₆₂, iIT₂-C₆Si and iIT₂-Si₂.

The first studies on isoindigo-based molecular BHJ solar cells revealed the existence of crystalline domains in the active layer when iIT₂-C₆₂ and PC₆₀BM were blended. Two processing methods focusing on additives have been investigated to tune the morphology of the iIT₂-C₆₂/PC₆₀BM bulk heterojunction. These additives are electro-optically inactive molecules that change the crystallization behavior of the
blend components when added in small amounts to the solution used for device fabrication. The three molecules described in this section were synthetically designed to provide a similar level of BHJ morphology control without the use of electro-optically inactive additives in the blend solutions. Specifically, it was anticipated that by disrupting the crystallization process of the symmetrical iT2-C62 by adding some percent of unsymmetrical iT2-C6Si in the blend solution, the final size of the crystalline domains in the active layer could be tuned, influencing the overall solar cell efficiency.

3.5.1 Electrochemical, Thermal and Optical Properties.

Before studying the effect on the solar cell active layer morphology by varying the side-chain nature of the oligomers, the electro-optical characteristics of each molecule should be understood. Their electrochemistry was studied in solution as displayed in Figure 3-18, all potentials being referenced against Fc/Fc+. The CVs and DPVs for each molecule dissolved at 1 mM in a DCM electrolyte containing 0.1 M TBAPF6 were plotted the same potential scale to facilitate their comparison. The two dotted vertical lines overlapping the three graphs are set at 0.42 V and -1.16 V, which correspond to the onset of oxidation and reduction of the DPVs for iT2-C62, respectively. All three oligomers showed two quasi-reversible reduction processes, centered at half-wave potentials between -1.27 and -1.28V for the first one and between -1.67 V and -1.72 V for the more cathodic one. In the positive potentials range, two overlapping oxidation waves could be distinguished for iT2-C62 and iT2-C6Si, centered at 0.54/0.55 V and 0.66/0.68 V respectively. The oxidation of iT2-Si2 only showed one wave centered at 0.62 V.
Figure 3-18. Cyclic voltammograms of iT$_2$C$_6$$_2$ (top), iT$_2$C$_6$Si (center) and iT$_2$Si$_2$ (bottom), and the corresponding differential pulse voltammograms (dashed lines) in 0.1 M TBAPF$_6$ in dichloromethane. Approximately 1mM concentration in oligomer.

Overall, the electrochemical processes as recorded by CV in solution occurred at very similar potentials, which was further supported by the DPV measurements. The DPV results showed that the onsets of oxidation and reduction for all three molecules are within 0.08 V and 0.03 V of one another respectively, and likewise for the DPV peak currents. This sets the HOMO and LUMO levels of the three molecules around -5.50/-5.60 eV and -3.90 eV respectively, with electrochemical energy gaps between 1.58 eV and 1.66 eV. These results support that the comparison of the molecular structure effect
on the solar cell performance in this study could be based mostly on morphological considerations, dispensing significant influence from the oligomers’ electronic characteristics.

Next, the thermal properties of the oligomers were investigated, employing TGA and DSC. The DSC results are shown in Figure 3-19, with the TGA thermograms displayed in the inset. From a 5% weight loss set as threshold for thermal decomposition, it appeared from the TGA (recorded under a flow of nitrogen) that all three oligomers are thermally stable up to at least 340°C. The DSCs were recorded for each oligomer separately all at 10°C/min from -50°C to 250°C. The thermograms shown in Figure 3-19 are the first cooling (a) and second heating (b) cycles for each oligomer.

![Figure 3-19. DSC and TGA (inset) thermograms of iIT<sub>2</sub>-C<sub>6</sub>2, iIT<sub>2</sub>-C<sub>6</sub>Si and iIT<sub>2</sub>-Si<sub>2</sub> (endo up).](image)

The thermogram for iIT<sub>2</sub>-C<sub>6</sub>2 showed a melting peak at 185°C upon heating and a sharp crystallization peak at 170°C (dash-dot line). For iIT<sub>2</sub>-C<sub>6</sub>Si (dashed line), a broad melting peak centered at 132°C appeared upon heating, and no crystallization peak was
observed. Rather, during the second heating scan after a featureless cooling scan, a cold crystallization broad peak starting at 90°C appeared before the melting peak. The thermogram for the symmetrical disilyl derivative iIT₂-Si₂ shows one melting peak at 145°C and a faint crystallization peak at 63°C. The differences in melting temperatures are consistent with an increased ability of the n-hexyl side-chain oligomers to pack more tightly compared to the bulkier triisobutylsilyl side-chain oligomers. More energy is required to separate molecules into a melt for iIT₂-C₆₂ than for iIT₂-C₆Si, and even more so than for iIT₂-Si₂, which would explain the 185°C, 145°C and 132°C decrease in melting temperature, respectively. This is further supported by the cooling cycles, where iIT₂-C₆₂ appears to crystallize well with a sharp peak and little hysteresis, while iIT₂-Si₂ barely crystallizes at the same cooling rate. iIT₂-C₆Si does not even crystallize well enough for a peak to be observed during cooling at that rate. The material appears to reorganize upon reheating starting at 85°C. These results confirm a significant difference between the crystallization behaviors of the three oligomers designed in this study. Specifically, iIT₂-C₆₂ crystallizes more readily than iIT₂-Si₂ and even more so than iIT₂-C₆Si₂.

The absorption of the three oligomers was measured, in solution and in the solid state. Figure 3-20 gathers the UV-vis spectra of iIT₂-C₆₂ (a), iIT₂-C₆₂ (b) and iIT₂-C₆₂ (c) in chloroform solution (solid lines) and as thin films spin-coated from chloroform solution (ca. 10 mg/mL, 2000 rpm) onto glass slides. The solid state spectra were recorded for the films as spun prior to thermal annealing (dotted lines), and after thermal annealing (dash-dot lines). Annealing was carried out by placing the films in an oven held at 90°C for 20 minutes.
Figure 3-20. UV-vis absorption of iIT$_2$-C$_6$ (a), iIT$_2$-C$_6$Si (b) and iIT$_2$-Si$_2$ (c) in chloroform (solid lines), as thin films spun-cast onto glass slides (dotted lines) and after thin film annealing (90°C, 20 min, dash-dot lines). Comparison of (d) solution absorption, (e) as spun thin film absorption and (f) annealed thin film absorption of the three oligomers.
The solution and as-spun spectra were normalized, while the annealed spectra were scaled to reflect the exact spectral changes observed from as-spun to after-annealing. As a means of comparison, Figure 3-20 also shows in the right hand side overlaid plots of the absorption profiles of the three oligomers in solution (d), as spun (e) and after thermal annealing (f). All spectra in the right hand side were normalized to ease comparison. The UV-vis absorption results are summarized in Table 3-2.

Focusing first on each oligomer, and starting with \textit{iIT}_2-\textit{C6}_2 (Figure 3-20.a), the solution absorption profile in chloroform features two absorption bands centered at 358 nm and 592 nm, with an absorption gap of approximately half the maximum intensities between 400 and 500 nm. The low-energy onset of absorption in solution is at 702 nm. In the spun-coated films, the absorption maximum is red-shifted by 66 nm to 658 nm, with a low-energy absorption onset at 745 nm, but the overall profile remains similar. Consequently, the deep purple-blue color in solution matched the blue color of the thin films. Annealing the film as described above did not have any effect on the as spun absorption profile aside from a slight decrease in intensity. This red-shift in the solid state suggests that the \textit{iIT}_2-\textit{C6}_2 oligomers are able to aggregate well likely through $\pi$-stacking. This is consistent with the sharp peaks observed in the DSC thermogram. Since there is essentially no change upon annealing, the \textit{iIT}_2-\textit{C6}_2 molecules seem to acquire a rather thermodynamically stable packing phase in the short time of solvent evaporation during spin-coating.

In Figure 3-20.b, the solution absorption of the unsymmetrical \textit{iIT}_2-\textit{C6Si} is identical as that of \textit{iIT}_2-\textit{C6}_2 (see Figure 3-20.d for comparison), while the solid state absorption broadened slightly with an increased intensity at higher energy compared to the solution
A significant spectral change was observed upon annealing, whereby the contribution of the low energy band peaking at 598 nm increased by 30% compared to the high-energy one. The as spun films were purple, and a clear switch to blue was observed upon annealing. The low-energy onset of absorption increased from 702 nm in solution to 710 nm as spun to 720 nm after annealing. The small red-shift in absorption onset observed from solution to as spun, to be contrasted with the blue-shift of the $\lambda_{\text{max}}$ by 13 nm, suggests that $\text{iIT}_2\text{C}_6\text{Si}$ does not undergo significant aggregation upon spin coating. Rather, annealing at 90°C—which was identified as within the cold crystallization temperature range in the DSC thermograms—led to further red-shifts of both the absorption onset and the $\lambda_{\text{max}}$, with an overall profile more alike the solution one. This suggests that while frozen in a less aggregated morphology during spin-coating, thermal treatment can allow the molecules to rearrange in a more thermodynamically stable morphology, which is consistent with the thermal behavior observed by DSC.

Table 3-2. Solution peak and onset absorptions, solution optical energy gap, and the corresponding values for the as-spun films and annealed films.

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\text{max}}$ sol. (nm)</th>
<th>$\lambda_{\text{onset}}$ sol. (nm)</th>
<th>$\Delta E_{\text{sol.}}$ (eV)</th>
<th>$\lambda_{\text{max}}$ as spun (nm)</th>
<th>$\lambda_{\text{onset}}$ as spun (nm)</th>
<th>$\lambda_{\text{max}}$ ann. (nm)</th>
<th>$\lambda_{\text{onset}}$ ann. (nm)</th>
<th>$\Delta E$ ann. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{iIT}_2\text{C}_6\text{C}_2$</td>
<td>358, 592</td>
<td>702</td>
<td>1.77</td>
<td>602, 658</td>
<td>745</td>
<td>601, 658</td>
<td>745</td>
<td>1.66</td>
</tr>
<tr>
<td>$\text{iIT}_2\text{C}_6\text{Si}$</td>
<td>358, 592</td>
<td>702</td>
<td>1.77</td>
<td>579</td>
<td>710</td>
<td>564, 598</td>
<td>720</td>
<td>1.72</td>
</tr>
<tr>
<td>$\text{iIT}_2\text{Si}_2$</td>
<td>358, 592</td>
<td>702</td>
<td>1.77</td>
<td>478, 540</td>
<td>700</td>
<td>460, 538</td>
<td>700</td>
<td>1.77</td>
</tr>
</tbody>
</table>
The solution absorption of the disilyl \( \text{iIT}_2\text{-Si}_2 \) derivative (Figure 3-20.c) is also identical to the two other derivatives (see Figure 3-20.d for comparison). The as spun films show no shift in the absorption onset, and a significant blue-shift of the \( \lambda_{\text{max}} \) from 592 nm to 540 nm, with most of the absorption between 350 nm and 600 nm. The color of the films was brown, and did not change upon annealing although a small blue-shift of the absorption was observed spectroscopically as a result of the thermal treatment.

Comparing the as spun and annealed solid state absorption profiles of the three oligomers, as plotted in Figures 3-20.e and 3-20.f, \( \text{iIT}_2\text{-C}_6\text{Si}_2 \) has the most red-shifted absorption, followed by \( \text{iIT}_2\text{-C}_6\text{Si} \) and finally \( \text{iIT}_2\text{-Si}_2 \), with approximately 50 nm shifts from one another. This is an important parameter to consider when selecting the main component for p-type material in the solar cell active layer. Essentially, and as already reported, the main component should be \( \text{iIT}_2\text{-C}_6\text{Si}_2 \), since it is able to crystallized best and has the most extended absorption. Then, \( \text{iIT}_2\text{-C}_6\text{Si} \) or \( \text{iIT}_2\text{-Si}_2 \) should be chosen as molecular additive to investigate its effect on the active layer morphology.

Electrochemistry shows little difference in the electronics of the two additives (Figure 3-18), which is also supported by their identical solution absorption, but thermal analysis and solid state absorption suggest that \( \text{iIT}_2\text{-C}_6\text{Si} \) is a good candidate as additive, since it offers a more extended absorption balanced with a likely more effective crystal size disruption.

### 3.5.3 Crystallization Behavior and Influence on Solar Cell Performance

It was hypothesized that the bulky triisobutylsilyl group would not insert as well as the \( n \)-hexyl chain into the \( \text{iIT}_2\text{-C}_6\text{Si}_2 \) crystal lattice as it develops, naturally creating a triisobutylsilyl-bithiophene-rich grain boundary. Monitoring the crystal sizes by optical
microscopy as a function of percent added \textit{iIT}_2\text{-C6Si} to the main \textit{iIT}_2\text{-C6}_2 component would provide a semi-quantitative insight on this effect. This was performed by Danielle Salazar in the Reynolds group by recrystallizing small amounts of \textit{iIT}_2\text{-C6}_2 and \textit{iIT}_2\text{-C6}_2/\textit{iIT}_2\text{-C6Si} mixtures from hexanes at low concentrations. By dispersing 0.05 mg of solids per mL of hexanes and heating the suspension to 60°C until complete dissolution, crystals of either pure \textit{iIT}_2\text{-C6}_2 or of the \textit{iIT}_2\text{-C6}_2/\textit{iIT}_2\text{-C6Si} mixture were obtained upon cooling. Their sizes were recorded using an optical microscope under polarized light at crossed polarizer/analyzer to enhance the contrast. Figure 3-21 (left) shows representative pictures of the pure \textit{iIT}_2\text{-C6}_2 crystals (0% \textit{iIT}_2\text{-C6Si} added) and the crystals obtained when 2%, 5% and 10% of \textit{iIT}_2\text{-C6Si} was added to the main \textit{iIT}_2\text{-C6}_2 component.

![Representative pictures of crystals](image)

Figure 3-21. Polarized light microscope images showing \textit{iIT}_2\text{-C6}_2 crystals as a function of added \textit{iIT}_2\text{-C6Si} in solution.

The graph in Figure 3-21 (right) shows the evolution of the average crystal size (population of 32 to 74 crystals depending on the ratio) as a function of the percent unsymmetrical oligomer added. The average crystal sizes decreased from $172 \pm 18 \, \mu m$ to $46 \pm 6 \, \mu m$ as the relative concentration of \textit{iIT}_2\text{-C6Si} is increased from 0 to 10%.
These results confirmed the anticipation of a iiT$_2$-C$_6$ crystal size reduction effect upon addition of small amounts of the unsymmetrical molecular additive iiT$_2$-C$_6$Si.

To test the hypothesis in solar cells, devices based on [iiT$_2$-C$_6$/ iiT$_2$-C$_6$Si]:PC$_{61}$BM (1:1 by weight) blend films were prepared by Dr. Ken Graham in a conventional architecture (ITO/PEDOT:PSS/[iiT$_2$-C$_6$/ iiT$_2$-C$_6$Si]:PC$_{61}$BM/Al) and the active layer surface morphologies were imaged using AFM. Figure 3-22 shows the AFM images of devices made with varying iiT$_2$-C$_6$Si to iiT$_2$-C$_6$ ratios of 0% to 50%. At 0% additive, well-defined crystalline features were visible with sizes at 200 nm scale.

Figure 3-22. AFM height images of [iiT$_2$-C$_6$/ iiT$_2$-C$_6$Si]:PC$_{61}$BM (1:1 by weight) blend films with varying mole % of iiT$_2$-C$_6$Si after 100°C thermal annealing, 5 × 5 μm images and 20 nm height scale (top); 1 × 1 μm images and 10 nm height scale (center). PCE of [iiT$_2$-C$_6$/ iiT$_2$-C$_6$Si]:PC$_{61}$BM cells (bottom right) with varying mole % iiT$_2$-C$_6$Si.
As the concentration of iIT$_2$-C6Si was increased, the crystalline features remained sharp with decreasing sizes on the order of 20 to 50 nm for up to 30% additive. At 50% additive, the definition of features worsened, suggesting a transition to a more amorphous morphology. A more detailed morphological study was performed by Dr. Ken Graham involving top-down and cross-sectional TEM imaging to support the hypothesis that the asymmetric iIT$_2$-C6Si oligomer disrupts crystallization and at high concentration leads to an amorphous morphology. The detailed solar cell characteristics were described and corroborated with the AFM and TEM imaging performed by Dr. Ken Graham as part of his PhD dissertation. The general trend is summarized here in Figure 3-22 (bottom), as the power conversion efficiencies for each set of cells described above were recorded and their average value plotted against the cells’ percent content in iIT$_2$-C6Si. The short-circuit currents, open-circuit voltages and fill factors all increased in going from 0% to 30% additive, although the J$_{sc}$ started decreasing after 20% added iIT$_2$-C6Si. This resulted in the trend in Figure 3-22, where the average efficiencies increased from 1.34% ± 0.41 to 2.24% ± 0.16 as 0% to 20% iIT$_2$-C6Si was added, stabilizing around 2% PCE from 20 to 30% additive, followed by a steady decrease to 0.71% ± 0.05 at 50% additive.

In summary, substituting a linear side chain for a bulkier group at one end of a conjugated molecule significantly changes its solid state properties, as observed by DSC and solid state spectroscopy. This was used to alter the crystallization of the parent symmetrical molecule, which was observed for simple mixtures of the two. The hypothesis that reduced crystal size would translate into reduce crystalline domains in
the active layer of molecular BHJ solar cell was verified by AFM, with a positive influence on the overall solar cell performance.

3.6 Synthetic Details

2-((6-(thiophen-2-yl)hexyl)oxy)tetrahydro-2H-pyran (3-2). In a dry flask was added thiophene (3.8 g, 45 mmol) which was then diluted with anhydrous tetrahydrofuran (200 mL). The mixture was stirred and cooled to -78°C under a flow of nitrogen. To the cooled mixture was then added a solution of n-butyllithium in hexanes (30 mL, 39.3 mmol) dropwise over 30 minutes. Stirring was continued at low temperature for 30 minutes after the addition of n-BuLi was complete, and then the flask was removed for the cooling bath to be stirred at room temperature of 1 hour. After cooling back to -78°C, compound 3-1 dissolved in 30 mL of tetrahydrofuran was added dropwise to the mixture. After the addition was complete, the mixture was allowed to warm up to room temperature and stirred for 12 hours. Water was then added to the flask, and the organics were extracted with diethyl ether and washed with water and brine. After drying the combined organics over magnesium sulfate, evaporation of the volatiles yielded a yellow oil. This was purified using bulb-to-bulb distillation in a Kugelrohr apparatus (140°C, 0.05 mmHg) to afford the title compound as a colorless oil (5.0 g, 22 mmol, 63%). $^1$H NMR (CDCl$_3$): $\delta$ 7.10 (dd, $J = 5.1, 1.1$ Hz, 1H), 6.91 (dd, $J = 5.1, 3.4$ Hz, 1H), 6.77 (dd, $J = 3.4, 1.1$ Hz, 1H), 4.57 (dd, $J = 4.3, 2.8$ Hz, 1H), 3.86 (m, 1H), 3.74 (dt, $J = 9.6, 6.6$ Hz, 1H), 3.50 (m, 1H), 3.38 (dt, $J = 9.6, 6.6$ Hz, 1H), 2.82 (t, $J = 7.6$ Hz, 2H), 1.84–1.25 (m, 14H). $^{13}$C NMR (CDCl$_3$): $\delta$ 145.68, 126.58, 123.88, 122.69, 98.82, 67.52, 62.32, 31.70, 30.75, 29.80, 29.68, 28.89, 25.97, 25.45, 19.69.
Trimethyl(5-(2-(tetrahydro-2H-pyran-2-yloxy)hexyl)thiophen-2-yl)stannane (3-3). To a solution of 1 (1.61 g, 6.0 mmol) in THF (20 mL) cooled at 0°C was added n-butyllithium (1.31 M in hexanes, 5.50 mL, 7.2 mmol). The cooling was removed for one hour, then recooled to 0°C prior to the addition of trimethyltin chloride (1 M in hexanes, 7.2 mL, 7.2 mmol) dropwise. The reaction mixture was allowed to warm up to room temperature overnight, after which the solvent was evaporated. The residue, a light brown slurry, was used with no further purification. $^1$H NMR (CDCl$_3$): $\delta$ 7.01 (d, $J$ = 3.2 Hz, 1H), 6.89 (d, $J$ = 3.2 Hz, 1H), 4.57 (m, 2H), 3.86 (m, 1H), 3.75 (m, 1H), 3.49 (m, 1H), 3.38 (dt, $J$ = 9.6, 6.5 Hz, 1H), 2.86 (t, $J$ = 7.5 Hz, 2H), 1.84–1.25 (m, 14H), 0.35 (s, 9 H).

5,5''-dibromo-2,2'-bithiophene (3-4). In the absence of light, N-bromosuccinimide (5.60 g, 31.5 mmol) was added portion wise to a solution of bithiophene (2.50 g, 15.0 mmol) in anhydrous dimethylformamide (80 mL). The reaction was left stirring at room temperature for three hours and subsequently poured onto ice whereupon a white precipitate forms. Filtration and recrystallization from ethanol affords the title compound (4.32 g, 13.30 mmol, 89%) as white crystals. $^1$H NMR (CDCl$_3$): $\delta$ 6.96 (d, $J$ = 3.8 Hz, 1H), 6.85 (d, $J$ = 3.8 Hz, 1H). $^{13}$C NMR (CDCl$_3$): $\delta$ 138.00, 130.88, 124.37, 111.74.

General procedure for 2-bromination of 3-hexylthiophene species: 2-bromo-3-hexylthiophene (3-5). To a solution of 3-hexylthiophene (2.52 g, 15 mmol) in dry dimethylformamide (DMF, 130 mL) cooled to 0°C was added N-bromosuccinimide (NBS, 3.20 g, 18 mmol) portionwise in the absence of light. The reaction mixture was stirred at 0°C for 3 hours, then poured in water (150 mL) and extracted with diethyl ether.
(3x100 mL). The combined organic extracts were washed with water, brine and dried over magnesium sulfate. After evaporation of the solvent, the residue was distilled on Kugelrohr to yield the pure title compound (3.44 g, 13.90 mmol, 93 %) as a colorless liquid.\(^1\)H NMR (CDCl\(_3\)): \(\delta 7.18\) (d, \(J = 5.6\) Hz, 1H), 6.79 (d, \(J = 5.6\) Hz, 1H), 2.57 (t, \(J = 7.5\) Hz, 2H), 1.58 (quintet, \(J = 7.7\) Hz, 2H), 1.32 (m, 6H), 0.89 (t, \(J = 6.7\) Hz, 3H).\(^1\)C NMR (CDCl\(_3\)): \(\delta 142.20, 128.45, 125.34, 109.00, 31.84, 29.92, 29.61, 29.11, 22.82, 14.30\). Note: Dry THF instead of dry DMF was used for brominations of the trimer and the seximer of 3-hexylthiophene.

