METHODOLOGIES FOR THE SYNTHESIS OF 3,4-DIOXYPYRROLE-BASED π-CONJUGATED MATERIALS

By

FRANK ANTONIO ARROYAVE MONDRAGON

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

2011

To my wife and my family

ACKNOWLEDGMENTS

I would like to thank my advisor Prof. John R. Reynolds, for giving me the opportunity to join his research group, and also for his teachings about science, writing and life. He gave me the support, tools and freedom to continue developing my scientific thinking and also allowed me to freely pursue and get involved in various aspects of organic synthesis and polymer science. I can sincerely say that he is the Ph. D. advisor that every graduate student should have.

I would like to thank all the professors who have contributed to my scientific education at the University of Florida. In particular, Professor Ken Wagener, who through his lectures showed me a new level of polymer science.

I would like to thank Drs. Svetlana Vasilyeva, and Aubrey Dyer for their teachings and help in electrochemistry, and Drs. Mike Craig, Leandro Estrada, Dan Patel, Chad Amb, Ryan Walczak, Ken Graham, Eric Shen and David Liu for sharing their knowledge through very useful scientific discussions. Thanks to Coralie Richard for listening and carrying out my crazy ideas, which in many cases turned out not to be crazy at all. Also, I would like to thank all the Butler lab and Reynolds group members who have made the lab a pleasant and dynamic place to work.

I would like to thank Giovanni Rojas and Mariela Rodriguez, Fabio Zuluaga, Paula Delgado, and Henry Martinez for their friendship.

I would like to thank my wife and my family for their unconditional support and love, since they are the motivation behind my personal and professional achievements. And finally, thanks God for making everything possible.

TABLE OF CONTENTS

page

LIST OF TABLES

LIST OF FIGURES

LIST OF SCHEMES

Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

METHODOLOGIES FOR THE SYNTHESIS OF 3,4-DIOXYPYRROLE-BASED π-CONJUGATED MATERIALS

By

Frank A. Arroyave

December 2011

Chair: John R. Reynolds
Major: Chemistry

Organic π-conjugated polymers are attractive due to a combination of their electronic properties, relatively low cost production and processability. Due to these features, π-conjugated materials are envisioned to replace many inorganic materials in various applications. Synthetic methodology plays an important role in the development and understanding of π-conjugated polymers by allowing the construction of new materials with diverse electronic properties, higher molecular weights and purities. The work presented herein focuses on developing new chemistries for the synthesis of novel π-conjugated materials—oligomers and polymers—based on the electron rich heterocycle 3,4-dioxypyrrole (XDOP). The work presented in Chapter 2 and 3 describes the efforts to synthesize 3,4-dioxypyrrole-based π-conjugated molecules, by taking advantage of the inherent ability of 3,4-dioxypyrroles to undergo decarboxylation. Chapter 2 describes how various π-conjugated molecules based on XDOPs were synthesized *via* Pd-mediated decarboxylative cross coupling. The optimization of the experimental conditions lead to an efficient cross-coupling reaction for *N*-alkyl-3,4-

propylenedioxypyrroles (ProDOPs), and acceptable to high reaction yields were observed for various ProDOP carboxylates and aryl bromides that were employed.

Chapter 3 describes an alternative synthetic methodology towards *N*-functionalized poly-XDOPs. The method was modified from the previously reported route by Walczak and coworkers. This reaction, a deiodination polycondensation, proved to be a convenient and efficient polymerization procedure for the synthesis of ProDOP-based polymers and oligomers.

Chapter 4 describes the synthesis of fused-aromatic diketones and how these molecules can be employed to generate a wide variety of monomers—both donors and acceptors—as potential precursors for the synthesis of new π-conjugated materials. This work is significant given that access to novel donor and acceptor molecules is vital to generate new π-conjugated materials with improved physical and electronic properties.

CHAPTER 1
INTRODUCTION

Conjugated Polymers: History, Synthesis, Properties and Applications

Brief History of Conjugated Polymers

The first synthetic appearance of a π-conjugated polymer in a laboratory can be traced to the 19th century. Interestingly at that time, scientists did not know about the existence of polymers or macromolecules and the general knowledge of organic chemistry was quite limited. Three of the most important representatives of these materials, polyaniline (PANI), polypyrrole (PPy), and polyacetylene, shown in Figure 1-1, were the first conjugated polymers to be synthesized. In 1862 Henry Letheby reported the anodic polymerization and the electrochromic properties of polyaniline—a blue electrochromic material;[1] a similar observation was previously made, under chemical oxidation in acidic media, by Runge in 1834 and Fritzsche in 1840.[2]

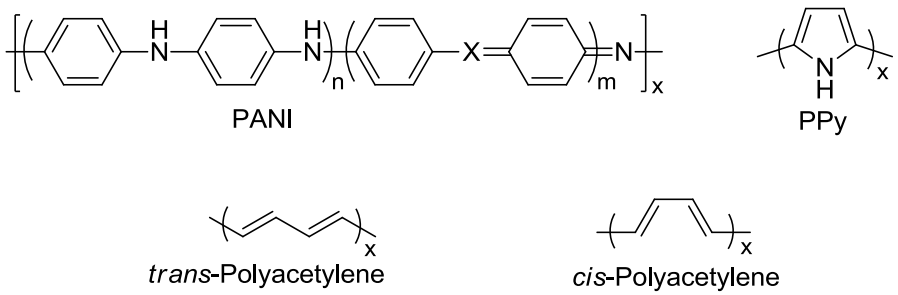


Figure 1-1. Chemical structures for polyaniline (PANI), polypyrrole (PPy), and polyacetylene (*cis*- and *trans*-).

In 1963, Weiss and coworkers reported the synthesis of iodide-doped polypyrrole prepared *via* deiodo-polycondensation. The material produced by this method had conductivities of ~1 S/cm,[3-5] and in 1968, Dall'Olio *et al.* also reported the synthesis of "pyrrole black", as polypyrrole was called at that time, *via* electrolysis of pyrrole in dilute sulfuric acid.[6] Unfortunately, Weiss' and Dall'olio's reports on conducting polypyrrole remained unnoticed for several decades. Polyacetylene, on the other hand, had a more

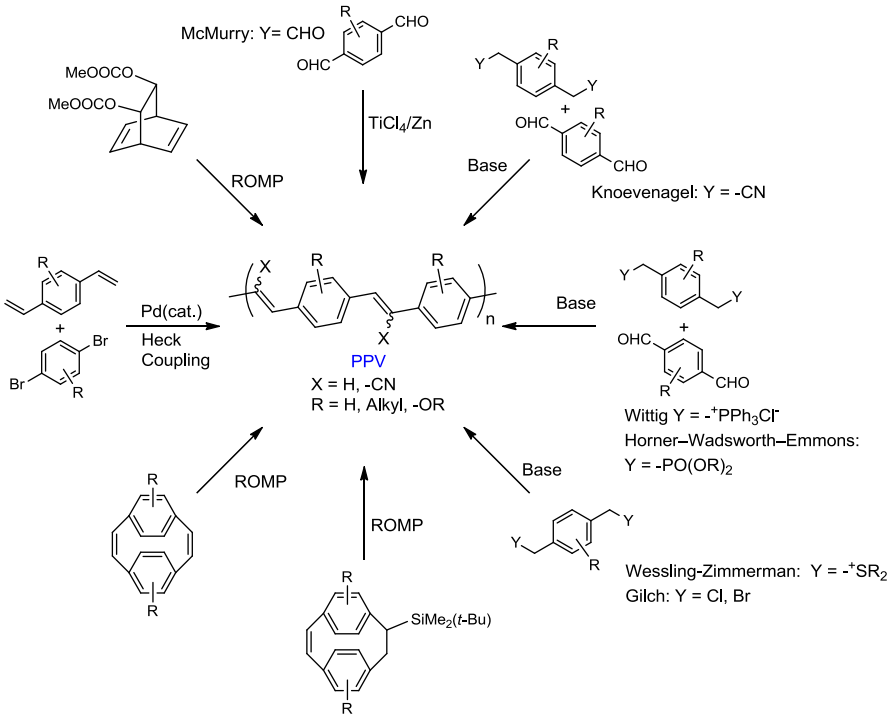
fruitful history: in 1953 and 1954 Ziegler and Natta developed new organometallic catalytic systems for the polymerization of polyolefins. This method had a high impact on polymer science and industry, culminating with Ziegler and Natta being awarded the Nobel prize in Chemistry in 1963.[7-9] Natta and co-workers used this methodology in 1958 to prepare polyacetylene (a semiconductor),[10] and this methodology was further exploited by several research groups in the area of materials sciences.[11-13] In 1977 Shirakawa, Heeger and MacDiarmid collaborated to prepare and study polyacetylene by using the Ziegler-Natta methodology and their knowledge about the doping of semiconductors, obtaining high conductivities (~10^3 S/cm) on halogen-doped polyacetylene.[14] This achievement was a significant breakthrough which launched the field of conducting polymers.[15] So far, due to its low stability and processability, polyacetylene has yet to find practical applicability. Nevertheless, polyacetylene laid the groundwork for the study and understanding of conjugated polymers, and the basic polyacetylene structure is a common motif in many polymers today.[16]