\textbf{3,3'''-bis(hexyl)-2,2':5',2'''-quaterthiophene (3-6).} To a suspension of magnesium turnings (319 mg, 13.1 mmol) in anhydrous diethyl ether (20mL) is added compound 7 (3.10 g, 12.54 mmol) dropwise while heating gently. After refluxing for 2 hours, the Grignard reagent is transferred dropwise to a solution of compound 3-4 (1.62g, 5.02 mmol) and Ni(dppp)Cl\(_2\) (35 mg, 0.07 mmol) in a mixture of toluene and diethyl ether (50mL, 3:2). The reaction mixture was refluxed at 55~60°C overnight, then quenched with a saturated aqueous solution of ammonium chloride (100mL) and extracted twice with chloroform. The combined organic extracts were washed with saturated aqueous sodium hydrogen carbonate, brine and water, and then dried over magnesium sulfate. The solvent was evaporated and the residue, an orange-brown oil, was purified by column chromatography on silica gel with pure hexanes as eluent to yield the title compound (2.15g, 4.31 mmol, 86% ) as a yellow oil.\(^1\)H NMR (CDCl\(_3\)): \(\delta 7.18\) (d, \(J = 5.2\) Hz, 1H), 7.13 (d, \(J = 3.8\) Hz, 1H), 7.03 (d, \(J = 3.8\) Hz, 1H), 6.94 (d, \(J = 5.2\) Hz, 1H), 2.79 (t, \(J = 7.6\) Hz, 2H), 1.66 (quintet, \(J = 7.7\) Hz, 2H), 1.36 (m, 6H), 0.89 (t, \(J = 6.7\) Hz, 3H).\(^1\)C NMR (CDCl\(_3\)): \(\delta 140.08, 137.00, 135.53, 130.52, 130.30, 126.73,\)
5,5'''-dibromo-3,3'''-bis(hexyl)-2,2':5',2''':5'',2'''':5'''',2''''':5'''',2'''''':5''''',2'''''':5''''''-quaterthiophene (3-7). A solution of 3-6 (2.00 g, 4.01 mmol) in anhydrous dimethylformamide (30mL) is stirred at 0°C and N-bromosuccinimide (1.50 mg, 8.42 mmol) is added portion wise to the reaction mixture in the absence of light. After stirring for five hours while warming up to room temperature, a precipitate crashes out of the solution. Filtration and washing with methanol yields the title compound (2.32 g, 3.53 mmol) as a yellow powder, which is then recrystallized from a hexanes/ethanol mixture to afford yellow crystals (2.05 g, 3.12 mmol, 78%) Mp 67-68°C. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 7.11 (d, \(J = 3.8\) Hz, 1H), 6.96 (d, \(J = 3.8\) Hz, 1H), 6.90 (s, 1H), 2.71 (t, \(J = 7.5\) Hz, 2H), 1.61 (m, 2H), 1.33 (m, 6H), 0.89 (t, \(J = 6.6\) Hz, 3H). \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 140.76, 137.25, 134.30, 132.92, 131.91, 127.19, 124.22, 110.88, 31.82, 30.71, 29.43, 29.31, 22.79, 14.30. HRMS (ESI–TOF): m/z calcd for C\(_{28}\)H\(_{32}\)Br\(_2\)S\(_4\)H (M+H)\(^+\) 656.9782 found 656.9806. Anal. calcd for C\(_{28}\)H\(_{32}\)Br\(_2\)S\(_4\): C 51.22, H 4.91 found C 51.07, H 5.02.

4',3''''-bis(hexyl)-5,5'''''-bis(6-(tetrahydro-2H-pyran-2-ylolxy)hexyl)-2,2':5',2''':5'',2'''':5'''',2'''':5'''',2''''':5''''',2''''''':5'''''''-hexathiophene (3-8). A solution of compound 3-7 (1.80 g, 2.74 mmol), compound 3-3 (38.4 mM in anhydrous THF, 200mL, 7.67 mmol), and dichlorobis(triphenylphosphine)palladium (II) (77 mg, 0.1 mmol) was degassed and then stirred at reflux overnight. The reaction mixture is subsequently poured in water and extracted with dichloromethane. The combined organic extracts are then washed with water and dried over magnesium sulfate. After filtration and concentration to a dark
oil, the residue is purified by flash chromatography (hexanes:ethyl acetate, 9:1) to yield the title compound (2.61 g, 2.53 mmol, 92%) as a red waxy oil. $^1$H NMR (CDCl$_3$): $\delta$ 7.12 (d, J = 3.8 Hz, 1H), 7.02 (d, J = 3.8 Hz, 1H), 6.97 (d, 1H), 6.93 (s, J = 3.5 Hz, 1H), 6.68 (d, J = 3.5 Hz, 1H), 4.57 (m, 1H), 3.88 (m, 1H), 3.75 (dt, J = 9.6, 6.7 Hz, 1H), 3.51 (m, 1H), 3.40 (dt, J = 9.6, 6.7 Hz, 1H), 2.80 (m, 2H), 2.76 (m, 2H), 1.86-1.30 (m, 22H), 0.91 (m, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ 145.50, 140.50, 136.68, 135.91, 135.30, 134.68, 128.84, 126.29, 126.07, 125.04, 123.98, 123.47, 99.03, 67.71, 62.52, 31.84, 31.66, 30.95, 30.56, 30.29, 29.81, 29.70, 29.42, 29.04, 26.18, 25.68, 22.79, 19.88, 14.29. HRMS (ESI–TOF): m/z calcd for C$_{58}$H$_{78}$O$_4$S$_6$ (M$^+$) 1030.4219 found 1030.4221. Anal. calcd for C$_{58}$H$_{78}$O$_4$S$_6$: C 67.53, H 7.62 found C 67.47, H 7.71.

**6,6'-(4',3'''-bis(hexyl)-2,2':5',2''':5''':2'''''hexitathiohexane-5,5'''''-diyl)dihexan-1-ol (T6-diol).** Compound 3-8 (800 mg, 0.78 mmol) is dissolved in a dichloromethane:methanol (3:2, 250mL) mixture and stirred at room temperature, to which are then added 10 drops of hydrochloric acid (12 N). The reaction mixture is stirred at room temperature for five hours, concentrated and slowly poured in hexanes (400 mL). The resulting orange precipitate is filtered to yield the title compound (636 mg, 0.736 mmol, 95%) as an orange solid. Further purification by flash chromatography (hexanes:ethyl acetate, 6:4) affords **T6-diol** (540 mg, 0.625 mmol, 80%) with excellent purity. Mp. 103.5-104.5°C. $^1$H NMR (CDCl$_3$): $\delta$ 7.12 (d, J = 3.8 Hz, 1H), 7.02 (d, J = 3.8 Hz, 1H), 6.97 (d, J = 3.5 Hz, 1H), 6.93 (s, 1H), 6.68 (d, J = 3.5 Hz, 1H), 3.65 (t, J = 6.5, Hz 2H), 2.80 (m, 2H), 2.75 (m, 2H), 1.80-1-30 (m, 16H), 0.91 (m, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ 145.45, 140.58, 136.74, 135.92, 135.33, 134.75, 128.89, 126.36, 126.14, 125.10, 124.04, 123.52, 63.13, 32.84, 31.87, 31.70, 30.63, 30.30, 29.72, 29.44, 29.01, 25.69,
22.82, 14.32. HRMS (ESI–TOF): m/z calcd for C_{48}H_{62}O_{2}S_{6} (M^+) 862.3054 found 862.3069. Anal. calcd for C_{48}H_{62}O_{2}S_{6}: C 66.77, H 7.24 found C 66.63, H 7.21.

6,6'-(4',3'''-Bis(dodecyl)-2,2':5',2':5''',2''''':5'''''',2''''''':5''''''''-hexathiophene-5,5''''''''-diyl)bis(hexane-6,1-diyl) dibenzoate (3-9). To a solution of T6-diol (129 mg, 0.15 mmol) and anhydrous pyridine (0.1 mL, 1.3 mmol) in dry THF (5 mL) is added a solution of benzoyl chloride (90 mg, 0.64 mmol) in dry THF (1 mL) dropwise at room temperature. After two hours of stirring at room temperature, the reaction mixture is diluted with dichloromethane and poured in water. After three extractions with dichloromethane (3x15 mL), the combined organic extracts are washed with water and brine and dried over magnesium sulfate. After evaporation of the solvent, the red viscous residue is dissolved in 2 mL of dichloromethane and precipitated in methanol (40 mL) at -10°C, to which hexanes (10 mL) is slowly added. Shiny crystals form after 10 minutes, which proved to be the title compound (124 mg, 0.12 mmol, 80%) after filtration and dryness, as a golden solid. Mp. 50-51°C. $^1$H NMR (CDCl$_3$): $\delta$ 8.05 (m, 2H), 7.56 (m, 1H), 7.44 (m, 2H), 7.12 (d, $J = 3.8$ Hz, 1H), 7.02 (d, $J = 3.8$ Hz, 1H), 6.07 (d, $J = 3.5$ Hz, 1H), 6.93 (s, 1H), 6.68 (d, $J = 3.5$ Hz, 1H), 4.33 (t, $J = 6.5$ Hz, 2H), 2.82 (m, 2H), 2.75 (m, 2H), 1.85-1.30 (m, 16H), 0.90 (m, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ 166.86, 145.34, 140.60, 136.75, 135.93, 135.35, 134.79, 133.02, 130.67, 128.90, 126.39, 126.16, 125.15, 124.06, 123.54, 65.18, 31.86, 31.64, 30.64, 30.28, 29.73, 29.44, 28.87, 28.85, 26.04, 22.82, 14.32. HRMS (ESI–TOF): m/z calcd for C$_{62}$H$_{70}$O$_4$S$_6$Na (MNa$^+$) 1093.3491 found 1093.3478. Anal. calcd for C$_{62}$H$_{70}$O$_4$S$_6$: C 69.49, H 6.58 found C 69.12, H 6.50.
Diethyl thiophen-2-ylphosphonate (3-11). 2-bromothiophene (10 g, 62.5 mmol) and anhydrous nickel chloride (387 mg, 3.1 mmol) were added in a dry flask equipped with a stir bar, an addition funnel and a short path distillation apparatus under a flow of argon. The mixture was heated to 145°C while stirring, at which point triethylphosphite was added dropwise from the addition funnel into the reaction mixture. The mixture alternates from deep blue to brown at each drop of triethylphosphite, with a concomitant evolution of ethylbromide which is distilled off. The reaction is left to stir at 145°C for 3 hours until the phosphite addition was complete and no more ethylbromide evolution was observed. The mixture is then allowed to cool back to room temperature, and the crude is distilled under reduced pressure (1 mtorr). After some of the starting material is collected off at 30°C under reduced pressure, the title compound is collected at 85°C as a pale yellow oil. (7.58 g, 34.4 mmol, 55 %). \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 7.70-7.62 (m, 2H), 7.16 (quartet, J = 3.3 Hz, 1H), 4.20-4.00 m (4H), 1.31 (t, J = 7.1 Hz, 6H). \(^{13}\)C NMR (CDCl\(_3\)): \(\delta\) 136.98, 136.81, 133.63, 133.53, 128.35, 128.10, 62.88, 62.81, 16.46, 16.37. \(^{31}\)P NMR (CDCl\(_3\), against H\(_3\)PO\(_4\)): 13.07.

Diethyl (5-(trimethylstannyl)thiophen-2-yl)phosphonate (3-12). Thienylphosphonate 13 was diluted with anhydrous tetrahydrofuran (40 mL) in a dry flask equipped with stir bar under argon flow, and cooled down to -78°C. Lithium diisopropylamine was prepared in a separate flask by adding \(n\)-butyllithium (4.5 mmol, 1.4 M in hexanes) to a diisopropylamine (0.71 mL, 5 mmol) solution in anhydrous THF (7mL) cooled to -78°C and stirring at -78°C for 30 minutes. The LDA solution was then added slowly to the cooled thienylphosphonate reaction mixture over the course of five minutes, and left to stir at such temperature for 3 hours, after which trimethyltin chloride
(solid) was added to the reaction flask in one portion. The mixture was left stirring while slowly warming up to room temperature over 3 hours. The solvent was then evaporated, and the crude was redissolved in 3 mL of dichloromethane to which the addition of 20 mL of hexanes results in white precipitates. The salts were filtered off, and the clear yellow solution was evaporated to afford the title compound as a clear oil in 85-90 % purity (by ¹H NMR), which was used without further purification. ¹H NMR (CDCl₃): δ 7.74 (dd, J = 4.2, 3.3 Hz, 1H), 7.23 (t, J = 2.7, 1H), 4.20–4.00 (m, 4H), 1.33 (t, J = 7.1, 6H), 0.40 (s, 9H).

**General procedure for 5-borylation of 3-hexylthiophene species: 2-(4-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3-13).** To a solution of freshly distilled diisopropylamine (4.22 g, 41.8 mmol) in anhydrous THF (50 mL) cooled to 0°C was added n-butyllithium (2.08 M in hexanes, 19.1 mL, 39.7 mmol) dropwise. The reaction mixture was stirred at 0°C for 30 minutes, after which the freshly made lithium diisopropylamine (LDA) solution was transferred dropwise over 30 minutes to a solution of 3-hexylthiophene (6.68 g, 39.7 mmol) in anhydrous THF (300 mL) cooled to -78°C. After stirring the reaction mixture at -78°C for two hours, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2) (8.88 g, 47.7 mmol) was slowly added. The mixture was allowed to warm up to room temperature while stirring overnight, and subsequently poured in water/diethyl ether and extracted with diethyl ether (2x250 mL). After drying over magnesium sulfate, the combined organic extracts were concentrated and purified by flash column chromatography using pure hexanes as eluent, to afford the title compound (10.1 g, 34.3 mmol, 86 %) as a colorless oil. ¹H NMR (CDCl₃): δ 7.47 (s, 1H), 7.21 (s, 1H), 2.62 (t, 2H), 1.61 (m, 2H), 1.34 (s, 12H), 1.29 (m, 6H), 0.88 (t,
General procedure for Suzuki-Miyaura coupling reactions of 3-hexylthiophene species: 3,4'-dihexyl-2,2'-bithiophene (3-14).\textsuperscript{184}

Tris(dibenzylideneacetone)dipalladium(0) (Pd\textsubscript{2}(dba)\textsubscript{3}, 202 mg, 0.22 mmol) and tri(o-tolyl)phosphine (P(\textsubscript{o}-toly)\textsubscript{3}, 269 mg, 0.88 mmol) were added in a dry flask and purged with argon/vacuum three times. A degassed solution of 3-13 (4.33 g, 14.71 mmol) and 3-5 (4.0 g, 16.18 mmol) in toluene (50 mL) was added to the flask containing the catalyst. A degassed 1M aqueous solution of tetraethylammonium hydroxide (22 mL, 22 mmol) was then added to the mixture, which was stirred vigorously and at 80~85°C for 12 hours, after which it was diluted with hexanes and poured in water. The organic phase was washed with water and brine and dried over magnesium sulfate. The solvents were then evaporated and the crude residue was filtrated though a short plug of silica using hexanes as eluent, then bulb-to-bulb distilled on Kugelrohr (60°C, 0.02 torr) to yield the title compound with a small amount of the head-to-head and tail-to-tail coupled isomers (3.93 g, 11.70 mmol, 72%) as a light yellow oil. No further purification was performed before the next step. \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \textgreek{d} 7.14 (d, 1H), 6.94 (s, 1H), 6.92 (d, 1H), 6.88 (s, 1H), 2.74 (t, 2H), 2.61 (t, 2H), 1.63 (m, 4H), 1.40-1.20 (m, 12H), 0.89 (m, 6H).

5'-bromo-3,4'-dihexyl-2,2'-bithiophene (3-15).\textsuperscript{184} To a solution of 3-14 (3.93 g, 11.7 mmol) in DMF (80 mL) cooled to 0°C and covered from light was added NBS (2.40 g, 12.48 mmol) in one portion. The reaction mixture was allowed to stir at 0°C for 3 hours in the absence of light. The mixture was then poured in water and extracted with
diethyl ether. The combined organic extract were washed with water and brine and dried over magnesium sulfate. After evaporation of the volatiles, the crude oil was purified using column chromatography with pure hexanes as eluent. The fractions containing the pure product were evaporated to afford the title compound (2.64 g, 6.38 mmol, 55 %) as a light yellow oil. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 7.16 (d, 1H), 6.91 (d, 1H), 6.80 (s, 1H), 2.71 (t, 2H), 2.57 (t, 2H), 1.62 (m, 4H), 1.34 (m, 12H), 0.90 (m, 6H). \(^1\)^C NMR (CDCl\(_3\)): \(\delta\) 142.54, 140.15, 135.90, 130.23, 130.12, 127.07, 124.12, 108.68, 31.86, 31.85, 30.92, 29.87, 29.76, 29.39, 29.33, 29.13, 22.83, 14.31, 14.30. Note: Because of the presence in the starting material of some head-to-head and tail-to-tail isomers, a slight excess of NBS was added.

**3,4',4''-Trihexyl-2,2':5',2''-terthiophene (3-16).** The general procedure for Suzuki-Miyaura coupling using 3-13 was followed (see compound 3-14). Purification by flash column chromatography using hexanes a pure eluent afforded the title compound (2.42 g, 4.83 mmol, 80 %) as thick yellow oil. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 7.15 (d, 1H), 6.97 (s, 1H), 6.94 (s, 1H), 6.93 (d, 1H), 6.90 (s, 1H), 2.78 (t, 2H), 2.76 (t, 2H), 2.62 (t, 2H), 1.65 (m, 6H), 1.40-1.20 (m, 18H), 0.90 (m, 9H). \(^1\)^C NMR (CDCl\(_3\)): \(\delta\) 143.79, 139.68, 135.76, 134.07, 131.09, 130.80, 130.23, 128.80, 127.31, 123.66, 120.13, 31.89, 30.87, 30.78, 30.71, 30.61, 29.48, 29.44, 29.23, 22.85, 14.31.

**5-Bromo-4,3',3''-trihexyl-2,2':5',2''-terthiophene (3-17).** The general procedure for 2-bromination of 3-hexylthiophene was followed (see compound 3-5), using dry THF instead of dry DMF. After evaporation of the solvent, the crude residue was purified by flash column chromatography using pure hexanes as eluent, affording the title compound (160 mg, 0.28 mmol, 71 %) as a yellow oil. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 7.16
(d, 1H), 6.93 (d, 1H), 6.92 (s, 1H), 6.81 (s, 1H), 2.77 (1, 2H), 2.70 (t, 2H), 2.57 (t, 2H),
1.63 (m, 6H), 1.40-1.20 (m, 18H), 0.89 (m, 9H). $^{13}$C NMR (CDCl$_3$): $\delta$ 142.63, 140.27,
139.91, 135.59, 134.65, 130.55, 130.03, 128.78, 126.83, 123.89, 108.75, 31.87,
31.84, 30.86, 30.79, 29.87, 29.76, 29.47, 29.42, 29.41, 29.13, 22.84, 22.82, 14.31.

2-(3,4',4''-trihexyl-2,2':5',2''-terthiophen-5-yl)-4,4,5,5-tetramethyl-1,3,2-
dioxaborolane (3-18).$^{183}$ The general procedure for 5-borylation was followed (see
compound 3-13) to afford the title compound (980 mg, 1.56 mmol, 52 %) as a thick
yellow oil. $^1$H NMR (CDCl$_3$): $\delta$ 7.46 (s, 1H), 7.01 (s, 1H), 6.97 (s, 1H), 6.90 (s, 1H), 2.79
(t, 2H), 2.75 (t, 2H), 2.62 (t, 2H), 1.66 (m, 6H), 1.36 (s, 12H), 1.40-1.20 (m, 18H), 0.90
(m, 9H).

3,4',4'',4''',4''''-hexa-hexyl-2,2':5',2''':5'',2''''':5'''',2'''''-sexithiophene (3-
19). The general procedure for Suzuki-Miyaura coupling was followed (see compound
3-14). Extraction was done with chloroform instead of diethyl ether. Purification by flash
column chromatography using pure hexanes as eluent afforded the title compound (610
mg, 0.61 mmol, 39 %) as an orange solid. $^1$H NMR (CDCl$_3$): $\delta$ 7.16 (d, 1H), 7.00 (s, 1H),
6.99 (s, 1H), 6.98 (s, 2H), 6.96 (s, 1H), 6.94 (d, 1H), 6.91 (s, 1H), 2.81 (m, 8H), 2.78 (t,
2H), 2.63 (t, 2H), 1.69 (m, 12H), 1.45-1.25 (m, 36 H), 0.92 (m, 18H). $^{13}$C NMR (CDCl$_3$):
$\delta$ 143.86, 140.03, 139.99, 139.84, 139.83, 135.75, 134.32, 133.96, 133.86, 133.75,
131.24, 130.80, 130.77, 130.71, 130.64, 130.29, 129.00, 128.80, 128.77, 128.67,
127.39, 123.78, 120.22, 31.92, 30.87, 30.79, 30.74, 30.63, 29.67, 29.53, 29.46, 29.24,
22.86, 14.31. HRMS (APCI–TOF): $m/z$ calcd for C$_{60}$H$_{86}$S$_6$H (MH$^+$) 999.5127 found
999.5098. Anal. calcd for C$_{60}$H$_{86}$S$_6$: C 72.08, H 8.67 found C 72.24, H 9.14.
5''''-bromo-3',4'',4''',4'''''-hexahexyl-2,2':5',2''':5'',2'''':5'',2''''':5'''''-sexithiophene (3-20). The general procedure for the 2-bromination of 3-hexylthiophene (see compound 3-5), was followed, using dry THF instead of dry DMF. Extraction was done with chloroform instead of diethyl ether. Purification by flash column chromatography using pure hexanes as eluent afforded the title compound (360 mg, 0.34 mmol, 83%) as an orange solid. Mp 50-51°C. 1H NMR (CDCl₃): δ 7.17 (d, 1H), 7.01 (s, 2H), 7.00 (s, 1H), 6.99 (s, 1H), 6.96 (d, 1H), 6.87 (s, 1H), 2.84 (m, 8H), 2.76 (t, 2H), 2.61 (t, 2H), 1.80-1.65 (m, 12H), 0.96 (m, 18H). 13C NMR (CDCl₃): δ 142.62, 140.29, 140.11, 140.02, 139.94, 139.75, 135.57, 134.31, 134.26, 134.05, 134.00, 130.72, 130.54, 130.46, 130.27, 130.11, 128.91, 128.71, 128.52, 126.75, 123.73, 108.82, 31.91, 31.88, 31.86, 31.82, 30.86, 30.79, 30.72, 29.94, 29.88, 29.76, 29.67, 29.52, 29.48, 29.44, 29.14, 22.87, 14.33. HRMS (ESI–TOF): m/z calc for C₆₀H₈₅BrS₆H (M+H) 1079.4222 found 1079.4207. Anal. calc for C₆₀H₈₅BrS₆: C 66.81, H 7.94 found C 67.27, H 8.53.

Diethyl (3',3'',3''',3'''',3'''''-hexahexyl-[2,2':5',2''':5'',2'''':5'',2''''':5''''''-septithiophen]-5-yl)phosphonate (rrT7-PE). In a dry Schlenk tube were added compound 3-20 (450 mg, 0.42 mmol), Pd₂(dba)₃ (40 mg, 0.04 mmol, chloroform adduct) and P(o-tyl)₃ (30 mg, 0.1 mmol) and kept under vacuum during 30 minutes while being subjected to three vacuum/argon purge cycles, and finally refilled with argon. Compound 3-12 (400 mg, 1.05 mmol) was dissolved in degassed anhydrous toluene (5 mL) and transferred to the reaction flask trough a septum using a syringe. The mixture was heated to 90°C and stirred for 12 hours. After cooling back to room temperature, it was diluted with dichloromethane and washed with
water and brine. The solvents were evaporated and the dark thick oil was diluted with a minimum of dichloromethane and purified by column chromatography using pure dichloromethane as eluent (Rf = 0.3). After evaporation of the combined pure fractions, the title compound (145 mg, 0.12 mmol, 28 %) was obtained as a thick orange oil, which solidified over a period of several days. \(^1\)H NMR (CDCl\(_3\)): \(\delta 7.61 (dd, J = 4.2 \text{ Hz}, 1\text{H}), 7.20 (t, J = 3.6 \text{ Hz}, 1\text{H}), 7.15 (d, J = 5.2 \text{ Hz}, 1\text{H}), 7.02 (s, 1\text{H}), 7.00 (s, 1\text{H}), 6.99 (s, 1\text{H}), 6.97 (s, 1\text{H}), 6.95 (s, 1\text{H}), 6.93 (d, J = 5.2 \text{ Hz}, 1\text{H}), 4.30-4.10 (m, 12\text{H}), 2.80 (m, 12\text{H}), 1.80-1.65 (m, 12\text{H}), 1.50-1.30 (m, 44\text{H}), 0.92 (m, 18\text{H}). \(^{13}\)C NMR (CDCl\(_3\)): 144.54, 144.43, 141.43, 140.46, 140.15, 140.03, 139.93, 139.74, 137.26, 137.11, 135.36, 134.31, 134.26, 134.04, 133.97, 130.65, 130.47, 130.39, 130.35, 130.25, 130.06, 129.14, 129.11, 128.93, 128.89, 128.84, 128.82, 128.77, 128.69, 128.58, 128.53, 128.19, 126.34, 126.12, 125.40, 123.73, 62.93, 62.86, 31.85, 31.82, 30.81, 30.66, 30.56, 29.63, 29.47, 29.43, 29.37, 22.82, 22.78, 16.52, 16.43, 14.30, 14.25. Anal. calcd for C\(_{68}\)H\(_{97}\)O\(_3\)PS\(_7\): C 67.06, H 8.03 found C 67.22, H 8.05.

5-bromo-3,3''',5''''-trihexyl-2,2':5',2''':5'',2'''''-quinquethiophene (3-21). In a dry Schlenk flask, compound 3-7 (3.35 g, 5.1 mmol), Pd\(_2\)(dba)\(_3\) (114 mg, 0.11 mmol, chloroform adduct) and P(o-tol)_3 (70 mg, 0.23 mmol) were loaded under a flux of argon and then kept under vacuum for 30 minutes, during which the flask was subjected to three vacuum-argon purge cycles, and finally refilled with argon. 2-(5-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3-10, 2.25 g, 7.65 mmol) was dissolved in degassed toluene (50 mL), and the afforded solution was added to the reaction Schlenk flask through a septum, using a syringe. A degassed tetraethylammonium hydroxide aqueous solution (11.5 mL, 11.5 mmol) was then added to the reaction flask, and the
mixture was vigorously stirred under argon at 90 °C for twelve hours. After the mixture had cooled down, it was poured in water and washed several times with water and finally with brine, then dried over magnesium sulfate. The solvents were then evaporated to afford a dark red oil. Column chromatography on silica gel using pure hexanes as eluent (Rf = 0.45) yielded the title compound 12 as an orange oil (1.17 g, 1.6 mmol, 31 %). Note: With an Rf of 0.3 in pure hexanes, the dicoupled sexithiophene by-product was isolated as an orange solid (0.98 g, 1.18 mmol, 23 %). 1H NMR (CDCl₃): 7.12 (d, J = 3.8 Hz, 1H), 7.11 (d, J = 3.8 Hz, 1H), 7.02 (d, J = 3.8 Hz, 1H), 6.97 (d, J = 3.6, 1H), 6.96 (d, J = 3.8, 1H), 6.94 (s, 1H), 6.90 (s, 1H), 6.68 (d, J = 3.6, 1H), 2.80 (t, J = 7.8, 2H), 2.75 (t, J = 7.6, 2H), 2.72 (t, J = 7.8, 2H), 1.68 (m, 4H), 1.62 (m, 2H), 1.39 (m, 6H), 1.33 (m, 12H), 0.90 (m, 9H). 13C NMR (CDCl₃): 145.82, 140.68, 140.66, 137.56, 136.45, 136.11, 135.66, 134.65, 134.00, 132.90, 132.02, 128.75, 127.18, 126.38, 126.12, 125.04, 124.28, 123.97, 123.57, 110.77, 31.88, 31.83, 31.79, 31.77, 30.72, 30.65, 30.43, 29.74, 29.45, 29.44, 29.32, 28.97, 22.83, 22.81, 22.80, 14.32, 14.30. HRMS (APCI): m/z calcd for C₃₈H₄₇BrS₅H (MH⁺) 745.1510 found 745.1539. Anal. calcd for C₃₈H₄₇BrS₅: C 61.34; H 6.37 found C 61.27; H 6.39.

Diethyl (3'''',4',5''''-trihexyl-[2,2':5',2'':5'',2''':5''',2'''':5'''',2'''':-sexithiophen]-5-yl)phosphonate (T6-PE). In a dry Schlenk flask, compound 3-21 (1.82 g, 2.45 mmol), Pd₂(dba)₃ (40 mg, 0.04 mmol, chloroform adduct) and P(o-tyl)₃ (30 mg, 0.1 mmol) were loaded together and kept under vacuum during 30 minutes while being subjected to three vacuum/argon purge cycles, and finally refilled with argon. Compound 3-12 (3 mmol) was dissolved in degassed anhydrous toluene (30 mL) and transferred to the reaction flask through a septum using a syringe. The mixture was heated to 90°C and
stirred for 12 hours. After cooling back to room temperature, the mixture was diluted with ethyl acetate and washed with water and brine. After drying over magnesium sulfate, the solvent was evaporated and the crude was purified by column chromatography using 9:1 dichloromethane : ethyl acetate (Rf = 0.2) as eluent. This afforded the title compound as thick red oil which eventually solidifies to a red-orange solid over time (650 mg, 0.74 mmol, 30 %). $^1$H NMR (CDCl$_3$): $\delta$ 7.55 (dd, J = 4.2, 3.8 Hz, 1H), 7.18 (t, J = 3.5 Hz, 1H), 7.14 (s, 1H), 7.13 (s, 1H), 7.10 (s, 1H), 7.06 (d, J = 3.8 Hz, 1H), 7.03 (d, J = 3.8 Hz, 1H), 6.97 (d, J = 3.5 Hz, 1H), 6.93 (s, 1H), 6.68 (d, J = 3.6 Hz, 1H), 4.20–4.00 (m, 4H), 2.79 (t, J = 7.6 Hz, 2H), 2.77 (t, J = 7.9 Hz, 2H), 2.75 (t, 7.8 Hz, 2H), 1.68 (m, 6H), 1.40 (m, 6H), 1.36 (t, J = 7.1 Hz, 6H), 1.33 (m, 12H), 0.90 (m, 9H).

$^{13}$C NMR (CDCl$_3$): $\delta$ 145.75, 140.70, 140.58, 136.95, 136.6, 136.02, 135.46, 135.18, 135.03, 134.68, 129.72, 128.86, 126.77, 126.46, 126.34, 126.11, 125.03, 124.09, 124.05, 123.53, 31.90, 31.80, 31.77, 30.65, 30.63, 30.43, 29.79, 29.76, 29.49, 29.48, 28.99, 22.85, 22.80, 14.34, 14.31. $^{31}$P NMR (CDCl$_3$, against H$_3$PO$_4$): $\delta$ 11.80. HRMS (APCI): m/z calcd for C$_{46}$H$_{59}$O$_3$PS$_6$H (MH$^+$) 883.2599 found 883.2526. Anal. calcd for C$_{46}$H$_{59}$O$_3$PS$_6$: C, 62.55; H, 6.73 found C 62.93; H 7.04.

(3‴′,4‴,5‴‴-triethyl-[2,2′:5′,2″:5″,2‴″:5‴″′,2‴‴′:5‴‴‴-sexithiophen]-5-yl)phosphonic acid (T6-PA). T6-PE (300 mg, 0.34 mmol) was added in a dry flask equipped with a stir bar and under argon flow, then dissolved in anhydrous dichloromethane (10 mL). To the orange solution was added trimethylsilylbromide (0.45 mL, 3.4 mmol) dropwise at room temperature, over the course of five minutes. The mixture was stirred at room temperature for 5 hours, after which methanol (10 mL) was added to the flask and allowed to stir for an additional 3 hours at room temperature. The
precipitates that formed were filtered to give an orange solid. Only one spot with Rf = 0 was observed by TLC on silica gel plates eluting with a 1:1 mixture of dichloromethane : ethyl acetate, suggesting complete conversion. The solids were dissolved in a minimum of dichloromethane and reprecipitated in methanol then filtered, and repeating this twice afforded the title compound as an orange solid (240 mg, 0.29 mmol, 85%). \(^1\)H NMR ((CD\(_3\))\(_2\)SO): \(\delta\) 7.40-7.36 (br, 5H), 7.23 (br, 1H), 7.18 (br, 1H), 7.15 (br, 1H), 7.14 (br, 1H), 6.82 (br, 1H), 2.59-2.57 (br, 6H), 1.63 (br, 6H), 1.40-1.20 (br, 18H), 0.87 (br, 9H). \(^{31}\)P NMR ((CD\(_3\))\(_2\)SO, against H\(_3\)PO\(_4\)): \(\delta\) 5.91. HRMS (ESI): \(m/z\) calcd for C\(_{42}\)H\(_{51}\)O\(_3\)PS\(_6\)-H (M-H\(^-\)) 825.1827 found 825.1812. Anal. calcd for C\(_{42}\)H\(_{51}\)O\(_3\)PS\(_6\): C, 60.98; H, 6.21 found C 60.15; H 6.41.

4,7-bis(4-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (3-22).\(^{185}\) In a dry Schlenk flask, 4,7-dibromobenzo[c][1,2,5]thiadiazole (3.0 g, 10.3 mmol), Pd\(_2\)(dba)\(_3\) (283 mg, 0.23 mmol, chloroform adduct) and P(o-tyl)\(_3\) (338 mg, 1.11 mmol) were loaded under a flux of argon and then kept under vacuum for 30 minutes, during which the flask was subjected to three vacuum-argon purge cycles, and finally refilled with argon. 2-(4-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3-13, 7.3 g, 24.8 mmol) was dissolved in degassed toluene (40 mL), and the afforded solution was added to the reaction Schlenk flask through a septum, using a syringe. A degassed tetraethylammonium hydroxide aqueous solution (36 mL, 36 mmol) was then added to the reaction flask, and the mixture was vigorously stirred under argon at 90°C for twelve hours. After it cooled back to room temperature, the mixture was poured in 300 mL of cold methanol (0°C). The orange precipitates that formed were filtered and redissolved in 100 mL of hexanes and passé through a short plug of silica gel using pure hexanes.
After evaporation of the solvent, the title compound was obtained as a bright orange solid (4.58 g, 9.77 mmol, 92 %). $^1$H NMR (CDCl$_3$): $\delta$ 7.98 (d, $J = 1.3$ Hz, 1H), 7.83 (s, 1H), 7.04 (s, 1H), 2.70 (t, $J = 7.9$ Hz, 2H), 1.71 (quintet, $J = 7.7$ Hz, 2 H), 1.35 (m, 4H), 0.90 (t, $J = 6.9$ Hz, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ 152.81, 144.55, 139.20, 129.25, 126.20, 125.71, 121.72, 31.93, 30.87, 30.69, 29.28, 22.86, 14.34.

4,7-bis(5-bromo-4-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (3-23).$^{185}$ Compound 3-22 (4.58 g, 9.77 mmol) was dissolved in chloroform (150 mL) and cooled to 0°C while protecting the solution from light exposure. N-bromosuccinimide (3.97 g, 22.3 mmol) was then added to the mixture in one portion, followed by two drops of acetic acid. The mixture was allowed to stir while warming up to room temperature for 12 hours. The mixture was then poured in water and washed once with water. The solvent was evaporated and the crude was purified by column chromatography on silica gel using pure hexanes as eluent. Evaporating the collected fractions afforded the title compound as a thick red oil which eventually crystallized to a bright red solid (5.97 g, 9.53 mmol, 97 %). $^1$H NMR (CDCl$_3$): $\delta$ 7.74 (s, 1H), 7.69 (s, 1H), 2.63 (t, $J = 7.4$ Hz, 2H), 1.67 (quintet, $J = 3.9$ Hz, 2H), 1.36 (m, 6H), 0.91 (t, $J = 6.9$ Hz, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ 152.38, 143.26, 138.69, 128.29, 125.45, 124.98, 111.81, 31.87, 29.97, 29.90, 29.19, 22.85, 14.33.

4-(5-bromo-4-hexylthiophen-2-yl)-7-(3,5'-dihexyl-[2,2'-bithiophen]-5-yl)benzo[c][1,2,5]thiadiazole (3-24). In a dry Schlenk flask, compound 3-23 (5.97 g, 9.53 mmol), Pd$_2$(dba)$_3$ (250 mg, 0.20 mmol, chloroform adduct) and P(o-tol)$_3$ (275 mg, 0.90 mmol) were loaded under a flux of argon and then kept under vacuum for 30 minutes, during which the flask was subjected to three vacuum-argon purge cycles, and
finally refilled with argon. 2-(5-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-
dioxaborolane (3-10, 2.26 g, 7.69 mmol) was dissolved in degassed toluene (100 mL),
and the afforded solution was added to the reaction Schlenk flask through a septum,
using a syringe. A degassed tetraethylammonium hydroxide aqueous solution (11.5 mL,
11.5 mmol) was then added to the reaction flask, and the mixture was vigorously stirred
under argon at 90°C for twelve hours. The mixture was allowed to cool down to room
temperature, diluted with 100 mL of hexanes and poured in water. The organic phase
was washed with water twice, dried over magnesium sulfate and evaporated. The red
oil was then purified by column chromatography using pure hexanes as eluent (Rf = 0.5)
to afford the title compound as a red thick oil (1.75 mg, 2.45 mmol, 26 %). Note: With an
Rf of 0.75 in pure hexanes, the starting material 16 was recovered (3.16 g, 5.04 mmol).

1H NMR (CDCl3): \(\delta\) 7.93 (s, 1H), 7.72 (s, 1H), 7.70, 7.66 (ABq, \(J_{AB} = 7.7\) Hz, 2H), 7.02
(d, \(J = 3.6\) Hz, 1H), 6.75 (d, \(J = 3.6\) Hz, 1H), 2.84 (t, \(J = 8.1\) Hz, 2H), 2.81 (t, \(J = 9.2\) Hz,
2H), 2.63 (t, \(J = 7.5\) Hz, 2H), 1.72 (m, 6H), 1.45-1.30 (m, 12 H), 0.92 (m, 9H). 13C NMR
(CDCl3): \(\delta\) 152.52, 152.44, 146.72, 143.14, 140.01, 138.88, 136.29, 133.58, 133.39,
130.97, 127.93, 125.94, 125.88, 125.05, 125.00, 124.87, 124.69, 111.51, 31.92, 31.87,
31.79, 30.80, 30.39, 29.97, 29.90, 29.72, 29.55, 29.21, 29.05, 22.89, 22.86, 22.81,
14.34, 14.32. HRMS (APCI): \(m/z\) calcd for C_{36}H_{45}BrN_2S_4H (MH^+) 713.1649 found
713.1665. Anal. calcd for C_{36}H_{45}BrN_2S_4: C, 60.56; H, 6.35; N 3.92 found C, 60.68; H,
6.23; N 3.72

**Diethyl (5'-(7-(3,5'-dihexyl-[2,2'-bithiophen]-5-yl)benzo[c][1,2,5]thiadiazol-4-
yl)-3'-hexyl-[2,2'-bithiophen]-5-yl)phosphonate (T4BTD-PE).** In a dry Schlenk flask,
compound 3-24 (1.75 g, 2.45 mmol), Pd_2(dba)_3 (60 mg, 0.05 mmol, chloroform adduct)
and P(o-tyl)$_3$ (70 mg, 0.23 mmol) were loaded under a flux of argon and then kept under vacuum for 30 minutes, during which the flask was subjected to three vacuum-argon purge cycles, and finally refilled with argon. Compound 3-12 (9 mmol) was dissolved in degassed toluene (30 mL), and the afforded solution was added to the reaction Schlenk flask through a septum, using a syringe. The mixture was then heated to 90°C and stirred for 12 hours. After cooling down to room temperature, the mixture was diluted with chloroform (100 mL) and washed once with water. The solvent was evaporated to a dark red oil. The crude was purified by column chromatography using 7:3 hexanes : ethyl acetate as eluent, followed by a second column using 9:1 dichloromethane : acetone as eluent, to afford the title compound as a dark red thick oil (1.34 g, 1.57 mmol, 64 %). $^1$H NMR (CDCl$_3$): $\delta$ 7.90 (s, 1H), 7.88 (s, 1H), 7.69, 7.65 (ABq, $J_{AB} = 7.7$ Hz, 2H), 7.62 (dd, $J = 4.2$, 3.7 Hz, 1H), 7.24 (d, $J = 3.6$ Hz, 1H), 7.01 (d, $J = 3.6$ Hz, 1H), 6.73 (d, $J = 3.6$ Hz, 1H), 4.21 (m, 4H), 2.85-2.75 (m, 6H), 1.71 (m, 6H), 1.50-1.30 (m, 24H), 0.90 (m, 9H). $^{13}$C NMR (CDCl$_3$): $\delta$ 152.46, 152.44, 146.64, 144.65, 144.54, 141.85, 139.91, 138.33, 137.26, 137.12, 136.18, 133.529, 133.418, 130.958, 130.837, 130.807, 130.438, 128.353, 126.542, 126.319, 125.975, 125.79, 125.56, 125.50, 124.82, 124.67, 124.64, 62.94, 62.87, 31.86, 31.84, 31.75, 31.73, 30.73, 30.60, 30.33, 29.82, 29.68, 29.51, 29.46, 29.00, 22.84, 22.81, 22.76, 16.54, 16.45, 14.30, 14.27. $^{31}$P NMR (CDCl$_3$, against H$_3$PO$_4$): $\delta$ 12.00. HRMS (APCI): m/z calcd for C$_{44}$H$_{57}$N$_2$O$_3$PS$_5$H (MH$^+$): 853.2783 found 853.2790. Anal. calcd for C$_{44}$H$_{57}$N$_2$O$_3$PS$_5$: C, 61.94; H, 6.73; N, 3.28 found: C, 61.60, N, 7.10, H, 3.16.
(5’-(7-(3,5’-dihexyl-[2,2’-bithiophen]-5-yl)benzo[c][1,2,5]thiadiazol-4-yl)-3’-hexyl-[2,2’-bithiophen]-5-yl)phosphonic acid (T4BTD-PA). In a dry round-bottom flask equipped with a stir bar, T4BTD-PE (300 mg, 0.35 mmol) was added and dissolved in 10 mL of anhydrous dichloromethane. The mixture was stirred under a flow of argon, and trimethylsilylbromide (0.46 mL, 0.35 mmol) was added dropwise at room temperature. The mixture was stirred at room temperature for five hours, after which methanol (10 mL) was added and left to stir at room temperature for 3 hours. The mixture was then diluted with dichloromethane (50 mL) and washed with water (100 mL). After the emulsion decanted, the organic phase was collected and evaporated without drying, and kept under vacuum to afford the title compound as a dark purple solid (265 mg, 0.33 mmol, 94 %). \(^1\)H NMR (CDCl\(_3\)): \(\delta 7.70-7.55\) (br, 3H), 7.15-7.00 (br, 3H), 6.90 (br, 1H), 6.68 (br, 1H), 2.80 (br, 2H), 2.75-2.55 (br, 4H), 1.80-1.50 (m, 6H), 1.50-1.35 (m, 18H), 1.00-0.85 (m, 9H). \(^{31}\)P NMR (CDCl\(_3\), against H\(_3\)PO\(_4\)): \(\delta 12.44\). Anal. calcd for C\(_{40}\)H\(_{49}\)N\(_2\)O\(_3\)PS\(_5\): C, 60.27; H, 6.20; N, 3.51 found 60.17, 6.22, 3.31

(5’-bromo-[2,2’-bithiophen]-5-yl)triisobutylsilane (3-26). 5,5’-dibromo-2,2’-bithiophene (3.24 mg, 10 mmol) was loaded in a 250 mL dry flask under an argon flow, and dissolved in anhydrous tetrahydrofuran (100 mL). The solution was stirred and cooled to -78°C, after which as solution of n-butyllithium (7.1 mL, 10 mmol) was added dropwise to the reaction mixture over the course of 30 minutes. The solution was then stirred at -78°C for two hours, and then chlorotriisobutylsilane (2.58 g, 11 mmol) was added using a syringe via a septum, in one portion. The mixture was allowed to warm up to room temperature while stirring for 12 hours. The solution was then concentrated and rediluted with hexanes (100 mL). The afforded white precipitate is filtered off, and
the remaining clear solution is concentrated to a brown slurry. This was purified by column chromatography using pure hexanes as eluent, to afford the title compound (1.51 g, 3.5 mmol, 35 %) as a clear oil. $^1$H NMR (CDCl$_3$): $\delta$ 7.15 (d, J = 3.5 Hz, 1H), 7.12 (d, J = 3.5 Hz, 1H), 6.96 (d, J= 3.8 Hz, 1H), 6.93 (d, J= 3.8 Hz, 1H), 1.83 (nonuplet, J = 6.6 Hz, 3H), 0.92 (d, J = 6.6 Hz, 18H), 0.86 (d, J = 6.9 Hz, 6H). $^{13}$C NMR (CDCl$_3$): $\delta$ 141.44, 139.32, 139.28, 135.59, 130.78, 125.22, 123.85, 125.22, 123.85, 110.94, 26.69, 25.38, 25.07.