Syntheses of Conjugated Polymers

Synthetic methodology has played an important role in the development of π-conjugated polymers; in fact, the understanding of π-conjugated polymers has advanced in parallel with new methods of synthesis, which have allowed the construction of materials with higher molecular weights and purities. Pyrolysis and chemical or electrochemical oxidation were commonly used by researchers during the initial efforts to produce conjugated polymers. Unfortunately, these methods often produced insoluble products, and it was not possible to obtain reliable structural information about the polymers. New synthetic developments led to numerous methods

to produce conjugated polymers, not only with the desired physical and electronic features but also with high processability.

Chemical or electrochemical oxidation is still used for the synthesis of various conjugated polymers, but this methodology is mainly restricted to a few monomers and commonly only used to acquire preliminary data on a specific conjugated monomer or polymer. In many cases, chemical or electrochemical oxidation has been replaced by other synthetic methods, in particular organometallic cross couplings, possessing a broader scope. In general, the methodology to be utilized depends on the polymeric systems being synthesized.



Scheme 1-1. Various synthetic routes toward poly(*p*-phenylene vinylene), PPV.

A clear example of the different strategies employed to synthesize a particular type of polymer is shown in Scheme 1-1. This scheme shows various methods employed to produce poly(*p*-phenylene vinylene), PPV, a material studied for various applications, such as light-emitting diodes (LED) and photovoltaic devices.[17,18] The most common

pathways towards the synthesis of PPVs involve the reaction of a functionalized *para*-xylene derivative with base to generate a quinodimethane intermediate, which then polymerizes to form a *pre*-polymer. Typically, the *pre*-polymer is then transformed into PPV by heating under reduced pressure. The predominant quinodimethane routes include Wessling-Zimmerman, Vanderzande, and Gilch.[17,18] The Wessling-Zimmerman method uses sulfonium salts as leaving groups; due to the unpleasant odors however, as well as the toxic byproducts, this route is typically avoided. The Vanderzande group developed a variant of the Wessling-Zimmerman method (not shown in Scheme 1-1). This method combines a halide with a sulfinyl leaving group (Y = Cl and -SOR) in the same molecule. Although, the monomer synthesis is longer and less efficient than in the Wessling-Zimmerman method, this method produces higher quality PPVs. Another method is the Gilch route, which makes use of halide leaving groups. This method is now the most widely used for making soluble PPVs. In this case, it is also possible to isolate the halide precursor (*pre*-polymer) to convert it to the final conjugated material by thermal treatment under vacuum or using an excess of base.

The quinodimethane methods described can be only employed for making homopolymers or random copolymers. There are direct routes that allow the synthesis of copolymers with two different alternating arylene moieties, and these direct routes avoid the formation of defects that are frequently seen in the quinodimethane routes. Molecular weights obtained by these direct routes are typically lower than those obtained by the *pre*-polymer routes. Direct routes include Schrock metathesis (ROMP), Heck coupling, and McMurry, Knoevenagel, Wittig and Horner polycondensations, shown in Scheme 1-1.

The physical and electronic properties of PPV-based materials depend highly on the stereochemistry of the double bonds (*cis*- or *trans*-), and the R and X groups. In some cases the final conjugated polymer has limited solubility, but since some of these methods produce *pre*-polymers that have higher solubility than the final PPV, processing of the pre-polymer circumvents the need to handle PPV. It is noteworthy that PPVs can be seen as polyacetylene derivatives since they contain the basic polyacetylenic structure in their backbones. Thus, PPVs contain many of the same attractive electronic properties as polyacetylene while also having considerably higher stability and processability.

Properties and Applications of Conjugated Polymers

Many uses have been envisioned for conjugated polymers, especially since the discovery of their conducting properties, particularly as materials that could potentially replace inorganic materials in various electronic applications. Two of the most attractive characteristics of π-conjugated polymers are their relatively low production costs and their processability. Some of the applications that have been envisioned for conjugated polymers include solar cells, thermoelectrics, electrodes, displays, supercapacitors, batteries, sensors, and antistatic agents. The applications of a particular polymer depend on various factors, such as electronic band gap, conductivity, HOMO and LUMO energy levels, processability and stability among others.[16]

Typically, conjugated polymers are insulators or semiconductors with low conductivities, and an intrinsically organic conducting π-conjugated polymer has not yet been developed. The semiconductor behavior comes from the separation between the valence band (VB) and the conduction band (CB), which is too big to allow the

movement of electrons from one band to another. All the polymers shown in Figure 1-1 are semiconductors, but once the conjugated polymers are doped—typically by removal of electrons using an oxidizing agent, such as iodine—the conductivities can dramatically increase up to several hundreds S/cm (up to several kS/cm for polyacetylene), and in some cases, with values comparable to the conductivity in metals. Band gaps (E_g), which is the energy difference between the valence band (VB) and the conduction band (CB), in polymers depend heavily on the physical and electronic properties of the polymer backbone, as well as the degree of polymerization (X_n), which is the number of repeat units in the polymers.

The evolution of the band gap (E_g) with increasing X_n and the effects of chemical doping in polypyrrole are shown in Figure 1-2**.** Figure 1-2 (left) shows how the π-orbitals in polypyrrole evolve as the number of monomeric units in the chain increases. As X_n increases to an effective conjugation length (not necessarily to ∞), the π-orbital distribution gap reaches a threshold value called the band gap (E_g). Typically, band gaps for organic π-conjugated polymers fall between 1 – 3 eV, and although there is a high electron delocalization due to the long π-conjugated system, the difference in energy between the VB and the CB (E_g) is too high and does not allow the material to behave as a conducting material—i. e. the thermal energy is not enough to move an electron from the VB to the CB; therefore, these materials behave as semiconductors. The main reason why the E_g of organic π-conjugated material does not reach values close to zero as X_n tends to ∞ is due to the bond length alternation in the polymer backbone, also known as Peierls distortion,[19] which states that 1D lattices with ½-filled (and indeed, $1/n$-filled) bands are susceptible to distort in a way that permits the opening

of a gap at the Fermi energy level, resulting in a decrease in the energy of the system and an increase in the stability of the system. π-Conjugated organic materials can be seen as quasi-one-dimensional periodic lattices, and therefore are susceptible to Peierls distortion.

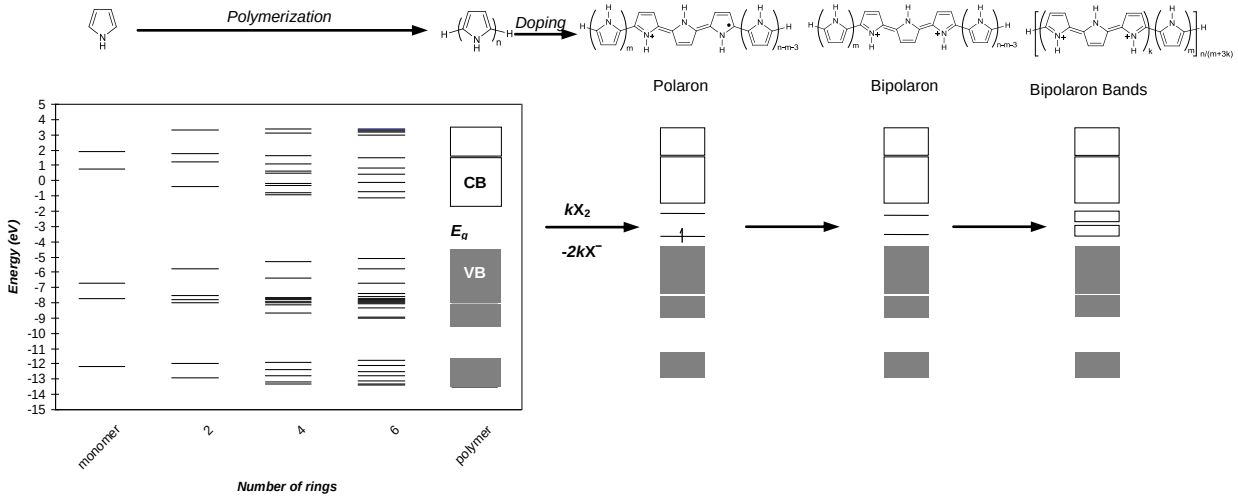


Figure 1-2. Evolution of the energy band gap in polypyrrole, from the monomer to the polymer (left), and from the neutral polymer to the p-doped polymer (right). For clarity purposes electrons in the VB were omitted, and counter ions are not shown in the doped polymers. Adapted from: Synthetic Metals 1998, 96, 177-189,[20] and Phys. Rev. B 1982, 26, 5843.[21]