Triisobutyl(5’-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[2,2’-bithiophen]-5-yl)silane (3-27). Compound 3-26 (650 mg, 1.47 mmol) was dissolved in a dry flask with anhydrous tetrahydrofuran (10 mL) and cooled to -78°C. A solution of n-butyllithium in hexanes (1.25 mL, 1.75 mmol) was added dropwise to the reaction mixture and the solution was then stirred at -78°C for two hours. 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (355 mg, 1.91 mmol) was added using a syringe via a septum, in one portion. The mixture was allowed to warm up to room temperature while stirring for 12 hours. The mixture was then diluted with hexanes, poured in water and extracted twice with hexanes. After washing the combined organic extracts with brine, the solution was dried over magnesium sulfate. The volatiles were then evaporated to afford a yellow oil. The crude contained 70 % of the title compound, the remaining being unreacted starting material as determined by NMR. This was used without further purification. $^1$H NMR (CDCl$_3$): $\delta$ 7.51 (d, J = 3.6 Hz, 1H), 7.27 (d, J = 3.8 Hz, 1H), 7.19 (d, J= 4.3 Hz, 1H), 7.14 (d, J= 4.8 Hz, 1H), 1.83 (nonuplet, J = 6.6 Hz, 3H), 1.35 (s, 12H), 0.92 (d, J = 6.6 Hz, 18H), 0.86 (d, J = 6.9 Hz, 6H).
(E)-1,1'-bis(2-ethylhexyl)-6,6'-bis(5'-hexyl-[2,2'-bithiophen]-5-yl)-[3,3'-biindolinylidene]-2,2'-dione (IT$_2$-C$_6$)$_2$ and (E)-1,1'-bis(2-ethylhexyl)-6-(5'-hexyl-[2,2'-bithiophen]-5-yl)-6'-((5'-triisobutylsilyl)-[2,2'-bithiophen]-5-yl)-[3,3'-biindolinylidene]-2,2'-dione (IT$_2$-C$_6$Si) In a purged Schlenk flask, (E)-6,6'-dibromo-1,1'-bis(2-ethylhexyl)-[3,3'-biindolinylidene]-2,2'-dione (291 mg, 0.45 mmol) and 2-(5-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3-10, 296 mg, 0.79 mmol), Pd$_2$(dba)$_3$ (30 mg, chloroform adduct) and P(o-tol)$_3$ (20 mg) were loaded under a flux of argon and then kept under vacuum for 30 minutes, during which the flask was subjected to three vacuum-argon purge cycles, and finally refilled with argon. Degassed toluene (4 mL) was then added to flask, followed by a degassed aqueous solution of tetraethylammonium hydroxide (1.8 mL, 1.8 mmol). The mixture was stirred and heated up to 90°C. The progression of the reaction was monitored by TLC, using a 3:2 mixture of hexanes:dichloromethane as eluent. When complete consumption of the dibromoisoindigo (red spot, $R_f = 0.5$) starting material was confirmed by TLC, a solution of compound 3-27 (166 mg, 0.34 mmol) in degassed toluene (2 mL) was added to the flask. The mixture was kept stirring at 90°C for 12 hours, then allowed to cool to room temperature and slowly precipitated in methanol (40 mL). The precipitates were filtered and collected in a 100 mL round-bottom flask, to which a minimum amount of hot chloroform (~15mL) was added in order to dissolve the solids completely. Silica gel (15 mL) was then added to the flask and swirled to absorb the solution. Careful evaporation of the solvent adsorbed the crude on the dry silica gel, which was loaded onto a silica gel column packed with 2:1 hexanes:dichloromethane. Eluting with 2:1 and then 3:2 hexanes:dichloromethane separated and purified the two title compounds, affording
**iiT$_2$-C6$_2$** (178 mg, 0.18 mmol, 40%) and **iiT$_2$-C6Si** (144 mg, 0.13 mmol, 29%) as dark purple-blue solids. **iiT$_2$-C6$_2$** $^1$H-NMR (CDCl$_3$) : $\delta$ 9.01 (d, J = 8.7, 2H), 7.25-7.18 (m, 4H), 7.05 (d, J = 3.6 Hz, 2H) 7.02 (d, J = 3.6 Hz, 2H), 6.78 (s, 2H), 6.70 (d, J = 3.3 Hz), 3.68-3.41 (m, 4H), 2.80 (t, J = 4.2 Hz, 4H), 1.82-1.65 (m, 6H), 1.44-1.20 (m, 28H), 0.98-0.81 (m, 18H) $^{13}$C-NMR (CDCl$_3$) : $\delta$ 168.73, 146.34, 145.61, 142.10, 138.90, 137.43, 134.72, 131.68, 130.34, 125.12, 125.07, 124.19, 123.90, 121.18, 118.80, 104.53, 44.24, 38.05, 31.79, 31.75, 31.12, 30.41, 29.26, 29.03, 24.54, 23.35, 22.81, 14.45, 14.36, 11.03. HRMS (ESI-TOF) Calculated for C$_{60}$H$_{74}$N$_2$O$_2$S$_4$ (M+H)$^+$: 983.4706 Found: m/z 983.4741. Anal. Calcd. for C$_{60}$H$_{74}$N$_2$O$_2$S$_4$: C, 73.27; H, 7.58; N, 2.85. Found: C, 73.39; H, 7.57; N, 2.80. **iiT$_2$-C6Si** $^1$H-NMR (CDCl$_3$) : $\delta$ 9.10 (dd, J = 3.0, 1.8 Hz, 1H), 9.08 (dd, J = 3.0, 1.8 Hz, 1H), 7.29 (d, J = 3.8 Hz, 1H), 7.28 (d, J = 3.5 Hz, 1H), 7.27 (d, J = 3.8 Hz, 1H), 7.25 (dd, J = 4.2, 1.6 Hz, 1H), 7.23 (dd, J = 4.0, 1.6 Hz, 1H), 7.17 (d, J = 3.8 Hz, 1H), 7.16 (d, J = 3.4 Hz, 1H), 3.71-3.53 (m, 4H), 2.80 (t, J = 7.4 Hz, 2H), 1.86 (nonuplet, J = 6.6 Hz, 3H), 1.86-1.76 (br, 2H), 1.70 (quintet, J = 7.2 Hz, 2H), 1.43-1.28 (m, 24H), 0.95 (d, 6.6 Hz, 18H), 0.88 (d, J = 6.8 Hz, 6H), 0.96-0.87 (m, 15H) $^{13}$C-NMR (CDCl$_3$) : $\delta$ 168.81, 146.34, 145.79, 145.77, 142.73, 142.16, 142.14, 139.52, 138.97, 138.48, 137.56, 137.47, 135.78, 134.71, 131.87, 131.75, 130.38, 130.37, 125.35, 125.23, 125.20, 125.18, 124.96, 124.22, 123.99, 121.30, 121.19, 118.97, 118.91, 104.69, 104.65, 44.27, 38.03, 31.83, 31.08, 30.48, 29.21, 29.18, 29.03, 26.75, 26.70, 25.44, 25.13, 24.56, 23.35, 22.83, 14.42, 14.34, 11.07. Anal. calcd for C$_{66}$H$_{88}$N$_2$O$_2$S$_4$Si: C, 72.21; H, 8.08; N, 2.55; found: C, 72.51; H, 8.56; N, 2.48

(E)-1,1’-bis(2-ethylhexyl)-6,6’-bis(5’-(triisobutylsilyl)-[2,2’-bithiophen]-5-yl)-[3,3’-biindolinyldiene]-2,2’-dione (iiT$_2$-Si$_2$) In a purged Schlenk flask, (E)-6,6’-dibromo-
1,1'-bis(2-ethylhexyl)-[3,3'-biindolylidene]-2,2'-dione (220 mg, 0.34 mmol), compound 3-27 (470 mg, 0.89 mmol), Pd$_2$(dba)$_3$ (15 mg, chloroform adduct) and P(o-tyl)$_3$ (10 mg) were loaded under a flux of argon and then kept under vacuum for 30 minutes, during which the flask was subjected to three vacuum-argon purge cycles, and finally refilled with argon. Degassed toluene (5 mL) was then added to flask, followed by a degassed aqueous solution of tetraethylammonium hydroxide (1.4 mL, 1.4 mmol). The mixture was stirred and heated to 90°C for 12 hours. After cooling back to room temperature, the mixture was slowly poured in methanol (30 mL) and the precipitates were collected by filtration. The solids had enough solubility that they were dissolved in a minimum of a 3:2 hexanes:dichloromethane, and purified by column chromatography using 3:2 hexanes:dichloromethane as eluent. This afforded the title compound (265 mg, 0.22 mmol, 64%) as a dark gray-purple solid. $^1$H NMR (CDCl$_3$): $\delta$ 9.13 (dd, $J$ = 4.2, 1.6 Hz, 1H), 7.32 (d, $J$ = 3.8 Hz, 1H), 7.29 (d, $J$ = 3.5 Hz, 1H), 7.27 (dd, $J$ = 4.2, 1.7 Hz, 1H), 7.20 (d, $J$ = 3.8 Hz, 1H), 7.17 (d, $J$ = 3.5 Hz, 1H), 6.92 (t, $J$ = 1.7 Hz, 1H), 3.76-3.60 (m, 2H), 1.86 (nonuplet, 6.6 Hz, 4H), 1.46-1.30 (m, 8H), 1.00-0.90 (m, 30H). $^{13}$C NMR (CDCl$_3$): $\delta$ 168.86, 145.88, 142.71, 142.14, 139.55, 138.53, 137.60, 135.75, 131.92, 130.37, 125.34, 125.27, 124.95, 121.29, 119.06, 104.77, 38.01, 31.05, 29.16, 26.71, 25.41, 25.09, 24.51, 23.33, 14.38, 11.04. Anal. calcd for C$_{72}$H$_{102}$N$_2$O$_2$S$_4$Si$_2$: C, 71.35; H, 8.48; N, 2.31; found: C, 71.62; H, 9.04; N, 2.23.

**Poly(6,6'-(4',3'''-bis(hexyl)-2,2':5',2''':5''',2'''':5'''''-hexathiophene-5,5''''''-diyl)dihexyl) carbonate (T6PC).** To a solution of T6-diol (259 mg, 0.30 mmol) and triphosgene (32.8 mg, 0.11 mmol) in dry THF (5 mL) is added anhydrous pyridine (0.1 mL) diluted in dry THF (1 mL) dropwise at room temperature. Gelation occurs after
90 minutes, after which 5 mL of dry THF are added to the reaction mixture, which is then left stirring at room temperature overnight. The reaction mixture is subsequently diluted with chloroform and poured in water, extracted twice with chloroform. After drying over magnesium sulfate, the combined organic extracts are concentrated to a red solid, which is dissolved in a minimum amount of chloroform and precipitated in methanol. The filtered precipitate is then fractionated using methanol, hexanes and chloroform in a Soxhlet apparatus. Precipitation of the concentrated chloroform fraction in methanol affords **T6PC** (210 mg, 0.236 mmol, 79 %) as an orange solid after filtration. $^1$H NMR (CDCl$_3$): $\delta$ 7.10 (d, J = 3.7 Hz, 1H), 7.01 (d, J = 3.8 Hz, 1H), 6.96 (d, J = 3.5 Hz, 1H), 6.93 (s, 1H), 6.67 (d, J = 3.5 Hz, 1H), 4.14 (t, J = 6.6 Hz, 2H), 2.85-2.65 (m, 4H), 1.68 (m, 6H), 1.43 (m, 6H), 1.34 (m, 4H), 0.90 (m, 3H). $^{13}$C NMR (CDCl$_3$): $\delta$ 155.60, 145.30, 140.58, 136.75, 135.90, 135.34, 134.80, 128.93, 126.38, 126.17, 125.14, 124.04, 123.54, 68.11, 31.88, 31.59, 30.64, 30.27, 29.74, 29.46, 28.81, 25.70, 22.83, 14.33. Anal. calcd for C$_{49}$H$_{60}$O$_3$S$_6$: C 66.17, H 6.80 found C 66.08, H 6.73.
CHAPTER 4
ISOINDIGO, A VERSATILE ELECTRON-DEFICIENT UNIT FOR P-TYPE AND N-TYPE ORGANIC ELECTRONIC APPLICATIONS

4.1 The isoindigo molecule

In the indigoid family, the most prominent structural isomer of isoindigo (II) is the well-known and widely used indigo molecule. The latter is one of the oldest natural dyes, whose structure was first proposed by Adolf von Baeyer in the late 1800s. The structure of the indigo chromophore is shown in Scheme 4-1 (left). Another dye outside of the indigoid family, diketopyrrolopyrrole (DPP, Scheme 4-1, center), was introduced by Ciba in 1983, as a vibrant red pigment in its bis-phenyl N-H form, although its synthesis was first reported in 1974. Soluble derivatives of the latter have become very popular in the field of organic electronics, mostly in the bis-thiophene form for high mobility and photovoltaic applications. Isoindigo itself, depicted in Scheme 4-1 (right), has not been widely employed as a dye nor pigment, probably because of the rather dull tone of the N-H form. Only since 2010, isoindigo was deemed a useful electron-deficient moiety for organic electronic applications, as first reported by the Reynolds group.

![Scheme 4-1. Structures of indigo, diketopyrrolopyrrole and isoindigo.](image)

As a most studied analog of isoindigo, a few characteristics of indigo are worth describing in order to understand isoindigo itself. The chromogen in the indigo molecule
has been identified as the central double bond decorated with two electron-donating (blue arrows) nitrogens and two electron-accepting (red arrows) carbonyls (Scheme 4-2, left).

![Scheme 4-2. Donor-acceptor pattern, substituents positions and conjugation extent of indigo.](image)

These electron-donors (N) and acceptors (C=O) are arranged in a *trans*-configuration, hence the so-called cross-conjugated or H-chromophore.\textsuperscript{189} Calculations showed that the outer benzene rings only play a secondary role in chromophore of indigo. Each donor (N) and acceptor (C=O) is also bonded to the outer benzene ring, for which the substituents pattern has a significant impact on the absorption of the derivatized indigo.\textsuperscript{189}

**Table 4-1. Effect of substituent on the longest wavelength absorption maxima of indigo.**

<table>
<thead>
<tr>
<th>Substituent X</th>
<th>Absorption maxima (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5,5’ position</td>
</tr>
<tr>
<td>None</td>
<td></td>
</tr>
<tr>
<td>-OEt</td>
<td>645</td>
</tr>
<tr>
<td>-NO₂</td>
<td>580</td>
</tr>
</tbody>
</table>

For instance, as depicted in Scheme 4-2 (center) and summarized in Table 4-1, the central chromogen is influenced by electron-donating ethoxy substituents on the
outer benzene 5,5’ positions induce a 40 nm bathochromic shift of the peak absorption. The opposite is true for the 6,6’ positions, with a 35 nm hypsochromic shift of the $\lambda_{\text{max}}$ compared to the unfunctionalized indigo. The reverse effects are observed for electron-withdrawing nitro groups. This strong dependence on the nature of the substituent and its position is explained by the strengthening of the electron donor character of the chromophore nitrogen by a para ethoxy group (5,5’ positions), and the strengthening of the electron accepting character of the carbonyl by a para nitro group (6,6’ positions), thus increasing the donor-acceptor effect. The latter effect is decreased when the reverse substitution pattern occurs, explaining the observed hypsochromic shifts for an ethoxy at the 6,6’ and a nitro at the 5,5’ positions. Calculations have shown that despite the strong substituents effect, the outer benzene ring itself only plays a secondary role in chromophore of indigo. As shown in Scheme 4-2 (right), the central double bond is not directly bonded to the benzene rings, hence the limited conjugation. Although the synthetic ability to tune the absorption of the chromophore is attractive, indigo is therefore not a valuable unit for fully conjugated systems a priori.

The diketopyrrolopyrrole unit is also based on a central donor-acceptor chromogen involving electron donating nitrogens and electron-accepting carbonyls (Scheme 4-3).

![Scheme 4-3. Donor-acceptor pattern, substituents positions and conjugation extent of DPP.](image-url)
Whether to call it a cross-conjugated chromophore is debatable, since each of the two central double bonds is only bonded to one N and one C=O; although when combined into the conjugated 1,3-butadiene core, a crossed D-A pattern is visible.

Unlike indigo, there is only one substitution position available at the 3 and 6 positions in the DPP unit (Scheme 4-3, center), and this is inherently aryl substituted because of the synthesis DPP itself. The electron donating strength of the aryl groups at the 3 and 6 positions have an influence on the chromophores’ absorption maxima. More importantly, there is an extended conjugation of the Pi system across the molecule, visible as a 1,4-diarylbuta-1,3-diene core depicted in Scheme 4-3 (right). This extended conjugation is responsible for the extensive use of DPP as an acceptor unit in fully conjugated molecules and polymers.

The subject of this Chapter, isoindigo, also has a cross-conjugated chromophore as part of the indigoids family. Displayed in Scheme 4-4 (left), the double D-A pattern across the central double bond can be understood as a direct electron-withdrawing effect (red) of the trans carbonyls on the double bond, and an indirect donating effect (blue) of the nitrogens via conjugation through the ortho positions of the benzene rings.

Scheme 4-4. Donor-acceptor pattern, substituents positions and conjugation extent of isoindigo.
Compared to the direct donating effect of the nitrogen in indigo (Scheme 4-2, left), one could stipulate that this indirect donating effect in isoindigo could be responsible for a reduced D-A interaction, which is consistent with the blue-shifted absorption of N,N'-dihexyl isoindigo ($\lambda_{\text{max}} = 496$ nm, in CHCl$_3$) compared with N,N'-diethyl indigo ($\lambda_{\text{max}} = 653$ nm, in CHCl$_3$). Another contributing factor could be the poorer electron-accepting character of the carbonyl in the amide of isoindigo compared to the ketone in indigo. As for indigo, significant substituent position and strength effects are expected on the benzene ring of isoindigo (Scheme 4-4, center). The 4 and 6 positions are conjugated with the central double bond, while the 5 and 7 positions are ortho and para to the nitrogen. A detailed study of the various substituent/position effects is underway, but is not part of this Chapter, mainly because of the applications targeted herein. As for DPP, isoindigo has a fully conjugated $\pi$-system, which is based on trans-stilbene as shown in Scheme 4-4 (right). Because the organic electronic applications here are based on fully conjugated systems, only the 4,4’ and the 6,6’ positions are of interest a priori. The 4,4’ positions can be ruled out already as steric hindrance with the carbonyls is likely to impair efficient $\pi$-system extension ortho to the central double bond. The para 6,6’ positions are thus the preferred functionalization sites for all compounds described in this Chapter. By comparison with indigo and DPP, 6,6’-functionalized isoindigo can be viewed as a structural hybrid of the latter two molecules: it displays the cross-conjugated chromophore and likely significant substituent/position effects on the benzene rings characteristic of indigo; but also, as DPP, it has an extended $\pi$-system across the central double bond through the 6,6’ positions.
4.2 Isoindigo model compounds.

The extension of conjugation at the 6,6' positions is possible via two precursors described in Scheme 4-5. Importantly, the two building blocks 6-bromoxindole and 6-bromoisatin are commercially available. Their acid-catalyzed condensation in refluxing acetic acid affords 6,6'-dibromoisoindigo in quantitative yields, with little purification required as simple filtration and washing with water, ethanol and ethyl acetate provides the pure compound 4-1. This is readily alkylated in high yields under basic conditions, using potassium carbonate in refluxing anhydrous DMF in the presence of the proper alkyl bromide or using sodium hydride in anhydrous DMF at room temperature followed by the addition of the alkyl bromide. For solubility purposes, 6,6'-dibromoisoindigo was alkylated with linear n-hexyl chains (4-2) for model compounds, but with branched 2-ethylhexyl (4-3) and 2-hexyldecyl chains (4-4) in the case of more extended conjugated molecules and polymers. These dibrominated isoindigos are the first set of precursors used to extend the conjugation at the 6,6' positions.

Scheme 4-5. Synthesis of the dibromo and diboron isoindigo precursors. a) 6-bromoxindole, 6-bromoisatin, HCl conc., AcOH, 90°C, 95%. b) 1.NaH, DMF, r.t. 2. n-hexyl bromide, 80°C, 95% for 4-2 or K$_2$CO$_3$, DMF, alkyl bromide, 100°C, 85% for 4-3 and 70% for 4-4. c) Pinacolester diboron, PdCl$_2$(dpdf), KOAc, dioxane, 80°C, 75%.

The second precursor involves converting the bromides into boron pinacol ester via the Miyaura borylation route using the pinacol ester of diboron in anhydrous dioxane.
in the presence of potassium acetate and catalytic amounts of PdCl$_2$(dppf) (Scheme 4-5). This affords compound 4-5 in high yields with little purification as simple precipitation in cold methanol and washing the filtered solids with methanol suffices.

With precursor 4-2 in hand, model compounds were synthesized as described in Scheme 4-6. By reacting 4-2 with the pinacol ester of benzene under Suzuki cross-coupling conditions, the 6,6'-diphenylisoindigo P-II-P molecule was obtained. Reacting 4-2 with 2-trimethyltin-thiophene or 2-trimethyltin-3,4-ethylenedioxythiophene (EDOT) under Stille cross-coupling conditions afforded 6,6'-dithiophene isoindigo (T-II-T) and 6,6'-diEDOT isoindigo (E-II-E).

![Scheme 4-6. Synthesis of the bisphenyl, bisthiophene and bisEDOT isoindigo model compounds. a) Phenyl boronic ester, Pd$_2$(dba)$_3$, P(o-tyl)$_3$, Et$_4$NOH, toluene, 90°C, 74%. b) 2-tributyltin-thiophene, Pd$_2$(dba)$_3$, P(o-tyl)$_3$, toluene, 90°C, 94%. c) 2-trimethyltin-3,4-ethylenedioxythiophene, Pd$_2$(dba)$_3$, P(o-tyl)$_3$, toluene, 100°C, 87%.]

The absorption spectra of all three model compounds were recorded in chloroform and are displayed in Figure 4-1.a (molar absorptivities vs wavelength), along with that of
the unfunctionalized N,N'-dihexyl isoindigo (H-ii-H) recorded in the same conditions. All spectra have two absorption bands, the high-energy ones being confined below 450 nm and the low-energy ones above 500 nm. The molar absorptivities at the low energy absorption peaks increase from 3,700 M\(^{-1}\)cm\(^{-1}\) for H-ii-H to 26,800 M\(^{-1}\)cm\(^{-1}\) for E-ii-E.

Figure 4-1. Solution absorption spectra (a) of the isoindigo model compounds, and solution electrochemistry (b) of isoindigo, along with the reduction DPVs of the isoindigo model compounds, recorded in 0.1M TBAPF\(_6\) in DCM.

The fact that the absorption of the unfunctionalized H-ii-H shows two bands typical of donor-acceptor systems is consistent with the intrinsic D-A character of isoindigo discussed in the previous section. As the electron-donating strength of the aryl group linked to isoindigo increases from phenyl (P-ii-P) to thiophene (T-ii-T) to EDOT (E-ii-E), the charge transfer band increases in intensity and red shifts from 496 nm for H-ii-H to 567 nm for E-ii-E.