To illustrate how polarons and bipolarons are formed in conjugated polymers, we can consider an example of a film of poly-pyrrole in the presence of an oxidant such as iodine, represented as X_2 in Figure 1-2. As the doping process starts, one or more electrons are extracted from the π-conjugated polymer, which generates a radical cation, called a polaron (see Figure 1-2). In a polaron, the radical and the cation are paired by resonance, and two new energy levels are generated in the gap (SOMO and LUMO), with one of these energy levels occupied by an unpaired electron (SOMO).[21,22] Two polarons can combine to form a bipolaron, with the two radical species forming a double bond, leaving behind two cations; these two cations are also associated by

resonance, and the separation between them can vary depending on the π-conjugated polymer, typically, 3 – 5 rings for polypyrrole. Upon increase the doping level, new bipolarons are formed in the same polymer chain and in other polymer chains in the film, leading to two bipolaronic bands. At high doping levels these two bands can merge.

For poly-dioxypyrroles, and many other doped π-conjugated materials, polarons and bipolarons are the main species responsible for charge transport (conductivity); but for *trans*-polyacetylene the mechanism is slightly different. *trans*-polyacetylene is unique among conducting polymers because it possesses a degenerate ground state—i. e., two geometric structures corresponding exactly to the same total energy, and the two structures differ from one another by the exchange of the carbon-carbon single and double bonds. Due to this degeneracy, two polarons, instead of forming a bipolaron, can readily separate in the polymer chain without being associated with each other, forming two solitons. This process is favored since the geometric structure that appears between the two charges has the same energy as the geometric structure on the other sides of the charges, thus, there is no increase in distortion energy if the two charges separate.[21]

The appearance of a soliton leads to the formation of a new energy level in the middle of the electronic gap as shown in Figure 1-3, and an increase in the doping level leads to the formation of a soliton band, which can also serve as the conduction band. Solitons can be positive, neutral or negative, and as previously mentioned, their formation does not occur in polypyrrole and is only observed in π-conjugated materials with a degenerate ground state, such as polyacetylene.

At any given moment—and even at high doping levels—it is possible to have polarons, bipolarons and solitons in the same polymeric material, but the formation of soliton and bipolaron bands are the two main phenomena responsible for conduction in doped π-conjugated polymers, which allow electrons (e^-) or holes (h^+) to move along (by resonance) and between (by hopping) the polymer chains; emulating the conductivity in metals, where the separation between VB and CB is minimum or does not exist. It is noteworthy that doping in π-conjugated polymers can also be achieved upon exposure to light and electrochemically, and that most of the charge density (>90%) is typically located close to the counter ion (for clarity, the counter ions are omitted in Figures 1-2 and 1-3).

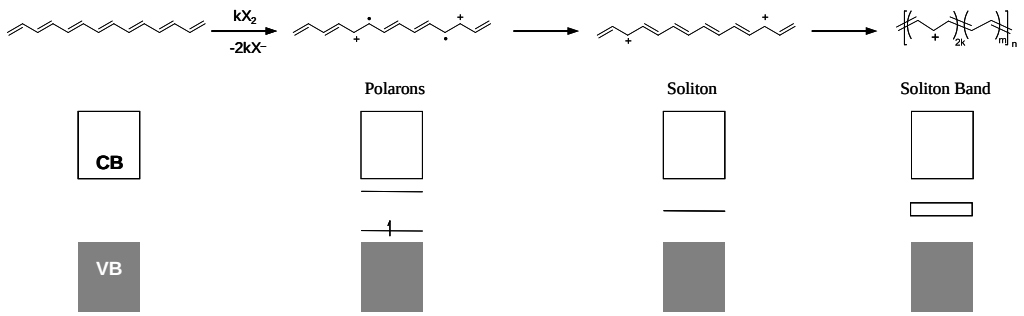


Figure 1-3. Evolution of the energy band gap in polyacetylene, from the neutral polymer (left) to the p-doped polymer (right). For clarity purposes electrons in the VB were omitted, and counter ions are not shown in the doped polymers. Adapted from: Phys. Rev. B 1982, 26, 5843.21