The electrochemistry of H-ii-H in solution (CV and reductive DPV) was recorded as shown in Figure 4-1.b; all potentials are calibrated against Fc/Fc\(^+\). The reductive CV shows two reversible reduction processes centered at half-wave potentials of -1.38 V and -1.85 V, while the oxidative CV shows one irreversible oxidation process at potentials higher than 1V. The accessible reduction of H-ii-H is consistent with its
electron deficient nature. The reductive DPV of H-il-H was recorded (black dashed line) in the same experimental conditions. With an onset of reduction in the DPV at -1.17 V, the LUMO energy level of isoindigo alone is calculated a 3.93 eV. Interestingly, when the reductive DPVs were measured for the phenyl, thiophene and EDOT model compounds (colored dashed lines, Figure 4-1.b), the onset of reduction for each compound was confined between -1.10 and -1.20 V. Therefore, the nature of the aryl substituent at the 6,6' positions has little effect on the energy of the LUMO of isoindigo model compounds. Because of the bathochromic shifts observed for increasingly electron-rich substituents, electron-rich aryl groups at the 6,6' positions of isoindigo seem to have a significant stabilizing effect on the HOMO energies of chromophore.

Calculations performed by Dr. Leandro Estrada in the Reynolds group were aimed at evaluating the electron density in the \( \pi \)-system of such compounds. The unconstrained geometry of T-il-T in gas phase was optimized by Density Functional Theory (DFT) using the B3LYP/6-31G* level of theory. The solubilizing \( n \)-hexyl groups on isoindigo were replaced for methyl to speed up the computations. Figure 4-2 shows the optimized structures and frontier orbital isodensity distributions for T-il-T.

Figure 4-2. DFT optimized structures and frontier orbital density distributions for T-il-T.
It appears that the HOMO is dominated by a stilbene-like structure with electron delocalization along the whole molecule, while the LUMO is localized on the central (3,3'-bipyrrolidine)-2,2'-dione unit. This is consistent with the spectroscopy and electrochemical measurements suggesting that the 6,6’ electron-rich substituents influence mostly the HOMO energy levels.

The level of influence of the electron-donating character on the stabilization of the HOMO energy should be balanced with the contribution of dihedral angle twisting on the extent of π-system overlap. The higher the dihedral angle, the less stabilized the system becomes as a result of poor overlap. Geometry optimization in the DFT calculations already suggests that the thiophene and isoindigo units are quite coplanar. Attempts were made to grow crystals of the model compounds P-il-P and T-il-T to evaluate the difference in dihedral angle between the two. The initial attempts to slowly evaporate chloroform solutions at room temperature did not yield suitable crystals. The material did look crystalline, but the crystals were too small for X-ray analysis.

![Figure 4-3](image)

Figure 4-3. Pictures of T-il-T crystals grown by (a) slow evaporation of a chloroform solution and (b) vapor diffusion between chloroform and acetonitrile.

Millimeter scale single crystals were eventually obtained by the vapor diffusion method between a concentrated chloroform (good solvent) solution of either P-il-P or T-
**il-T** (ca. 10 mg/mL) and acetonitrile (poor solvent). Figure 4-3 shows representative crystals from the slow solvent evaporation (a) and vapor diffusion (b) methods for **T-il-T** samples, kept at room temperature without disturbance for 4 days.

X-ray analysis of the crystals resulted in the packing structure displayed in Figure 4-4.a for **P-il-P** and 4-4.b for **T-il-T**. The two compounds pack differently in the crystal lattice. For **P-il-P** (Figure 4-4.b), the π-stacking direction is the same for every molecule, and each molecule is slid half-way along the chromophore axis as compared to its closest neighbors, so that each phenyl ring overlaps with an isoindigo core.

![Figure 4-4. Crystal packing of **T-il-T** (a) and **P-il-P** (b).](image)

For **T-il-T**, the packing occurs in two orthogonal π-stacked sheet directions (Figure 4-5.a). For one molecule in one sheet, its π-stacked neighbor is slid two thirds of its length along the chromophore axis, such that the thiophene ring overlaps with the benzene ring of the neighboring isoindigo. Thus, only the benzene and thiophene rings are in π-overlap, leaving a gap on each side of the isoindigo central double bond. This gap is filled by two hexyl chains from adjacent molecules of the orthogonal sheet of π-stacked molecules.
For both compounds, the isoindigo unit is essentially flat in a trans configuration consistent with the DFT calculations. In the crystal structure of $\text{P-ii-P}$, the dihedral angle between the phenyl substituent and the isoindigo core is $36^\circ$, much greater than the $4^\circ$ dihedral extracted from the crystal structure of $\text{T-ii-T}$. The steric interaction between the protons ortho to the biphenyl linkages in $\text{P-ii-P}$ likely result is such a dihedral angle difference, as $\text{T-ii-T}$ is almost flat.

![Figure 4-5. Crystal structures of $\text{T-ii-T}$ (top) and $\text{P-ii-P}$ (bottom).](image)

Going beyond these simple model molecules, extending the donor unit to two thiophene rings resulted in a red-shifted absorption spectrum as described in the last part of Chapter 3: Figure 3-20d showed a peak absorption in solution at 592 nm for the bithiophene-capped isoindigo $\text{iIT}_2\text-C_6_2$. When the alkyl chains on the latter were linear $n$-hexyl chains, the crystallinity of the compound resulted in an even greater bathochromic shift in the solid state, up to 658 nm. This led to the first report of isoindigo as electron-acceptor in efficient molecular BHJ solar cells. Since then, Würthner and coworkers
have shown that functionalizing T-III-T with amines at the 5 position can increase the solution peak absorption up to 696 nm.\textsuperscript{191} Similar effects on the dependence of the HOMO energies on the nature of the electron donating substituent were reported. The following section describes the synthesis of donor-acceptor conjugated polymers incorporating isoindigo as an electron-deficient unit.

4.3 Isoindigo-Based Donor-Acceptor Conjugated Polymers.

4.3.1 Polymer Synthesis and Characterization

Six representative isoindigo-based conjugated polymers were synthesized by the palladium-catalyzed polycondensations of 6,6'-dibromoisoindigo compounds 4-3 and 4-4 with functionalized electron-rich moieties, as depicted in Scheme 4-7. The 2-ethylhexyl derivative 4-3 was used in most cases, but solubility issues for one polymer required the use of the 2-hexyldecyl monomer 4-4. The borylations of 3,4-dioctylthiophene, 1,4-bis(hexyloxy)benzene and 9,9-dihexylfluorene were performed according to previously reported procedures. The ditin-thiophene and ditin-3,4-propylene dioxythiophene (ProDOT) compounds were purchased or prepared by direct lithiation with \textit{n}-butyllithium followed by quenching with trimethyltin chloride.

The polycondensations were carried out under Stille or Suzuki coupling conditions depending on the nature of the electron-rich co-monomer, using \textit{Pd}_2(\textit{dba})_3 as palladium source and \textit{P}((\textit{o}-\textit{t}yl))_3 as phosphine ligand. A 20 wt\% degassed aqueous solution of \textit{Et}_4\textit{NOH} was selected as an organic base for the Suzuki polycondensations. The polymerizations were carried out at 85°C for 36 hours in degassed toluene/water mixture, where both the activated boronate salts and the monomers are soluble.
Scheme 4-7. Synthesis of a family of il-based D-A polymers. a) 2,7-diboron-fluorene, Pd$_2$(dba)$_3$, P(o-tyl)$_3$,Et$_4$NOH, toluene, 85°C, 93%. b) 2,5-diboron-2,4-dihexyloxybenzene, Pd$_2$(dba)$_3$, P(o-tyl)$_3$,Et$_4$NOH, toluene, 85°C, 63%. c) 2,5-diboron-3,4-diocylthiophene, Pd$_2$(dba)$_3$, P(o-tyl)$_3$,Et$_4$NOH, toluene, 85°C, 57%. d) 2,5-bis(trimethyltin)thiophene, Pd$_2$(dba)$_3$, P(o-tyl)$_3$, toluene, 85°C, 42% for P(ii-T)-EH and 74% for P(ii-T)-HD. e) 2,5-bis(trimethyltin)-ProDOT, Pd$_2$(dba)$_3$, P(o-tyl)$_3$, toluene, 85°C, 34%.

The polymers were collected by filtration after precipitation into methanol and purified by Soxhlet extraction using methanol, hexanes and chloroform fractions. The fractionation yields vary depending on the solubility of the material: for P(ii-OB), P(ii-AT) and P(ii-ProDOT), both the hexanes and the chloroform fractions contained significant amounts of polymer, while only the chloroform fraction of P(ii-F) contained significant amounts of material. After evaporation of the chloroform, P1 shows considerable mechanical strength, and a 20 cm-diameter free-standing film was easily obtained, as shown in Figure 4-6.a.

The lack of alkyl chains on the thiophene unit of P(ii-T)-EH resulted in a poorly soluble polymer even in hot chlorinated solvents and limited yields after extraction from
chloroform. This is why 4-4 was also polymerized with ditin-thiophene to afford \( P(\text{ii-T})\)-HD, which is soluble in THF (> 10 mg/mL) and chlorinated solvents (>20 mg/mL).

Figure 4-6. Picture (a) of 20 cm-diameter free-standing film of \( P(\text{ii-F}) \) and proton NMR spectrum (b) of \( P(\text{ii-F}) \) recorded in CDCl\(_3\).

The remainder of this study was carried out on samples from the chloroform fractions after Soxhlet extractions, which contain the higher molecular weights. Estimation of these molecular weights against polystyrene standards using size exclusion chromatography (SEC) with THF as eluent gives number average molecular weights \( (M_n) \) within 10 to 22 kDa for the polymers bearing alkyl chains on the donor unit. The recorded \( M_n \) for \( P(\text{ii-T})\)-EH suffered from poor solubility in THF for SEC analysis leading to a low \( M_n \) of 2.4. Poor solubility of the growing polymer chain in the toluene reaction solvent could also explain the low molecular weight of \( P(\text{ii-T})\)-EH. The 2-hexyldeyl version \( P(\text{ii-T})\)-HD was a higher molecular weight polymer of 19.9 kDa as measured by SEC in THF. The proton NMR spectra of all polymers show broad peaks in the 6.5 to 9.4 ppm range corresponding to the aromatic protons, as well as broad multiplets in the 0.70 to 1.80 ppm corresponding to the alkyl chain protons other than the ones on the tertiary carbon of the branched chains (around 1.90 ppm) and the ones on the carbon next to the isoindigo nitrogen (in the 3.50 to 3.90 ppm range). A
representative $^1$H NMR spectrum of the polymer set is shown for $\textbf{P(II-F)}$ in Figure 4-6.b. Thermogravimetric analysis (TGA) under nitrogen flow was used to evaluate the thermal stability of the purified polymers. A mass loss of 5% is defined as the threshold for thermal decomposition. All materials demonstrate good thermal stability with decomposition temperatures above 325°C. The thermal data and the SEC results are summarized in Table 4-2.

4.3.2 Electrochemistry and Optical Properties.

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments were carried out on thin films of each polymer to evaluate their redox properties. The CVs and DPVs of each polymer are displayed in Figure 4-7, all potentials being versus Fc/Fc$^+$. As a representative polymer, $\textbf{P(II-T)}$ shows a quasi-reversible oxidation, with a half-wave potential located at 0.91 V and two quasi-reversible reductions centered at -1.24 V and -1.62 V. While the generation of the anion radical during the first reduction process at -1.24 V is stable to repeated cycles, the second reduction process was unstable under the selected electrochemical conditions. The overall CV and DPV data for the six polymers is summarized in Table 4-2. The HOMO and LUMO energy levels can be calculated from the onsets of oxidation and reduction, respectively, with Fc/Fc$^+$ set at -5.1 eV. The onsets of oxidation and reduction from the solid state DPV displayed in Figure 4-7 (dashed lines) are also summarized in Table 4-2. The LUMO levels are comprised in a narrow range: the LUMO for $\textbf{P(II-T)-HD}$ is the deepest at -4.03 eV, while $\textbf{P(II-F)}$ has the highest at -3.84 eV. The deepest HOMO level is at -5.83 eV for $\textbf{P(II-F)}$, and the highest is at -5.68 eV for $\textbf{P(II-ProDOT)}$. This is consistent with the ProDOT unit being more electron-rich than the fluorene in $\textbf{P(II-F)}$, resulting in a stabilized HOMO for $\textbf{P(II-PrDOT)}$. 

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Figure 4-7. Cyclic voltammogram and differential pulse voltammogram of thin films of each polymer on Pt-button electrode, recorded at a 50 mV/s scan rate in 0.1M TBAPF₆ acetonitrile solution.

The electrochemistry of the polymers is consistent with the results observed for the model compounds is Section 4.2, as the energies of the LUMOs confined in a 0.2
eV range are only slightly influenced by the nature of the electron-donor moiety. The HOMO energies are also within 0.2 eV. The electrochemical band gaps were calculated to be between 1.70 and 2.0 eV (Table 4-2).

Before analyzing the difference in the absorption spectra of polymers with different electron-donor moieties, the absorption of the $P(\text{II-T})$-EH and $P(\text{II-T})$-HD should be compared. As shown in Figure 4-8, although the aromatic part of the repeat unit of the two polymers is the same, the solution spectrum $P(\text{II-T})$-HD is significantly red-shifted by 40 nm to 687 nm as compared to the maximum absorption of $P(\text{II-T})$-EH (dashed lines). In the solid state for $P(\text{II-T})$-HD, there is little difference with the solution spectrum (a 7 nm red-shift to 694 nm) while the solid state absorption of $P(\text{II-T})$-EH broadens towards the near-IR compared to its solution spectrum with a shoulder appearing at 687 nm.

Figure 4-8. Solution absorption spectra (dashed lines) of $P(\text{II-T})$-EH (blue) and $P(\text{II-T})$-HD (black) and the corresponding solid state (solid lines) absorption spectra.
Since the solution spectra for the two polymers are different, the polymer bearing the shorter alkyl chains $P(\text{ii-T})$-EH is likely to have a different conjugation length than its longer alkyl chains equivalent $P(\text{ii-T})$-HD. In particular, the solution UV-vis spectroscopy suggests that $P(\text{ii-T})$-EH has not reached its conjugation length high limit, because the 2-ethylhexyl side-chains on isoindigo are not sufficient solubilizing group to allow the growing polymer chains to attain high enough molecular weights. It is likely that only oligomers of isoindigo and thiophene were obtained during the polymerization for $P(\text{ii-T})$-EH, which is consistent with the broadening of its absorption in the solid state as shorter polymer backbones will be able to reorganize and aggregate more freely. Therefore, when comparing the absorption spectra for the set of D-A polymers synthesized here, $P(\text{ii-T})$-EH should be set aside as it is not representative of a fully conjugated polymer with isoindigo-co-thiophene as repeat unit. $P(\text{ii-T})$-HD will be used in the following.

As depicted in Figure 4-9.a, the UV-vis spectrum of the five high molecular weight polymers in solution displays two absorption bands characteristic of donor-acceptor systems: a high-energy band located in the 420 to 490 nm range attributed to the $\pi-\pi^*$ transition, and a low-energy band in the 520 to 800 nm range assigned to intramolecular charge transfer. Polymers $P(\text{ii-F})$ and $P(\text{ii-OB})$ have similar absorption spectra in solution with high-energy peaks at 462 and 452 nm respectively, and low-energy peaks at 564 and 555 nm respectively. For these two polymers, the relative intensities of these two bands are comparable and are close to unity. With red-shifted absorption maxima, the peaks for $P(\text{ii-AT})$ are located at 472 and 609 nm, with a decreased intensity of the high-energy band relative to the low-energy band. The trend on going from $P(\text{ii-F})$ or
**P**(ii-OB) to **P**(ii-AT) is accentuated for **P**(ii-T)-HD and even further for **P**(ii-ProDOT): bathochromic shifts of 35 nm and 89 nm for the low-energy absorption maxima of **P**(ii-T)-HD and **P**(ii-ProDOT) respectively compared to **P**(ii-AT). The intensities of their high-energy bands decrease further relative to their low-energy band, to a point where little absorption remains at high energy (below 500 nm) for the thiophene and ProDOT copolymers in solution.

![Graph](image)

**Figure 4-9.** Normalized UV-vis absorption spectra the five high molecular weight polymers (a) in chloroform solution and (b) as thin films on ITO-coated glass.

The trend for chromatic shifts in absorption maxima can be explained by the variations of the electron-donating character of the different electron-rich co-monomers to the overall $\pi$-system. For instance, the electron-donating character of the fluorene spacer in **P**(ii-F) is relatively weak. Arguably, this moderately electron-rich unit lies out of plane relative to the isoindigo unit because of steric interaction of the benzene rings, as suggested by the X-ray crystal structures on model compound **P**-ii-**P**. For the dialkoxybenzene donor in **P**(ii-OB), the donating effect of the alkoxy side chains into the polymer backbone could be impaired by an even greater dihedral twist of the alternating units, since the alkoxy chains are ortho to the backbone linkages. This could explain
why the absorption of \( P(\text{ii-F}) \) and \( P(\text{ii-OB}) \) are confined below 650 nm. The three thiophene-based spacers of the other three copolymers are more electron-rich than the benzene spacers, and X-ray crystal structures show a low dihedral angle between thiophene and isoindigo, which is why the absorption of \( P(\text{ii-AT}) \), \( P(\text{ii-T})\)-HD and \( P(\text{ii-ProDOT}) \) extend further towards the near-IR. For \( P(\text{ii-AT}) \), it is likely that steric hindrance arising from the presence of the dialkyl substituents on the thiophene of would explain the blue-shift in its UV-vis spectrum compared to \( P(\text{ii-T})\)-HD. The ProDOT spacer of \( P(\text{ii-ProDOT}) \) is the most electron-rich co-monomer, resulting in the greatest bathochromic shift. The extinction coefficients of the polymers in solution are between 22,000 and 40,000 M\(^{-1}\)cm\(^{-1}\).

Table 4-2. SEC results, optical properties and electrochemical data measured for the six polymers.

<table>
<thead>
<tr>
<th></th>
<th>UV-vis-NIR</th>
<th>Electrochemistry(^c)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>CV</td>
</tr>
<tr>
<td></td>
<td>( M_n )</td>
<td>( \lambda_{\text{max}}^a )</td>
</tr>
<tr>
<td>( P(\text{ii-F}) )</td>
<td>21.2</td>
<td>564</td>
</tr>
<tr>
<td>( P(\text{ii-OB}) )</td>
<td>10.5</td>
<td>555</td>
</tr>
<tr>
<td>( P(\text{ii-AT}) )</td>
<td>16.7</td>
<td>609</td>
</tr>
<tr>
<td>( P(\text{ii-T}))-EH</td>
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<td>647</td>
</tr>
<tr>
<td>( P(\text{ii-T}))-HD</td>
<td>19.9</td>
<td>687</td>
</tr>
<tr>
<td>( P(\text{ii-ProDOT}) )</td>
<td>19.3</td>
<td>701</td>
</tr>
</tbody>
</table>

\( a \) In chloroform solution. \( b \) Recorded for thin films spayed onto ITO coated glass. \( c \) Recorded for thin films drop-cast from toluene onto Pt button electrodes.

The solid state absorption spectra of the polymers are displayed in Figure 4-9.b. Thin films were prepared by spraying solutions of the polymers onto ITO-coated glass. The trend delineated for solution absorption still holds in the solid state, only red-shifted.
on the order of 10 nm compared to the solution spectra. The colors of the polymer thin films are consistent with their absorption profile: \( \text{P(il-F)} \) and \( \text{P(il-OB)} \) films are red-purple due to the broad absorption from 400 nm to \( \text{ca. 675 nm} \) and little absorption beyond 675 nm. Thin films of \( \text{P(il-T)} \) have a blue-gray color due to their long-wavelength absorption and the reduced intensity of the low-wavelength absorption band below 550 nm. With long-wavelength absorption even more red-shifted and further reduced low-wavelength absorption, \( \text{P(il-T)-HD} \) and \( \text{P(il-ProDOT)} \) have a blue-green hue. From the low-energy onset of absorption in the solid state, optical band gaps in the 1.55 to 1.90 eV range are calculated (Table 4-2), consistent with the measured electrochemical band gaps trend.

In summary, D-A conjugated polymers based on the isoindigo acceptor are able to absorb light up to 800 nm when thiophene-based electron-rich co-monomers are used. The LUMO energies of the polymers, much like the model compounds studied in the beginning of this Chapter, are rather insensitive to the nature of the electron-rich moiety and are confined between -3.80 and -4.00 eV, which are deep (high electron affinities) compared to other conjugated polymers. With bandgaps in the 1.55 to 2.00 eV range, the HOMO energy levels are also deep (high ionization potentials), in the -5.60 to -5.85 eV range.

### 4.4 All-Acceptor Isoindigo-Based Conjugated Polymers.

Motivated by such low-lying energy levels and extended light absorption, conjugated polymers were designed for n-type applications as a substitute for the widely used fullerene derivatives in BHJ solar cells, since the latter n-type materials have limited absorption. In the following, two new isoindigo-based conjugated polymers with backbones exclusively composed of electron-deficient units. In contrast to the more
common donor–acceptor approach widely used to synthesize n-type conjugated polymers, the versatile chemistry of isoindigo provided a synthetic route to two soluble high molecular weight all–acceptor polymers: a homopolymer of isoindigo, Poly(il), and a copolymer of isoindigo with 2,1,3-benzothiadiazole alternating in the repeat unit, Poly(il-BTD).

4.4.1 Polymer Synthesis and Optical Properties.

As shown in Scheme 4-8, diborylated isoindigo 4-5 was copolymerized with its dibrominated analogue 4-4 under Suzuki polycondensation conditions in degassed toluene at 80°C, using Pd₂(dba)₃ and tri(ortho-tolyl)phosphine as catalytic system, and a degassed 1M tetraethylammonium hydroxide aqueous solution as boron-activating base. These efficient Suzuki cross-coupling conditions afforded the homopolymer of isoindigo, Poly(il), in excellent yield. The purification process involved precipitation into methanol, followed by Soxhlet extraction with methanol and then hexanes to remove low molecular weight product. A soluble higher molecular weight fraction of Poly(il) was then extracted using chloroform, precipitated into methanol and filtered giving Poly(il) in an overall yield of 74%.

Scheme 4-8. Synthesis of the all-acceptor polymers Poly(il) and Poly(il-BTD). a) Pd₂(dba)₃, P(o-tolyl)₃, Et₄NOH, toluene, 85°C, 74%. b) Pd₂(dba)₃, P(o-tolyl)₃, Et₄NOH, toluene, 85°C, 95%.
The number average molecular weight of the chloroform soluble fraction of **Poly(iI)** is 28.7 kDa with a polydispersity index (PDI) of 2.4 as measured by size exclusion chromatography in THF against polystyrene standards. **Poly(iI)** is soluble in a range of common organic solvents, including tetrahydrofuran, toluene, dichloromethane, chloroform and chlorinated benzenes. The \(^1\)H NMR spectrum of the chloroform-soluble fraction shows broadened peaks in the aromatic region, between 8.8-9.1 ppm and 6.8-7.4 ppm, and a wide peak in the 3.6 to 4.3 ppm region with consistent integration corresponding to the methylene proton on the tertiary carbon of the 2-hexyldecyl side-chains. These chemical shifts are consistent with the repeat unit structure of **Poly(iI)**, further confirmed by elemental analysis.

By copolymerizing the diborylated isoindigo 4-5 with 4,7-dibromo-2,1,3-benzothiadiazole (Scheme 4-8), an alternating copolymer **Poly(iI-BTD)** was obtained. Similar high-yielding polymerization and purification procedures afforded **Poly(iI-BTD)** with an average molecular weight of 16.3 kDa and a PDI of 3.5 in 95 % yield for the chloroform fraction after Soxhlet extraction. The solubility of **Poly(iI-BTD)** is similar to **Poly(iI)** using the same solvents. The remainder of the study was conducted on the materials extracted from chloroform during Soxhlet purification to ensure the highest average molecular weights available. Setting a 5 % weight loss as the threshold for thermal decomposition, TGA under nitrogen flow to showed that the polymers were both thermally stable up to 380°C, as displayed in Figure 4-10.a. We recorded the UV–vis absorption spectra of **Poly(iI)** and **Poly(iI-BTD)** in solution and in the solid state. As displayed in Figure 4-10.b, the UV–vis spectra of the polymer in solution and in thin
films show little difference, suggesting little aggregation in the solid-state without further film treatment after spray-coating.

Figure 4-10. TGA thermograms (a) of Poly(il) and Poly(il-BTD) under nitrogen flow, and normalized absorption spectra (b) in solution (dashed lines) and in solid state (solid lines) of the two polymers.

In the solid state, Poly(il) absorbs light at wavelengths longer than 700 nm, with $\lambda_{\text{max}}$ at 690 nm, and a low-energy onset of absorption at 731 nm. Of the two main absorption bands in the 400-730 nm region, the low-energy absorption band centered at 690 nm for Poly(il) is more intense than its high-energy absorption band with a local maximum at 460 nm. Films of Poly(il) have a blue-green color in the neutral state, as most of the red light is absorbed by the polymer. Thin films of Poly(il-BTD) have a shorter $\lambda_{\text{max}}$ at 464 nm, with a low-energy absorption onset at 700 nm. The polymer absorbs from 400 to 600 nm. The measured molar absorptivities for Poly(il) and Poly(il-BTD) in toluene were 25,000 M$^{-1}$ cm$^{-1}$ and 22,300 M$^{-1}$cm$^{-1}$ respectively at their $\lambda_{\text{max}}$. From the low-energy onsets of the thin film absorption, solid-state optical bandgaps of 1.70 eV and 1.77 eV were calculated for Poly(il) and Poly(il-BTD), respectively.
4.4.2 Electrochemistry and Spectro electrochemical measurements.

In order to experimentally determine the energy levels of the polymers, and be able to compare them to that of soluble fullerenes, we investigated the electrochemistry of Poly(ii) and Poly(ii-BTD) as thin films drop-cast onto Pt button electrodes in a 0.1M TBAPF₆ acetonitrile solution under inert atmosphere. All potentials reported here are calibrated against Fc/Fc⁺. Figure 4-11.a shows the tenth CV cycles of the oxidation and reduction of Poly(ii), and the reductive DPV. The reductive CV of Poly(ii) thin films shows one reversible redox process with cathodic and anodic peak currents at -1.36 V and -1.24 V, respectively, and a half-wave potential at -1.30 V. We used the onset of reductive DPV (dashed line) to calculate the energy of the LUMO level. With a Fc/Fc⁺ redox standard set at -5.10 eV versus vacuum, the measured DPV reduction onset found at -1.26 V corresponds to a LUMO energy of -3.84 eV.

The reductive CV experiments on thin films of Poly(ii-BTD) performed under the same conditions (Figure 4-11.b) show one cathodic peak at -1.47 V and two anodic peaks upon reduction centered at -1.42 V and -1.21 V. From the reductive DPV (dashed
line), an onset of reduction was measured at -1.20 V corresponding to a LUMO energy of -3.90 eV.

When the scan rates were increased from 10 to 200 mV/s in the reductive CV of Poly(II), the half-wave potentials remained constant (Figure 4-12.a). With an anodic peak to cathodic peak potential difference under 160 mV even at relatively high scan rates, these results indicate a stable and relatively reversible redox process.

Figure 4-12. Overlaid reduction CVs (a) of Poly(II) recorded in 0.1M TBAPF₆/ACN, at increasing scan rates from 10mV/s to 200 mV/s with a 10mV/s rate increment, with scan rate dependence of peak currents in inset. Overlaid ten first oxidation CVs of (b) Poly(II) recorded in 0.1M TBAPF₆/ACN, at 50mV/s scan rate.

Displayed in the inset, the peak currents dependence on scan rate is close to linear, suggesting that the doping of the well-adhered film on the electrode surface is not diffusion limited at the chosen scan rates. Attempts to electrochemically oxidize Poly(II) resulted in an irreversible and unstable redox process with a peak potential at +1.40 V, as shown in Figure 4-12.b. Since the poor oxidation of the polymer prevents a viable electrochemical calculation of the HOMO energy level, we deduced it from the optical bandgap of the thin films: for an optical bandgap of 1.70 eV, the corresponding HOMO energy level is at -5.54 eV.
Similar scan rate dependence experiments were performed on the reduction of thin films of Poly(iI-BTD), shown in Figure 4-13.a. While the half-wave potentials remained constant at -1.31 V when the scan rate was increased from 10 to 200 mV/s, the peak-to-peak potential difference widened from 170 mV to 610 mV. In the inset, the peak currents dependence on scan rate is also close to linear, dismissing concerns of film deterioration or electrolytic limitations at the scan rates employed. This indicates that the reduction of Poly(iI-BTD) is less reversible than that of Poly(iI). In a similar way to Poly(iI), the oxidation process is irreversible and unstable with currents steadily decreasing with successive recording cycles (Figure 4-13.b). The solid state optical bandgap of 1.77 eV is equivalent to a HOMO energy of -5.67 eV.

![Graphs showing scan rate dependence](image)

Figure 4-13. Overlaid reduction CVs (a) of Poly(iI-BTD) recorded in 0.1M TBAPF$_6$/ACN, at increasing scan rates from 10mV/s to 200 mV/s with a 10mV/s rate increment, with scan rate dependence of peak currents in inset. Overlayed ten first oxidation CVs of (b) Poly(iI-BTD) recorded in 0.1M TBAPF$_6$/ACN, at 50mV/s scan rate.

Spectroelectrochemistry provides insight into the nature of the charged species generated along the conjugated backbone during the solid state reduction process. To investigate the spectroelectrochemical behavior of Poly(iI), films of the polymer were sprayed from toluene solutions onto ITO-coated glass slides, which serve as
transmissive working electrodes. Tetraethylammonium tetrafluoroborate in propylene carbonate (TEABF₄/PC) was selected as the supporting electrolyte for the reduction of the polymer films on ITO, since the redox processes proved to be more stable than when the TBAPF₆/ACN electrolyte was used. Figure 4-14 depicts the spectral changes upon application of successive step potentials from -1.26 V to -1.45 V, with 10 mV potential increments for a Poly(iI) film on ITO. This small voltage difference to attain full reduction from the neutral polymer suggests a narrow distribution of states and that each species being reduced is chemically similar.

![Figure 4-14](image_url)

Figure 4-14. Spectroelectrochemistry (left) of Poly(iI) sprayed onto an ITO-coated glass slide. The film was subjected to 20 mV potential increments (first five spectra) then 10mV increments (last nine spectra) from -1.26 V to -1.45 V vs Fc/Fc⁺ in a 0.1M TEABF₄/propylene carbonate electrolyte. Pictures (right) of the neutral and reduced Poly(iI) film.

No spectral change was observed when the potential was swept negative of 0 V up to -1.20 V: the blue line in Figure 4-14 with peak absorption at 688 nm in the neutral film remained steady until potentials close to −1.25 V were reached. Within 0.19 V of further reduction from -1.26 V to -1.45 V, the absorption bands at 459 nm and 688 nm of the neutral film decreased steadily to an almost complete bleaching of the absorption in the visible region. Concomitantly, a well-defined absorption band centered at 1522 nm
emerged stabilizing in intensity at -1.45 V (thick black line). While blue-green in the neutral state the polymer film cathodically bleaches at -1.45 V, as displayed in Figure 4-14, with a well-defined isosbestic point at 737 nm. We evaluated the color of the polymer films in the undoped and the reduced states as the human eye perceives them by measuring their L*a*b* values (CIE 1976 L*a*b* Color Space). The neutral film shown in Figure 4-14 with a maximum absorbance of 0.4 at 688 nm has a low optical density with a* and b* values of -16 and -4, respectively. These values confirm a green to blue-green color of the undoped polymer, which is consistent with the trough observed in its neutral UV–vis spectrum at 520 nm and the lower relative intensity of the band at 459 nm with respect to the one at 688 nm. In the reduced state, the a* and b* values of the polymer film are respectively 1 and 6, confirming a transmissive doped state with a slight yellow hue, as expected from the small remnant absorption band at 459 nm at -1.45 V. Aside from dioxythiophene-cyanovinylene-based copolymers, this is the only example of a stable colored to transmissive electrochromic polymer upon n-doping (i.e. anodically coloring material).\textsuperscript{17}

The spectroelectrochemistry of Poly(II-BTD) was studied under the same conditions. Starting from a neutral film previously subjected to ten reduction CV cycles from -0.5 to -1.5 V at 50 mV/s, potential steps with a 10mV increment were then applied from -1.05 V to -1.46 V and the spectra were recorded after each increment. Figure 4-15 shows the progression of chromatic changes upon stepping the potential from -1.21 V to -1.41 V, as little spectral changes were observed outside this potential window. In the absorption of the neutral film (red line), the two absorption bands at 468 nm and 594
nm decrease in intensity as a high wavelength band appears in the near-IR centered at 1134 nm.

Figure 4-15. Spectroelectrochemistry of Poly(ii-BTD) sprayed onto an ITO-coated glass slide. The film was subjected to 10 mV potential increments from -1.21 V to -1.41 V vs Fc/Fc⁺ in a 0.1M TEABF₄/propylene carbonate electrolyte.

Unlike for Poly(iI), the absorption of Poly(ii-BTD) in the visible is not fully bleached, as a band remains between 450 and 550 nm even at more negative potentials.

The electrochemical experiments showed a pronounced difference between the stable, reversible reduction processes compared to the unstable, irreversible oxidation processes, under the same electrochemical setup. The spectroelectrochemistry shows that the reversible generation of stable negative charges in Poly(iI) thin films takes place in less than 20 mV, from -1.26 V to -1.45 V. The excellent reversibility and speed of the reduction, and the well defined isosbestic point suggest a single-electron process which yields a radical anion on the repeat unit of isoindigo. The absorption band in the near IR centered at 1522 nm likely corresponds to that of the radical anion. The spectroelectrochemistry of Poly(ii-BTD) shows a similarly low potential range (20 mV)
for generation of negatively charged species in the film, although the process is not as reversible as for Poly(iI). This is an indication of the potential n-type character of all-acceptor polyisoindigos.

4.4.3 All-Polymer Solar Cells.

The electrochemistry results confirmed our expectations of high electron affinities (deep LUMOs) and high ionization potentials (deep HOMOs) for electron-deficient polyisoindigos. Figure 4-16.a depicts where the energy levels of Poly(iI) lie with respect of that of P3HT (electron-donor) and PC$_{60}$BM (electron-acceptor). Figure 4-16.b shows the electrochemical reduction of a solution PC$_{60}$BM carried out in 0.1M TBAPF$_6$ in DCM under inert atmosphere. The onset of reduction in the DPV was measured at -1.0 V vs Fc/Fc$^+$, corresponding to a LUMO energy of -4.1 eV for PC$_{60}$BM. The electron affinity of Poly(iI) around -3.9 eV approaches that of the commonly used PC$_{60}$BM, measured at -4.1 eV electrochemically and set at -4.2 eV in the literature.$^{30}$ As can be seen in Figure 4-16.a, the ionization potential of Poly(iI) around -5.6 eV is sufficiently high to drive exciton separation in BHJ cells with an appropriately chosen donor material.

![Figure 4-16. Band structure diagram (a) comparing the HOMO and LUMO levels of Poly(iI) and PC$_{60}$BM, and their offsets relative to the electron-donor P3HT. Solution electrochemistry (b) of PC$_{60}$BM, recorded in 0.1M TBAPF$_6$ in DCM.](image-url)
Having a bandgap below 1.8 eV allows for extended absorption throughout the visible spectrum—validating the candidacy of Poly(II) as electron-accepting material for all-polymer solar cells. We selected P3HT as the p-type counterpart to Poly(II) for all-polymer solar cells, since P3HT is a well characterized polymer with HOMO and LUMO energy levels around -5.2 eV and -3.2 eV respectively. This not only enables energy offsets greater than 0.3 eV between the HOMO (LUMO) of P3HT and Poly(II), but the latter has a complementary absorption to P3HT, extending the absorption of the resulting blend by almost 100 nm into the near IR in thin films, shown in Figure 4-17.b.

Bulk heterojunction photovoltaic cells were fabricated using P3HT as the donor and Poly(II) as the acceptor, by Caroline Grand in the Reynolds group and Dr. Jegadesan Subbiah in Dr. Franky So’s Research group. The polymers were dissolved separately in chlorobenzene under inert atmosphere and from the stock solutions, blends of 2:1, 1:1 and 1:2 P3HT:Poly(II) were spin cast onto adequately prepared patterned ITO slides.

Figure 4-17. Schematic diagram (a) of the all-polymer solar cell with conventional device geometry, and thin film absorption spectra (b) of the P3HT:Poly(II) blends at 2:1, 1:1 and 1:2 ratios.
A schematic diagram of an all–polymer solar cell with conventional device architecture is shown in Figure 4-17.a, along with the blend films absorptions for each ratio (Figure 4-17.b).

The level of contribution of Poly(il) in the overall film absorption for the 2:1 P3HT:Poly(il) is small, which is expected at such a ratio given the difference in molar absorptivities between the two polymers. At 1:2 P3HT:Poly(il) blend, the absorption band at 688 nm from the contribution of Poly(il) scales to approximately to 68 % of the maximum absorption of P3HT. The J-V characteristics of the devices made with three different P3HT:Poly(il) weight ratios of 2:1, 1:1 and 1:2 as the active layer are shown in Figure 4-18.a.

Figure 4-18. J-V curves (a) of the P3HT:Poly(il) based BHJ solar cells with various blend ratios under AM1.5 solar illumination, 100 mW.cm$^{-2}$ in conventional solar cell architecture. Photovoltaic parameters are inset: $J_{sc}$ in mA.cm$^{-2}$, $V_{oc}$ in V; FF and PCE in %. External quantum efficiency (b) of the 1:1 P3HT:Poly(il) device.

The photovoltaic parameters (short-circuit current ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill-factor (FF) and power conversion efficiency (PCE)) of these devices are summarized in the inset in Figure 4-18.a. The P3HT:Poly(il) weight ratio of 1:1 showed the best
device performance with a $V_{oc}$ value of 0.62 V, a FF of 41 %, and a $J_{sc}$ value of 1.91 mA.cm$^{-2}$, resulting in a PCE value of 0.47 %. We denote an increasing fill-factor of the devices with increasing Poly(II) content, which reaches a maximum value of 50 % when the blend ratio is 1:2. Meanwhile, increasing the Poly(II) content in the blend ratio from 1:1 to 1:2 decreases the $J_{sc}$, lowering the overall device performance. When AFM was used to probe the surface morphology of the active layer at different blend ratios, no significant difference in the feature sizes for the different blends was observed. Likewise, no significant information was obtained from TEM images of the blends.

Unlike blends of polymers and fullerenes, the difficulties in monitoring the surface morphology of polymer blends by AFM and low contrast in TEM are expected, since the two components are of similar physical and electronic nature on the scale of the latter two methods' sensitivities. The external quantum efficiency (EQE) of the P3HT:Poly(II) device with the blend ratio of 1:1 is shown in Figure 4-18.b. The EQE measurements showed that the best polyisoindigo-based device exhibited broad photo-response ranging from 350 to 750 nm with a maximum EQE of 12 % at 520 nm, confirming the contribution of Poly(II) to the photogenerated current.

In summary, the maximum PCE of 0.47 % obtained for the polyisoindigo-based all–polymer solar cells is to put in perspective of the best all–polymer solar cells efficiency of 2.2~2.3 % reported so far for BHJ devices. Better morphological control of the polymer blends could lead to increased efficiencies in the solar cells described above, although low electron mobilities in Poly(II) could impair the performance to a greater extent. Indeed, electron mobilities of $3.7 \times 10^{-7}$ cm$^2$V$^{-1}$s$^{-1}$ on average in pristine
films of Poly(II) were measured in an electron-only device based on a vertical architecture (Al/ Poly(II)/LiF/Al), in the space charge limited current regime.

4.5 Isoindigo-Based D-A Polymers for BHJ Polymer Solar Cells.

4.5.1 Isoindigo in Polymer Solar Cells.

From the previous sections, using donor moieties based on the thiophene unit result in polymers with a more extended absorption toward the near-IR rather than phenyl-based donors. The backbone is likely more planar for thiophene donor, at least as long as the thiophene ring itself is not alkylated in a way that would induce twisting (cf. P(II-AT)).

![Scheme 4-9. Structures of all the D-A conjugated polymer reported in the literature so far.](image)

At the same time, non-alkylated thiophenes worsen the solubility of the D-A polymer to an extent that not only would hamper solvent processing, but also can lead
to oligomeric species rather than actual polymers (cf. \textbf{P(iI-T)-EH} vs \textbf{P(iI-T)-HD}). As a general rule, isoindigo should bear 2-ethylhexyl chains when the donor is alkylated; 2-hexyldecyl chains when the donor is not alkylated.

Since the first report of molecular solar cells and conjugated polymers based on isoindigo by the Reynolds group, researchers in the field have followed with the synthesis of a variety of D-A conjugated polymers, for which the structures are displayed in Scheme 4-9.\textsuperscript{193-201} Remarkably, the LUMO energy levels of all il-based conjugated materials reported so far are confined to the −3.7 to −3.9 eV range. With bandgaps between 1.9 and 1.5 eV depending on the aromatic units conjugated with isoindigo, the HOMO energy levels are between −5.5 and −5.9 eV. Such high ionization potentials (deep HOMOs) for D–A polymers led to devices with high open circuit voltages (\(V_{oc}\)) for BHJs with fullerene derivatives. Some of these polymers performed very well, with 6.3% BHJ solar cell efficiency with PCBM reported by Andersson and coworkers\textsuperscript{200} for the copolymer of isoindigo and terthiophene and 0.79 cm\(^2\)V\(^{-1}\)s\(^{-1}\) in air-stable p-type OFETs reported by Lei and coworkers\textsuperscript{194} for the copolymer of isoindigo and unalkylated bithiophene. These remain the best performances reported for isoindigo-based materials so far.

\textbf{4.5.2. Polymer Synthesis and Characterization.}

In an effort to tailor the structure of isoindigo-based D–A polymers for optimized solar cells, the synthesis of the copolymer of isoindigo and dithieno[3,2-b:2′,3′-d]silole, \textbf{P(ii-DTS)}, is described in the following. The simplest electron-rich moiety serving this purpose is one thiophene ring, which was used by Andersson and co-workers in an il-based conjugated polymer similar to \textbf{P(ii-T)-HD} achieving 4.5% solar cell efficiency.\textsuperscript{195} Extending the donor unit length to two thiophene rings likely increases the delocalization
of positive charge carriers along the backbone thereby enhancing the p-type character
of the iI-based polymer, as demonstrated by Lei and co-workers\textsuperscript{194}. In copolymers
based on different acceptors than isoindigo, the presence of a bridging atom such as
carbon (cyclopentadithiophene, CPDT) or silicon (dithienosilole, DTS) between two
thiophene rings has been shown to further planarize the electron-rich unit\textsuperscript{44}, while
providing an alkylation site for solubility purposes. The silicon bridge of DTS is
advantageous as the alkyl chains stemming from silicon are able to remain in-plane to a
greater extent than in CPDT, resulting in a more planar backbone. Therefore, we
suspected DTS to be an electron-rich unit best suited for high efficiency D–A
copolymers based on isoindigo as a conjugated acceptor. For solubility purposes, both
monomers were functionalized with 2-ethylhexyl side-chains. The DTS moiety was
prepared and converted to its ditin derivative by Dr. Chad Amb following a previously
reported procedure\textsuperscript{46} and was purified by preparative HPLC in order to guarantee
proper functional group stoichiometry during polymerization. As shown in Scheme 4-10,
the 6,6′-dibromo-N,N′-(2-ethylhexyl)-isoindigo monomer 4-3 was then copolymerized
with 2,2′-bistrimethylstannyl-4,4′-bis-(2-ethylhexyl)-dithieno[3,2-b:2′,3′-d]silole under
Stille coupling conditions to afford P(iI-DTS) in 94% overall yield after purification. The
copolymerization was carried out using \( \text{Pd}_2(\text{dba})_3 \) as Pd source and \( \text{P(o-tyl)}_3 \) as ligand,
in dry degassed toluene at 85°C.

\[
\begin{align*}
\text{4-3} & \quad + \quad \text{Me}_3\text{Sn} \quad \xrightarrow{\text{a}} \quad \text{P(iI-DTS)} \\
\text{Scheme 4-10. Synthesis of P(iI-DTS) via Stille cross-coupling. a) } & \quad \text{Pd}_2(\text{dba})_3, \quad \text{P(o-tyl)}_3, \\
& \quad \text{toluene, } 85^\circ\text{C, 97%}. 
\end{align*}
\]
Before quenching the reaction, 2-bromothiophene and 2-trimethyltin thiophene were added in succession in the reaction medium as an attempt to replace undesired backbone chain-end groups with thiophene rings. After purification of the polymer in a Soxhlet extractor using methanol and hexanes, the high molecular weight fraction of P(II-DTS) extracted with chloroform was analyzed using size exclusion chromatography in THF against polystyrene standards.

Figure 4-19. TGA thermogram (a) of P(II-DTS) under nitrogen flow; CV and DPV (b) of the polymer film drop-cast onto a Pt-button electrode recorded in 0.1M TBAPF$_6$ in ACN; solution (dashed) and solid state (solid) absorption spectra (c) of P(II-DTS) and film absorption of a 1:4 blend of P(II-DTS):PC$_{70}$BM.