As was mentioned before, at any given moment it is possible to have polarons, bipolarons and solitons in the same polymeric material, which can be confirmed by different techniques, such as ESR (electron spin resonance) and absorption spectroscopy. Figure 1-4 shows the doping process using $NOPF_6$ for a pyrrole-based polymer, poly-ProDOP-*N*-*EtHx* [poly-(propyelene-3,4-dioxy)pyrrole-*N*-*EthylHexyl*],[23] which has a high optical band gap (~3.1 eV, onset shown at λ = 400 nm as a dashed gray line).

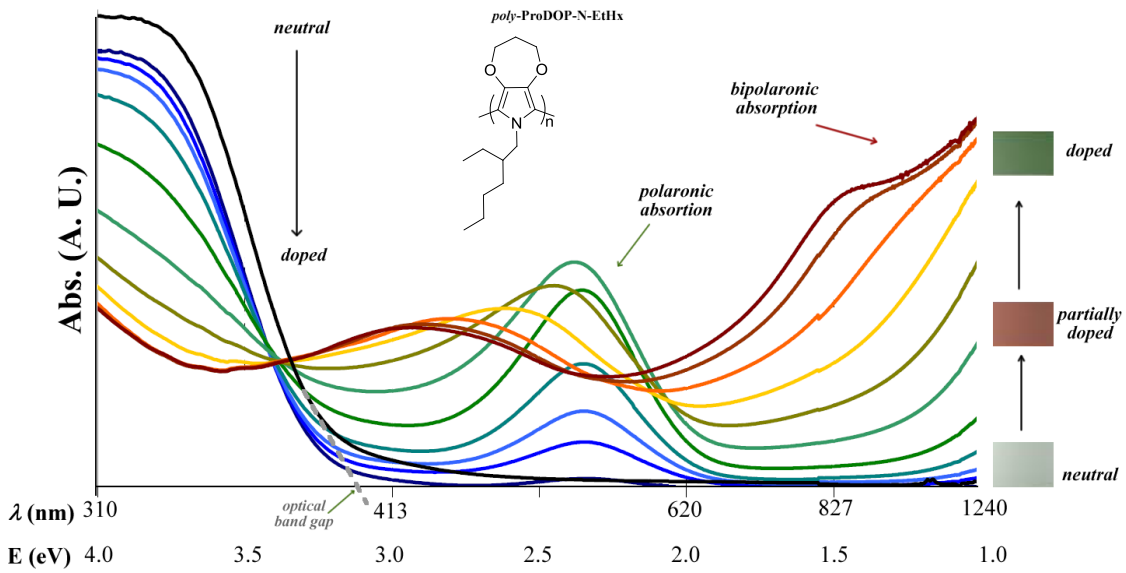


Figure 1-4. Uv-Vis-NIR of pristine (black line) and various levels of doping (colored lines) of a poly-ProDOP-*N*-EtHx solution in DCM, using $NOPF_6$ as dopant. Arrows indicate the evolution of the absorbance spectra for each region upon doping: a hypochromic shift for the π-π^* transition from neutral to doped in the UV region, and hyperchromic shift for the same transition in the near infrared. Color change of the solution, from neutral to doped, is also shown on the right side of the spectrum. Adapted from:[23] Macromolecules 2008, 41, (3), 691-700.

The black line in Figure 1-4 represents the optical absorption of the pristine solution, which only absorbs in the ultraviolet (Uv) region (λ_{max} ~ 315 nm), but once various aliquots of the dopant are added ($NOPF_6$), a hypochromic shift is observed for this absorption, but the opposite occurs in the visible (Vis) region, where the absorption corresponding to the radical cations (polarons) emerges as a hyperchromic shift. Once the level of doping is increased, the bipolaronic absorptions can be also observed as hyperchromic shifts, but these absorb in a lower energy region, which correspond to the near infrared (NIR). Due to its high band gap, poly-ProDOP-*N-EtHx* is colorless, but upon doping, a color change can be observed: red due to the polaronic absorption and green due to the combination of the polaronic and bipolaronic absorptions, as shown in Figure 1-3 for the polymer solution in dichloromethane (DCM).