The polymer from the chloroform fraction used in the following study has a number average molecular weight of 36.0 kDa and a polydispersity of 2.77, and is soluble in all chlorinated solvents and in THF and toluene. The analyzed elemental composition for
C, H and N is within 0.4% of the calculated elemental composition. From the thermogravimetric analysis (Figure 4-19.a) performed under nitrogen with a 5% weight loss set as decomposition threshold, the polymer was found to be thermally stable up to 410°C. The electrochemistry of P(ii-DTS) is displayed in Figure 4-19.b.

The CV and DPV were performed on thin films drop-cast onto Pt button electrodes, using 0.1M TBAPF₆ in acetonitrile as supporting electrolyte. In the oxidative CV one reversible oxidation process was observed with a half-wave potential at 0.69 V. In the oxidative DPV experiment, we recorded an onset of oxidation at 0.45 V. The corresponding HOMO energy level is −5.55 eV. The reductive CV shows two reversible reduction processes, with half-wave potentials at −1.17 V and −1.57 V. From the onset of reduction at −1.15 V in the DPV, the calculated LUMO energy level is −3.95 eV. The electrochemical bandgap of 1.60 eV is consistent with the optical bandgap of 1.54 eV. The UV–vis absorption spectrum of P(ii-DTS) in solution and in thin films is shown in Figure 4-19.c. With a peak absorption (λₘₐₓ) at 720 nm and a low-energy onset of absorption (λ_onset) at 805 nm in the solid state, the polymer absorbs strongly in the visible towards the near-IR with an optical bandgap of 1.54 eV as calculated from λ_onset. At wavelengths less than 550 nm, the absorption decreases, peaking at 435 nm with 33% of the intensity of the λₘₓ at 720 nm. Thin films of P(ii-DTS) thus look blue-green as they absorb mostly in the red region of the visible spectrum. This absorption gap at wavelengths lower than 550 nm is compensated by the absorption of PC₇₀BM, and blend films of P(ii-DTS):PC₇₀BM absorb broadly across the entire visible spectrum.

The high value of the LUMO at −3.95 eV is closer to that of PC₇₀BM than the ~0.3 eV offset recommended for efficient electron transfer, but the extended absorption of
the polymer, and the high ionization potential (deep HOMO) of $-5.55$ eV were promising for devices with high $V_{oc}$, as the latter is closely related to the offset of the LUMO of the fullerene derivative and the HOMO of the p-type polymer in BHJ solar cells.

### 4.5.3 Polymer/PCBM Solar Cells.

In collaboration with Dr. Franky So’s Research group, a conventional cell architecture was first investigated based on ITO/PEDOT:PSS/P(iI-DTS):PCBM/LiF/Al, with PC$_{60}$BM and PC$_{70}$BM as electron acceptors. After initial device testing, PC$_{70}$BM was deemed a better acceptor than PC$_{60}$BM, because of the enhanced photon absorption of the cells under AM1.5 illumination, due to the more extended absorption of PC$_{70}$BM in the visible.

![J–V curves](image1.png)

**Figure 4-20.** J–V curves of the P(iI-DTS):PC$_{70}$BM (1:4) based BHJ solar cells with and without DIO additive, under AM1.5 solar illumination, in conventional (circle and triangle lines) and inverted architecture (square line). AFM images of the P(iI-DTS):PC$_{70}$BM blend at 1:4 ratio, processed without (a) and with (b) 4% DIO additive (2 μm-side, 20 nm-height scales). TEM images of the aforementioned blend, processed without (c) and with (d) 4% DIO additive (200 nm scale bars).

The ratio of P(iI-DTS) to PC$_{70}$BM, solvent (chloroform (CF) and chlorobenzene (CB)), solution concentration, spin-coating speed and annealing conditions were
optimized. A donor/acceptor weight ratio of 1:4 in CB at a concentration of 25 mg/mL spun cast at 1000 rpm and annealed at 150°C before LiF/Al deposition gave the best efficiency. The J–V curves of the optimized BHJ obtained under AM1.5 illumination (100 mWcm\(^{-2}\)) are shown in Figure 4-20.a.

The use of solvent additives such as octanedithiol or diiodooctane (DIO) has previously been shown to decrease the domain sizes in the BHJ of PSCs.\(^ {46,65}\) Given the morphological limitations stated above, we monitored the effect of two solvent additives (1,8-diiodooctane (DIO), chloronaphthalene) on device performance. As shown in the AFM and TEM images in Figure 4-20.b, the addition of 4% in volume of DIO in the spin-casting solution significantly reduces the features sizes in the active layer.

Table 4-3. Solar cell characteristics of the P(ii-DTS):PC\(_{70}\)BM (1:4) blend.

<table>
<thead>
<tr>
<th>Device processing</th>
<th>(J_{sc}) (mA/cm(^2))</th>
<th>(V_{oc}) (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional cell without DIO</td>
<td>2.82</td>
<td>0.86</td>
<td>60</td>
<td>1.45</td>
</tr>
<tr>
<td>Conventional cell with DIO (4%)</td>
<td>8.26</td>
<td>0.76</td>
<td>42</td>
<td>2.62</td>
</tr>
<tr>
<td>Inverted cell with DIO (4%)</td>
<td>10.49</td>
<td>0.77</td>
<td>50</td>
<td>4.01</td>
</tr>
</tbody>
</table>

While the AFM images show a smoother surface morphology, the TEM images reveal an intricate network of donor/acceptor phases in the bulk of the film, similar to that observed in previously reported studies, with segregation scales reduced from 0.5 micron without additives to tens of nanometers with 4% DIO. Because of the reduced domain size, excitons are more likely to reach the P(ii-DTS)/PC\(_{70}\)BM interface and generate charge carriers. As can be seen in Table 4-3, 4% DIO additive leads to a three-fold increase of the \(J_{sc}\). To further improve carrier extraction at the electrodes,
devices using the inverted architecture ITO/ZnO/$\text{P(iI-DTS)}$:PC$_{70}$BM(1:4)/MoO$_3$/Ag were fabricated, while keeping the processing conditions for the active layer the same. As can be seen in Figure 4-20 and Table 4-3, this architecture leads to increased device performance from 2.62% to 4.01%, since as it is likely to take better advantage of a vertical phase separation present in the BHJ film.

In summary, the copolymer $\text{P(iI-DTS)}$ of isoindigo and dithienosilole is soluble at high molecular weight when functionalized with 2-ethylhexyl side chains on each conjugated unit, and absorbs light up to 800 nm in the solid state. With HOMO and LUMO energy levels at −5.55 and −3.95 eV vs vacuum respectively, this polymer has a bandgap of 1.60 eV as measured by DPV in the solid state, which correlates well with an optical bandgap of 1.54 eV. Despite its high electron affinity (deep LUMO) close to that of fullerene derivatives, $\text{P(iI-DTS)}$ still enables moderate PCE of 1.45% when blended with PC$_{70}$BM in PSCs processed without solvent additives: the high open circuit voltage of 0.86V is undermined by a low short circuit current. When 4% diiodooctane was used as an additive, a PCE increase to 2.62% was measured, accountable to improved film morphology for charge separation. When the device architecture was modified to enhance carrier extraction at the electrodes, the $\text{P(iI-DTS)}$:PC$_{70}$BM cells reached 4% PCE, one of the highest reported for isoindigo-based conjugated polymers.

4.6 Synthetic Details.

$\text{6,6' - dibromoisoindigo (4-1).}^{158}$ To a suspension of 6-bromoxindole (500 mg, 2.36 mmol) and 6-bromoisatin (533 mg, 2.36 mmol) in AcOH (15 mL), conc. HCl solution (0.1 mL) was added and heated under reflux for 24. The mixture was allowed to cool and filtered. The solid material was washed with water, EtOH and AcOEt. After drying under vacuum, it yielded brown $\text{6,6' - dibromoisoindigo}$ (951 mg, 95%). $^1$H-NMR
((CD₃)₂NCOD), DMF at 80°C) δ: 10.7 (bs, 2H), 9.14 (d, J = 8.7 Hz, 2H), 7.22-7.15 (m, 4H).\(^{13}\)C-NMR (CDCl₃) δ: 170.33, 147.25, 134.02, 132.36, 127.04, 125.35, 122.67, 113.93.

**6,6′-dibromo-N,N′-dihexyl-isoindigo (4-2).** Compound 4-1 (1.0 g, 2.38 mmol) was added in a dry flask, to which was added anhydrous DMF (20 mL). To the suspension was then added sodium hydride (0.24 g, 5.95 mmol) in one portion while stirring at room temperature. The reaction mixture turns blue-green after 5 minutes. This was allowed to stir for 30 minutes at room temperature under a flow of argon, after which n-hexylbromide (0.98 g, 5.95 mmol) was added to reaction using a syringe via a septum. The reaction mixture was then stirred at 80°C for 3 hours, upon which it turns bright red. It was then allowed to cool to room temperature, leading to the formation of bright red precipitates. This was poured in cold methanol (50 mL, -60°C), and the precipitates were filtered, to afford the title compound (1.33 g, 2.26 mmol, 95%) as bright red needles.\(^1\)H-NMR (CDCl₃) δ: 9.04 (d, J = 9 Hz, 2H), 7.14 (dd, J = 9 Hz, 1.8 Hz, 2H), 6.86 (d, J = 1.8 Hz, 2H), 3.71 (t, J = 7.2 Hz, 4H), 1.75-1.60 (m, 4H), 1.40-1.20 (m, 12H), 0.87 (t, J = 6.6 Hz, 6H); \(^{13}\)C-NMR (CDCl₃) δ: 167.94, 146.01, 132.91, 131.43, 127.06, 125.37, 120.60, 111.54, 40.53, 31.95, 29.22, 27.60, 22.87, 14.33. Anal. Calcd for C₂₈H₃₂Br₂N₂O₂: C, 57.16; H, 5.48; N, 4.76; Found: C, 57.07; H, 5.68; N, 4.65.

**6,6′-dibromo-N,N′-di(2-ethylhexyl)-isoindigo (4-3).**\(^{158}\) To a suspension of 6,6′-dibromoisoindigo (420 mg, 1 mmol) and potassium carbonate (829 mg, 5 mmol) in dimethylformaldehyde (DMF) (20 mL), 1-bromo-2-ethylhexane (425 g, 2.2 mmol) was injected through a septum under nitrogen. The mixture was stirred for 15 h at 100°C and then poured into water (200 mL). The organic phase was extracted by CH₂Cl₂, washed
with brine and dried over MgSO₄. After removal of the solvent under reduced pressure, the deep-red solids were purified by silica chromatography, eluting with (CH₂Cl₂: Hexane = 1:1) to give 6,6'-dibromo-N,N'-di(2-ethylhexyl)-isoindigo (548 mg, 85 %) 

\[ ^1H-\text{NMR (CDCl}_3\text{)} \delta: 9.00 (d, J = 8.7 Hz, 2H), 7.13 (dd, J = 8.7, 1.5 Hz, 2H), 6.81 (d, J = 1.5 Hz, 2H), 3.60-3.48 (m, 4H), 1.90-1.72 (m, 2H), 1.43-1.20 (m, 16H), 0.95-0.82 (m, 12H). \]

\[ ^{13}C-\text{NMR (CDCl}_3\text{)} \delta: 168.13, 146.24, 132.66, 131.22, 126.89, 125.20, 120.56, 111.66, 44.56, 37.63, 30.75, 28.72, 24.15, 23.21, 14.25, 10.87. \]


**6,6'-dibromo-N,N'-di(2-hexyldecyl)-dibromoisoindigo (4-4)** To a suspension of 6,6'-dibromoisoindigo (4.20 g, 10.0 mmol) and potassium carbonate (8.29 g, 60 mmol) in DMF (45 mL), 2-hexyl-bromodecane (9.16 g, 30 mmol) was injected through a septum under nitrogen. The mixture was stirred for 15 h at 100°C and then poured into water (200 mL). The organic phase was extracted by CH₂Cl₂, washed with brine and dried over MgSO₄. After removal of the solvent under reduced pressure, the dark red liquids were purified by silica chromatography, eluting with (CH₂Cl₂: Hexane = 1:2) to give 6,6'-dibromo-N,N'-di(2-hexyldecyl)-isoindigo (6.1 g, 70 %) as dark red solids. 

\[ ^1H-\text{NMR (CDCl}_3\text{)} \delta: 9.04 (d, J = 9 Hz, 2H), 7.14 (dd, J = 9 Hz, 1.8 Hz, 2H), 6.83 (d, J = 1.8 Hz, 2H), 3.56 (d, J = 7.5 Hz, 4H), 1.83 (bs, 2H), 1.40-1.24 (m, 48H), 0.88-0.84 (m, 12H); \]

\[ ^{13}C-\text{NMR (CDCl}_3\text{)} \delta: 168.25, 146.33, 132.65, 131.36, 126.92, 125.23, 120.64, 112.75, 44.91, 36.39, 32.10, 32.07, 31.75, 30.27, 29.87, 29.77, 29.59, 26.63, 22.89, 22.87, 14.34, 14.31. \]
6,6’-\(\text{N,N’-2-hexyldecyl}\)-pinacoldiboronisoindigo (4-5).\textsuperscript{201} 6,6’-\(\text{N,N’-2-hexyldecyl}\)-dibromoisoindigo (4.35 g, 5.0 mmol), pinacol ester of diboron (3.05 g, 12 mmol), \(\text{PdCl}_2\)(dpff) (220 mg), and potassium acetate (2.95 g, 30 mmol) were mixed at room temperature under an argon atmosphere. Anhydrous 1,4-dioxane (2 mL) was injected with a syringe through a septum. The solution was heated at 80°C for 30 h and then cooled to room temperature. The reaction mixture was filtered by passing through a short pad of silica gel, and washed by a mixture of methylene chloride and hexane (1:1). The collected filtration was concentrated and precipitated into cold methanol (100 mL). The precipitates was filtered and dried to give a dark red shiny powder (3.6 g, 75%).\textsuperscript{1}H-NMR (CDCl\textsubscript{3}) \(\delta\): 9.15 (d, \(J = 7.2\) Hz, 2H), 7.48 (d, \(J = 8.1\) Hz, 0.6 Hz, 2H), 7.15 (d, \(J = 0.6\) Hz, 2H), 3.69 (d, \(J = 7.5\) Hz, 2H), 1.95 (bs, 2H), 1.59-1.19 (m, 72H), 0.85 (t, \(J = 6.6\) Hz, 6H); \textsuperscript{13}C-NMR (CDCl\textsubscript{3}) \(\delta\): 168.35, 144.74, 134.51, 129.00, 128.96, 124.47, 113.73, 84.25, 44.62, 36.31, 32.16, 32.07, 31.83, 31.26, 29.84, 29.78, 29.51, 26.65, 25.10, 22.90, 22.88, 14.32, 14.30. HRMS (MALDI-TOF) Calculated for \(\text{C}_{60}\text{H}_{96}\text{B}_{2}\text{N}_{2}\text{O}_{6}\) (M+Na)\textsuperscript{+}: 963.7548 Found: \textit{m/z} 963.7583. Anal. Calcd for \(\text{C}_{60}\text{H}_{96}\text{B}_{2}\text{N}_{2}\text{O}_{6}\): C, 74.83; H,10.05; N,2.91. Found: C, 74.91; H,10.75; N, 2.80.

6,6’-\(\text{diphenyl-N,N’-dihexyl}-\text{isoindigo (P-il-P)}\). In a purged Schlenk flask, compound 4-2 (294 mg, 0.5 mmol), phenylboron pinacol ester (265 mg, 1.3 mmol), \(\text{Pd}_2\)(dba)\textsubscript{3} (18 mg, chloroform adduct) and \(\text{P(o-tyl)}_3\) (15 mg) were loaded under a flux of argon and then kept under vacuum for 30 minutes, during which the flask was subjected to three vacuum-argon purge cycles, and finally refilled with argon. Degassed toluene (5 mL) was then added to flask, followed by a degassed aqueous solution of tetraethylammonium hydroxide (1 mL, 1 mmol). The mixture was stirred and heated to
90°C for 12 hours. After cooling back to room temperature, the mixture was slowly poured in methanol (40 mL) and the precipitates were collected by filtration. The solids were purified by column chromatography using 2:1 hexanes:dichloromethane as eluent. This afforded the title compound (214 mg, 0.37 mmol, 74%) as a brown solid. $^1$H-NMR (CDCl$_3$) δ: 9.26 (d, J = 8.3 Hz, 1H), 7.65 (d, J = 7.3 Hz, 2H), 7.49 (t, J = 7.4 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 7.28 (dd, J = 4.2, 1.4 Hz, 1H), 6.98 (s, 1H), 3.83 (t, J = 7.4 Hz, 2H), 1.75 (quintet, J = 7.4 Hz, 2H), 1.44 (quintet, J = 7.4 Hz, 2H), 1.34 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H). $^{13}$C-NMR (CDCl$_3$) δ: 168.41, 145.51, 145.30, 140.78, 132.79, 130.50, 129.10, 128.37, 127.28, 121.14, 121.09, 106.59, 40.31, 31.74, 27.77, 26.96, 22.77, 14.24. Anal. Calcd for C$_{40}$H$_{42}$N$_2$O$_2$: C, 82.44; H, 7.26; N, 4.81. Found: C, 81.97; H, 7.98; N, 4.72.

6,6'-dithiophene-N,N'-dihexyl-isoindigo (T-il-T) In a dry Schlenk flask, compound 4-2 (294 mg, 0.5 mmol), Pd$_2$(dba)$_3$ (18 mg, chloroform adduct) and P(o-tyl)$_3$ (15 mg) were loaded under a flux of argon and then kept under vacuum for 30 minutes, during which the flask was subjected to three vacuum-argon purge cycles, and finally refilled with argon. Tributyl(thiophen-2-yl)stannane (485 mg, 1.3 mmol) was then added to the flask via syringe through a septum. Degassed toluene (5 mL) was then added to flask. The mixture was stirred and heated to 90°C for 12 hours. After cooling back to room temperature, the mixture was slowly poured in methanol (30 mL) and the precipitates were collected by filtration. The solids were dissolved in a minimum of a dichloromethane, and purified by column chromatography using 2:1 hexanes:dichloromethane as eluent. This afforded the title compound (280 mg, 0.47 mmol, 94%) as a dark dark brown solid. $^1$H-NMR (CDCl$_3$) δ: 9.17 (d, J = 8.3 Hz, 1H),
7.42 (dd, J = 1.7, 0.9 Hz, 1H), 7.36 (dd, J = 2.5, 0.9 Hz, 1H), 7.28 (dd, J = 4.2, 1.4 Hz, 1H), 7.12 (dd, J = 3.2, 3.7 Hz, 1H), 6.95 (s, 1H), 3.80 (t, J = 7.3 Hz, 2H), 1.72 (quintet, J = 7.3 Hz, 2H), 1.42 (m, 2H), 1.34 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H).

13C-NMR (CDCl3) δ:

6,6’-di(3,4-ethylenedioxythiophene)-N,N’-dihexyl-isoindigo (E-il-E) In a dry Schlenk flask, compound 4-2 (1.00 g, 1.7 mmol), Pd2(dba)3 (0.07 g, 80 μmol), P(o-tolyl)3 (0.05 g, 0.16 mmol), EDOT-SnMe3 (1.14 g, 3.7 mmol) were loaded under a flux of argon and then kept under vacuum for 30 minutes, during which the flask was subjected to three vacuum-argon purge cycles, and finally refilled with argon. The homogeneous dark brown solution was heated to 100−110°C and stirred overnight under argon atmosphere. The formed suspension was then evaporated to dryness, redissolved in chloroform and dry-packed over silica gel. This was purified by column chromatography using Hexanes/DCM gradients from 1:1 (1.5 L)→2:3 (1 L)→1:4 (rest of the column). Product containing fractions were combined and evaporated to dryness. The residual solid was suspended in MeOH at −60°C, filtered and washed with chilled MeOH (3×50 mL). After drying under vacuum in a dessicator overnight, brown powder was obtained (87% yield). m.p. > 200 °C; 1H NMR (CDCl3, 500 MHz) δ (ppm) 9.13−9.16 (d, J = 8.5 Hz, 2H), 7.32−7.36 (dd, J1 = 1.5 Hz, J2 = 8.5 Hz, 2H), 7.21−7.22 (d, J = 1.5 Hz, 2H), 6.38 (s, 2H), 4.26−4.37 (m, 8H), 3.78−3.83 (t, J = 7.5 Hz, 4H), 1.70−1.77 (quintet, J = 7.5 Hz, 4H), 1.30−1.45 (m, 12H), 0.86−0.91 (t, J = 7.0 Hz, 6H); 13C NMR (CDCl3, 125 MHz) δ (ppm) 14.36, 22.83, 27.07, 27.73, 31.71, 40.21, 64.69, 65.26, 99.57, 105.34,
HRMS (EI-DIP) [M+H]^+ 711.2557, calcd for [C_{40}H_{43}N_{2}O_{6}S_{2}]: 711.2563

**General procedure for Suzuki polycondensations: (P(iI-F), P(iI-OB) and P(iI-AT)).** In a 100 mL flame-dried Schlenk flask, the dibromoisoindigo monomer 4-3 (0.5 mmol, 1 equiv.), the bis(pinacolato)diboron comonomer (0.5 mmol, 1 equiv.), Pd_{2}(dba)_{3} (15 mg) and P(o-tyl)_{3} (10 mg) were subjected to three cycles of evacuation/argon purging, and then dissolved with 5 mL of degassed toluene after which 1.5 mL (1M) of degassed aqueous solution of Et_{4}NOH was added. The reaction mixture was stirred at 85°C for 36 hours under argon, and then cooled down to room temperature. The mixture was precipitated in 100 mL of methanol and filtered through a 0.45 μm nylon filter. The dark solids were purified using a Soxhlet apparatus with methanol until the extracts appeared colorless. The polymers were then fractionated in the Soxhlet apparatus using hexanes and chloroform fractions which contained varying amounts of polymer after complete extraction depending on the nature of the comonomer used. Concentration and reprecipitation in methanol allowed filtering the solids through a 0.45 μm nylon filter to afford the targeted polymer after complete drying in vacuo.

**Poly[9,9’-dihexyl-2,7-fluorene-alt-N,N’-(2-ethylhexyl)-6,6’-isoindigo], P(iI-F):**

The general Suzuki polymerization procedure was followed using 322 mg of compound 4-3 and 293 mg of 2,2’-(9,9-dihexyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) to afford a shiny brown solid. (466 mg, yield: 93%, chloroform fraction).

^{1}H NMR (300 MHz, CDCl_{3}, ppm): 9.40-9.30 (br, 2H), 7.90-7.80 (br, 2H), 7.70-7.60 (br, 4H), 7.45-7.35 (br, 2H), 7.10-7.05 (br, 2H), 4.00-3.50 (br, 4H), 2.15-1.90 (br, 2H), 1.65-1.30 (br, 16H), 1.10-1.05 (br, 20H), 1.05-0.95 (br, 6H), 0.95-0.80 (br, 6H), 0.80-0.70 (br,
6H). $M_n$: 21.2 kDa; PDI: 1.96. Anal. Calcd for C$_{57}$H$_{72}$N$_2$O$_2$: C, 83.78; H, 8.88; N, 3.43. Found: C, 82.72; H, 8.84; N, 3.42.

**Poly[2,5-dioctyloxy-1,4-phenyl-alt-N,N’-(2-ethylhexyl)-6,6’-isoindigo], P(il-OB):** The general Suzuki polymerization procedure was followed using 322 mg of compound 4-3 and 265 mg of 2,2’-(2,5-bis(octyloxy)-1,4-phenylene)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) to afford a dark brown fluffy solid. (116 mg, yield: 31%, hexanes fraction); (241 mg, yield: 63%, chloroform fraction). $^1$H NMR (300 MHz, CDCl$_3$, ppm): 9.30-9.20 (br, 2H), 7.35-7.25 (br, 2H), 7.20-7.15 (br, 2H), 7.10-7.05 (br, 2H), 4.05-3.90 (br, 4H), 3.85-3.65 (br, 4H), 1.95-1.85 (br, 2H), 1.85-1.65 (br, 4H), 1.40-1.20 (br, 32H), 1.00-0.75 (br, 18H). $M_n$: 10.5 kDa; PDI: 2.13. Anal. Calcd for C$_{50}$H$_{68}$N$_2$O$_4$: C, 78.91; H, 9.01; N, 3.68. Found: C, 78.97; H, 9.01; N, 3.57.

**Poly[3,4-dioctyl-2,5-thiophene-alt-N,N’-(2-ethylhexyl)-6,6’-isoindigo], P(il-AT):** The general Suzuki polymerization procedure was followed using 322 mg of compound 4-3 and 280 mg of 2,2’-(3,4-dioctylthiophene-2,5-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) to afford a dark brown fluffy powder. (109 mg, yield: 28%, hexanes fraction); (224 mg, yield: 57%, chloroform fraction). $^1$H NMR (300 MHz, CDCl$_3$, ppm): 9.35-8.90 (br, 2H), 7.40-7.10 (br, 2H), 7.10-6.75 (br, 2H), 3.90-3.45 (br, 4H), 3.05-2.50 (br, 4H), 2.05-1.80 (br, 2H), 1.80-1.15 (br, 40H), 1.15-0.75 (br, 12H), 0.75-0.45 (br, 6H). $M_n$: 16.7 kDa; PDI: 1.94. Anal. Calcd for C$_{52}$H$_{74}$N$_2$O$_2$S: C, 78.94; H, 9.43; N, 3.54. Found: C, 79.26; H, 9.45; N, 3.58.

**General procedure for Stille polycondensations:** P(il-T)-EH, P(il-T)-HD and P(il-ProDOT). The dibromoisoindigo monomer 4-3 (0.5 mmol, 1 equiv.), Pd$_2$(dba)$_3$ (15 mg) and P(o-tyl)$_3$ (10 mg) were added to a flame-dried Schlenk flask which was
evacuated and backfilled with argon three times. The bis(trimethylstannyl) comonomer (0.5 mmol, 1 equiv.) was dissolved in a dried separate vial in 5 mL of toluene, subsequently degassed with argon for one hour. The solution was then added to the Schlenk flask and the reaction mixture was stirred at 85°C for 36 hours. The mixture was precipitated in 100 mL of methanol and filtered through a 0.45 μm nylon filter. The dark solids were purified using a Soxhlet apparatus with methanol until the extracts appeared colorless. The polymers were then fractionated in the Soxhlet apparatus using hexanes and chloroform fractions which contained varying amounts of polymer after complete extraction depending on the nature of comonomer used. Concentration and reprecipitation in methanol allowed filtering the solids through a 0.45 μm nylon filter to afford the targeted polymer after complete drying in vacuo.

**Poly[2,5-thiophene-alt-N,N'-(2-ethylhexyl)-6,6'-isoindigo], P(ii-T)-EH:** The general procedure for Stille polymerization was followed using 322 mg of compound 4-3 and 205 mg of 2,5-bis(trimethylstannyl)thiophene to afford a deep blue solid after extraction. (120 mg, yield: 42%, chloroform fraction) ¹H NMR (300 MHz, CDCl₃, ppm):

9.20-8.90 (br, 2H), 7.30-7.15 (br, 2H), 7.15-6.90 (br, 2H), 6.75-6.60 (br, 2H), 3.75-3.45 (br, 4H), 1.95-1.70 (br, 2H), 1.55-1.20 (br, 16H), 1.20-0.80 (br, 12H). Mₙ: 2.4 kDa; PDI: 1.13. Anal. Calcd for C₃₆H₄₂N₂O₂S: C, 76.29; H, 7.47; N, 4.94. Found: C, 75.88; H, 7.31; N, 4.75.

**Poly[2,5-thiophene-alt-N,N'-(2-ethylhexyl)-6,6'-isoindigo], P(ii-T)-HD:** The general procedure for Stille polymerization was followed using 424 mg of compound 4-4 and 205 mg of 2,5-bis(trimethylstannyl)thiophene to afford a dark blue solid after extraction. (294 mg, yield: 74%, chloroform fraction) ¹H NMR (300 MHz, CDCl₃, ppm):
9.20-8.90 (br, 2H), 7.30-7.15 (br, 2H), 7.15-6.90 (br, 2H), 6.75-6.60 (br, 2H), 3.75-3.45 (br, 4H), 1.95-1.70 (br, 2H), 1.60-0.65 (m, 56H). Mₙ: 19.9 kDa; PDI: 2.5.

**Poly[2,5-propylenedioxythiophene-alt-N,N’-(2-ethylhexyl)-6,6’-isoindigo], P(ili-ProDOT):** The general procedure for Stille polymerization was followed using 322 mg of compound 4-3 and 383 mg of (3,3-bis(((2-ethylhexyl)oxy)methyl)-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine-6,8-diyl)bis(trimethylstannane) to afford a dark blue solid. (290 mg, yield: 63%, hexanes fraction); (161 mg, yield: 34%, chloroform fraction). ¹H NMR (300 MHz, CDCl₃, ppm): 9.20-9.05 (br, 2H), 7.45-7.35 (br, 2H), 7.35-7.25 (br, 2H), 4.30-4.15 (br, 4H), 3.65-3.50 (br, 4H), 3.55-3.45 (br, 4H), 3.45-3.25 (br, 4H), 1.95-1.75 (br, 4H), 1.50-1.20 (br, 32H), 1.05-0.80 (br, 24H). Mₙ: 19.3 kDa; PDI: 1.70. Anal. Calcd for C₅₇H₈₂N₂O₆S: C, 74.15; H, 8.95; N, 3.03. Found: C, 73.65; H, 8.65; N, 3.10.

**Poly[N,N’-(2-hexyldecy1)-6,6’-isoindigo], Poly(iii).** In a flame-dried Schlenk flask (50 mL), 4-4 (434.45 mg, 0.5 mmol) and 4-5 (481.52 mg, 0.5 mmol), Pd₂(dba)₃·CHCl₃ (18 mg) and P(o-tyl)₃ (12 mg) were added. The flask was evacuated and back-filled with argon three times, after which degassed toluene (15 mL) and tetraethylammonium hydroxide (3 mmol, 1M) was transferred to the mixture through a septum. The resulting solution was heated up to 85°C under argon and stirred for 36 h. The mixture was cooled to room temperature and poured slowly in methanol (300 mL). The precipitates were collected through a 0.45 μm PTFE filter. The crude polymer (711 mg of dark solids) was purified with Soxhlet extraction with methanol, hexane to remove low molecular species and catalyst residues. From the hexanes fraction, 150 mg of lower molecular weight species were collected. Last, the higher molecular weight fraction was extracted with chloroform, to which diethylammonium
diethyldithiocarbamate (as palladium scavenger, ~30 mg) was subsequently added in one portion. The latter mixture was then stirred for two hours at room temperature, and then poured slowly in methanol (300mL). The precipitates were filtered and dissolved in a minimum amount of chloroform, and precipitated a second time in methanol (100mL). The precipitates were collected via vacuum filtration through a 0.45 μm PTFE filter and dried, yielding dark blue solids (523 mg, 74%). \(^1\)H-NMR (CDCl\(_3\)) \(\delta\): 8.98-8.70 (M, 2H), 7.40-6.80 (m, 4H), 3.60-3.25 (m, 4H), 2.20-0.60 (m, 62H). GPC: \(M_n = 28.7\) kDa, PDI = 2.4. Anal. Calcd for \(C_{48}H_{72}N_2O_2\): C, 81.30; H,10.23; N,3.95. Found: C, 80.47; H, 10.52; N, 3.84.

**Poly[2,1,3-benzothiadiazole-alt-N,N’-(2-ethylhexyl)-6,6’-isoindigo], Poly(il-BTD).** In a flame-dried Schlenk flask (50 mL), 4,7-dibromobenzothiadiazole (73.49 mg, 0.25 mmol) and 4-5 (240.76 mg, 0.25 mmol), \(\text{Pd}_2\text{(dba)}_3\)-CHCl\(_3\) (9 mg) and \(\text{P(o-tyl)}_3\) (6 mg) were added. The flask was evacuated and back-filled with argon three times, after which degassed toluene (15 mL) and tetraethylammonium hydroxide (2 mmol, 1M) was transferred to the mixture through a septum. The resulting solution was heated up to 85°C under argon and stirred for 36 h. The mixture was cooled to room temperature and poured slowly in methanol (300 mL). The precipitates were collected through a 0.45 μm PTFE filter. The crude polymer (220 mg of dark solids) was purified with Soxhlet extraction with methanol to remove catalyst residues. The polymer was extracted with chloroform, to which fraction diethylammonium diethyldithiocarbamate (as palladium scavenger, ~20 mg) was added in one portion. The mixture was stirred for two hours at room temperature, and then poured slowly in methanol (300mL). The precipitates were filtered and dissolved in a minimum amount of chloroform, and precipitated a second
time in methanol (100mL). The precipitates were collected via vacuum filtration through a 0.45 μm PTFE filter and dried, yielding dark brown solids (202 mg, 95%). $^1$H-NMR (CDCl$_3$) δ: 9.42-8.95 (m, 2H), 7.78-5.98 (m, 8H), 3.60-3.20 (m, 4H), 2.20-0.45 (m, 62H). GPC: $M_n = 16.3$ kDa, PDI = 3.5. Calcd for C$_{54}$H$_{74}$N$_4$O$_2$S: C, 76.91; H, 8.85; N, 6.64. Found: C, 76.55; H, 8.86; N, 6.30.

**Poly[5,5'(4,4'-bis-(2-ethylhexyl)-dithieno[3,2-b:2',3'-d]silole)-alt-6,6'-N,N'-(2-ethylhexyl)-isoindigo], P(ii-DTS).** The faint yellow oil 2,2′-bistrimethylstannyl-4,4′-bis-(2-ethylhexyl)-dithieno[3,2-b:2',3'-d]silole$_{ref}$ was added in a tared clean glass vial, which was kept under vacuum. The oil, weighing 381.6 mg (0.510 mmol) once dry, was then diluted in 1 mL of hexanes and transferred to a dry Schlenk flask equipped with a stir bar. The dilution/transfer of 2 was repeated four times so that the compound was completely transferred to the reaction Schlenk flask, as a total of 5 mL of hexanes solution. The hexanes were then evaporated carefully under vacuum for 2 hours at room temperature. After refilling the reaction flask with argon, 6,6'-dibromo-N,N'- (2-ethylhexyl)-isoindigo (monomer 4-3, 330.4 mg, 0.510 mmol), Pd$_2$(dba)$_3$ (chloroform adduct, 15 mg, 0.015 mmol) and P(o-tyl)$_3$ (10 mg, 0.03 mmol) were added to the flask and purged with 3 vacuum/argon refill cycles. Degassed toluene (5 mL, 5 freeze-pump-thaw cycles prior to addition) was then added to the flask and the reaction medium was stirred and heated to 85°C under argon. The reaction medium viscosity had notably increased after 12 hours at 85°C, and was left to stir for an additional 2 days at 85°C after which the temperature was increased to 100°C for 2 hours. After the reaction medium was cooled back to 85°C, a solution of 2-bromothiophene (0.2 mmol) in degassed toluene (2 mL) was added to the flask along with a small amount of the
catalytic system and allowed to react for 6 hours. A solution of 2-(tributylstanny)-thiophene (0.2 mmol) in degassed toluene (2 mL) was subsequently added to the flask and allowed to react for 12 hours. At this point, the reaction medium was then cooled to 60°C and a spatula tip of diethylammonium diethyldithiocarbamate was added to the flask. After 2 hours of stirring at 60°C, the reaction medium was precipitated into methanol (200 mL). The precipitates were filtered and collected into a cellulose thimble, then purified in a Soxhlet apparatus using methanol (1 day), hexanes (12 hours) and chloroform (2 hours). The methanol and hexanes fractions were discarded, while the chloroform fraction was precipitated into methanol (200 mL). The precipitates were collected and dried to afford 445 mg of dark purple solids (0.494, 97%). GPC: Mn = 36,000 kDa; Mw = 99,600; PDI = 2.77. 

$^1$H-NMR (CDCl$_3$) δ: 9.4-8.8 ppm (br, 2H), 7.8-7.0 (br, 4H), 6.8-6.2 (br, 2H), 4.0-3.6 (br, 4H), 2.0-1.0 (br, 40H), 1.0-0.6 (br, 24H). Elemental Analysis Calc. for C$_{56}$H$_{76}$O$_2$S$_2$Si: C, 74.61; H, 8.50; N, 3.11. Found: C, 74.22; H, 8.61; N, 3.02.
CHAPTER 5
CONCLUSIONS AND PERSPECTIVES

Over the past 30 years of research on conjugated systems for organic electronics, several parameters have stood out as key to making a conjugated organic material part of efficient opto-electronic devices. This dissertation has illustrated how a synthetic chemist might contribute to the field, first by designing compounds which provide some degree of morphological control in the devices. Chapter 3 introduced three of such approaches. In the first one, a linear alternating aliphatic/chromophoric polymer was shown to retain electroactivity despite the inherent conjugation break in its backbone. It was observed to adopt some degree of ordering in the bulk, which could be further induced by mechanical stress. Another approach consisted in covalently binding organic conjugated oligomers onto inorganic nanocrystals to create electro-active hybrid materials. This was achieved thanks to the design of unsymmetrical oligomers bearing one reactive end-group. Their interaction with the nanocrystals was demonstrated, which led to the synthesis of the organic/inorganic complexes where a significant amount of oligomers were bound to the inorganic nanocrystals surface. One last approach dealt with the control of the crystallinity of molecular solar cells’ active layer. This was enabled via the synthesis of symmetrical and unsymmetrical oligomers based on the same chromophore, which were shown to have different solid state optical properties and morphological behavior, depending on the molecular structure. The use of an unsymmetrical oligomer as an additive to molecular solar cells was beneficial to the morphology of the active layer, leading to increased efficiencies.

With the development of isoindigo-based materials, access to conjugated oligomers and polymers with deep energy levels and low bandgaps was presented in
Chapter 4. The synthesis of donor-acceptor polymers showed the ability of isoindigo as an acceptor to extend the absorption of the materials towards the near-IR. Conjugated polymers with all-acceptor backbones were also presented, and spectroelectrochemical measurements gave insight on their n-type character. The homopolymer of isoindigo was used as an n-type material in all-polymer solar cells, with encouraging results. Efficient polymer/PCBM solar cells were also shown to be possible with isoindigo-based donor-acceptor polymers: the copolymer of isoindigo and dithienosilole demonstrated solar cell efficiencies up 4% when used with heterojunction with PC$_{70}$BM.

As a chemist, I believe that organic electronics have a bright future. The wide variety of synthetic tools available to tune the properties of the organic materials it relies on is far from being depleted. It is also a research field which brings together chemists, materials scientists and physicists in such an enthused and competitive way that it can only move forward faster and faster. Such collaborations can help to pinpoint the critical enhancement to be carried out, which sometimes leads to great success. They also lead to new, simple ideas. And sometimes, simple works. One should not forget the main strength of organic electronics: their low-cost. Parallel to the understanding of the materials and devices fundamental properties, the field is now also moving toward taking the technology to the production scale, which is a good indication of its success.
APPENDIX
CRYSTALLOGRAPHIC DATA

Table A-1. Crystal data and structure refinement for T6-benzoate 3-9.

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<td>Formula weight</td>
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<td></td>
<td>b = 17.200(3) Å, β = 95.279(3)°.</td>
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<td></td>
<td>c = 22.169(4) Å, γ = 116.120(4)°.</td>
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</tr>
<tr>
<td>Crystal size</td>
<td>0.17 x 0.11 x 0.05 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.35 to 22.50°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-18≤h≤18, -18≤k≤15, -20≤l≤23</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>26182</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>14855 [R(int) = 0.0846]</td>
</tr>
<tr>
<td>Completeness to theta = 22.50°</td>
<td>100.0 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Integration</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9858 and 0.9528</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>14855 / 15 / 1280</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.025</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0903, wR2 = 0.1578 [6973]</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.1928, wR2 = 0.1970</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.392 and -0.474 e.Å⁻³</td>
</tr>
</tbody>
</table>

\[
R1 = \frac{\sum(||F_o|| - |F_c||)}{\sum|F_o|} \quad wR2 = \frac{\sum[w(F_o^2 - F_c^2)^2]}{\sum[w(F_o^2)^2]}^{1/2}
\]
\[
S = \left[\frac{\sum[w(F_o^2 - F_c^2)^2]}{\sum w} \right]^{1/2}
\]
\[
w = \frac{1}{[\sigma^2(F_o^2) + (m*p)^2 + n*p]} \quad p = [\text{max}(F_o^2,0) + 2* F_c^2]/3, m & n \text{ are constants.}
\]
Table A-2. Crystal data and structure refinement for T-il-T.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C36 H38 N2 O2 S2</td>
</tr>
<tr>
<td>Formula weight</td>
<td>594.80</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C2/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>a = 23.7346(5) Å</td>
<td>α = 90°</td>
</tr>
<tr>
<td>b = 9.4569(2) Å</td>
<td>β = 123.740(1)°</td>
</tr>
<tr>
<td>c = 15.8426(4) Å</td>
<td>γ = 90°</td>
</tr>
<tr>
<td>Volume</td>
<td>2957.02(12) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.336 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.217 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>1264</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.31 x 0.16 x 0.04 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.06 to 27.50°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-30≤h≤30, -11≤k≤12, -20≤l≤20</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>16335</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>3400 [R(int) = 0.0514]</td>
</tr>
<tr>
<td>Completeness to theta = 27.50°</td>
<td>100.0 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Numerical</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9918 and 0.9349</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>3400 / 0 / 195</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.077</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0353, wR2 = 0.0928 [2694]</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0481, wR2 = 0.0987</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.366 and -0.271 e.Å⁻³</td>
</tr>
</tbody>
</table>

R1 = \[ \frac{\sum(|F_o| - |F_c|)}{\sum|F_o|} \]  
W = \[ \frac{\sum[w(F_o^2 - F_c^2)^2]}{\sum[w(F_o^2)^2]} \]^{1/2}  
S = \[ \frac{\sum[w(F_o^2 - F_c^2)^2]}{(n-p)} \]^{1/2}  

w = 1/[σ²(Fo²)+(m*²p)²+n*²p], p = [max(Fo²,0)+ 2* Fc²]/3, m & n are constants.
Table A-3. Crystal data and structure refinement for P-Il-P.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C40 H42 N2 O2</td>
</tr>
<tr>
<td>Formula weight</td>
<td>582.76</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 7.9552(3) Å, α = 69.237(2)°.</td>
</tr>
<tr>
<td></td>
<td>b = 10.0864(4) Å, β = 77.021(2)°.</td>
</tr>
<tr>
<td></td>
<td>c = 10.7629(4) Å, γ = 74.620(2)°.</td>
</tr>
<tr>
<td>Volume</td>
<td>770.39(5) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>1</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.256 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.077 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>312</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.27 x 0.25 x 0.19 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.05 to 27.50°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-10 ≤ h ≤ 10, -13 ≤ k ≤ 13, -13 ≤ l ≤ 13</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>18073</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>3547 [R(int) = 0.0438]</td>
</tr>
<tr>
<td>Completeness to theta = 27.50°</td>
<td>100.0 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Numerical</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9853 and 0.9796</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>3547 / 0 / 200</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.063</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0348, wR2 = 0.0915 [3099]</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0403, wR2 = 0.0956</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.345 and -0.186 e.Å⁻³</td>
</tr>
</tbody>
</table>

\[
R1 = \frac{\sum(||F_o|-|F_c||)}{\sum|F_o|}, \quad wR2 = \sqrt{\frac{\sum[w(F_o^2 - F_c^2)^2]}{\sum[w(F_c^2)^2]}}^{1/2} \\
S = \sqrt{\frac{\sum[w(F_o^2 - F_c^2)^2]}{(n-p)}}^{1/2} \\
w = \frac{1}{[\sigma^2(F_o^2)+(m*p)^2+n*p]}, \quad p = [\max(F_o^2,0)+2*F_c^2]/3, \quad m \& n \text{ are constants.}
\]
LIST OF REFERENCES


(190) Stalder, R.; Estrada, L. A.; Reynolds, J. R. *Work in Progress*.


BIOGRAPHICAL SKETCH

Romain Stalder was born in April of 1984, in Saint-Avold, France. His parents, both teachers, were hired by the Michelin tire company in 1986 to become expatriate teachers for Michelin personnel’s children in small schools abroad. Romain thus became an expatriate at the age of two, living for two years in Campo Grande, Brazil; followed by two years in Pusan, South Korea; five years in Pattaya, Thailand; and four years in Ashikaga, Japan. When he was fourteen years old, his family settled back to France, where he was able to (re)discover his native country and begin high school in the Lycee Berthollet of Annecy. After obtaining his baccalaureat in science, Romain remained in Annecy to study advanced topics in maths, physics and chemistry in the classes preparatoires of the Lycee Berthollet. The Concours aux Grandes Ecoles gave him access to the Graduate School of Physics and Chemistry of Bordeaux (ENSCBP), France. He spent two years in Bordeaux learning the principles of chemical engineering, for which he obtained his Masters in Chemical Engineering. He then joined the chemistry graduate school at the University of Florida (UF) in Gainesville, Florida. At UF Romain joined the group of Professor John Reynolds, working in the area of organic chemistry, synthesizing conjugated molecules and polymers for charge transport and organic solar cell applications, which resulted in the present dissertation. Romain received his Ph.D from the University of Florida in the spring of 2012.