Poly-Dioxypyrroles (Poly-XDOPs) and their Place in the World of π-Conjugated Polymers

Poly-dioxypyrroles (poly-XDOPs) are pyrrole-based materials which display outstanding properties.[24] Poly-XDOPs inherit most of their properties from polypyrrole, and circumvent some of its drawbacks such as polypyrrole's tendency to crosslink during polymerization and its low processability. This can easily be explained, since the substitution with alkoxy groups on the 3 and 4 positions of the pyrrole ring avoids crosslinking during the polymerization, simultaneously increasing the material processability.

Polymeric materials based on pyrrole and 3,4-dioxypyrrole molecules (poly-XDOPs) possess characteristic optical and electrochemical properties; such as high conductivity, multicolor cathodic and anodic electrochromism, rapid redox switching, and stability to bio-reductants. [17,24,25] These outstanding properties make XDOP-based materials excellent candidates for various applications, such as sensors, supercapacitors, and electrochromic devices where high conductivity and processability are needed.[24]

The polymer previously shown in Figure 1-4 can be used to explain some of XDOP's properties. Poly-ProDOP-*N*-EtHx has a high band gap, due to the low degree of conjugation between the monomeric units, and this is caused by the repulsion between the alkyl chains (propylene and -2-ethylhexyl) on adjacent pyrrole rings, which hinders the two pyrrole rings from adopting a planar and more conjugated conformation; as a consequence, most *N*-alkyldioxypyrroles are colorless or pale yellow in their neutral state. Some of the poly-XDOP's properties, such as solubility and electronic band gaps, can be finely adjusted by including different functional groups by *N*- or *O*-

substitution of the XDOP monomers. The syntheses and properties of a wide variety of XDOP monomer have been reported.[24,26-29]

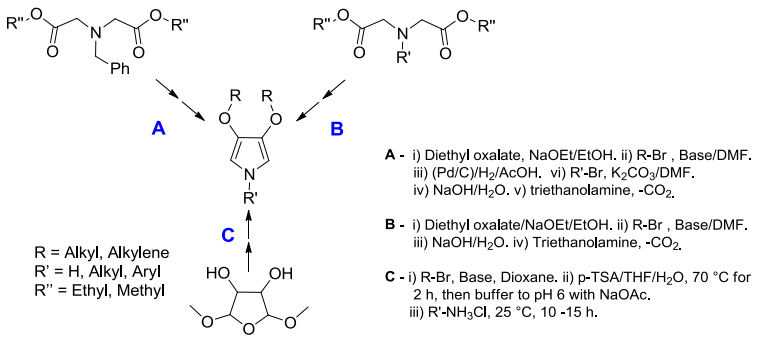
The work presented in this dissertation focuses on developing new chemistries for the synthesis of novel π-conjugated materials—oligomers and polymers—based on the electron rich heterocycle 3,4-dioxypyrrole (XDOP). The work presented in Chapter 2 and 3 describes the efforts to synthesize 3,4-dioxypyrrole-based π-conjugated molecules *via* the Pd-mediated decarboxylative cross coupling, and the deiodination polycondensation. Both methodologies proved to be convenient and efficient methods for the synthesis of ProDOP-based polymers and oligomers.

Chapter 4 describes the synthesis of fused-aromatic diketones and how these molecules can be employed to generate a wide variety of monomers—donors and acceptors—as potential precursors for the synthesis of new π-conjugated materials. This work attempts to provide new building blocks that can be combined with other available molecules to produce new materials with higher charge mobilities and unique electronic band gaps, two important elements in a π-conjugated polymer.

CHAPTER 2
ORGANOMETALLIC CROSS COUPLING OF DIOXYPYRROLES

Synthesis of 3,4-Dioxypyrroles

Although, some 3,4-dioxypyrrole (XDOPs) derivatives are commercially available, the custom synthesis of these materials are preferred, due to the low cost of the precursors and relatively easy scalability of the chemical reactions. XDOPs can be synthesized by a variety of methodologies, for example, *via* Hinsberg condensation from acyclic starting materials,[24,30,31] as shown in routes **A** and **B** in Scheme 2-1, and also from the heterocyclic starting material 3,4-dihydroxy-2,5-dimethoxytetrahydrofuran, *via* route **C**. It is noteworthy that the decarboxylation of the XDOP dicarboxylic acids is carried out in the last step in routes **A** and **B**, and as will be described later, this tendency of XDOPs to decarboxylate can be exploited in different ways to produce XDOP-based materials.



Scheme 2-1. Synthetic routes to XDOPs.

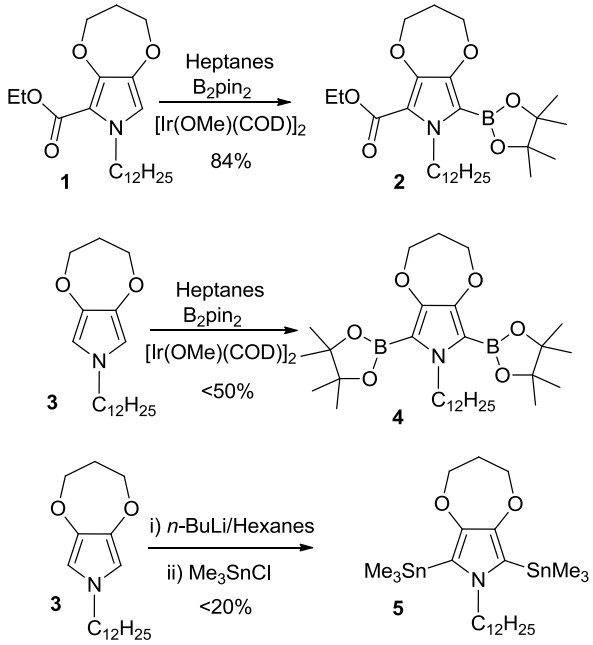
Palladium-Mediated Cross Coupling of 3,4-Dioxypyrroles

Suzuki Cross Coupling

Nowadays, organometallic cross coupling is the most common tool employed to synthesize π-conjugated oligomers and polymers. Unfortunately, organometallic coupling is almost unknown for the synthesis XDOPs; apart from a report by Merz *et al.*,[32] literature reports of organometallic coupling of XDOPs are unfamiliar. Hence, the

chemistry presented in this section will describe various synthetic approaches that allowed us to produce a variety of π-conjugated molecules based on XDOPs *via* organometallic cross coupling.

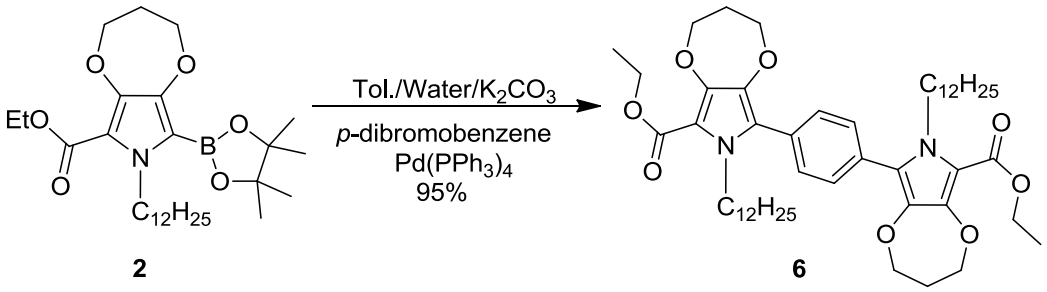
Halo derivatives can be seen as the natural precursors for many organometallic coupling reactions. Unfortunately, halo-XDOP derivatives tend to decompose, dimerize, or polymerize,[23,32] and as a result, handling and storage of 2,5-dihaloXDOP can be problematic, hindering their utility in organometallic cross couplings. Due to the complications when 2,5-dihaloXDOP derivatives are employed, other approaches were necessary in order to combine the XDOP moiety with other π-conjugated systems. Scheme 2-2 shows two approaches that can be employed to overcome the use of 2,5-dihaloXDOPs.



Scheme 2-2. Borylation and stannylation of two ProDOP-based molecules.

The approaches shown in Scheme 2-2 avoid the usage of halo-XDOPs by producing the organometallic reagent using iridium chemistry or *n*-butyllithium. Compounds **1** and **3** can be made by saponification and further decarboxylation of the

respective diesters. These compounds can then be subjected to direct borylation[33] using $[Ir(OMe)(COD)]_2$ and stannylation[34,35] (in the case of compound **3**). Compound **2** was isolated in high yield and purified easily, but compounds **4** and **5** were isolated in low yields, and starting material (compound **3**) as well as mono substituted products, were also present in the reaction crude. These compounds can only be purified by HPLC since they decompose on silica or alumina, although high vacuum distillation may be used if shorter alkyl chains than $-C_{12}H_{25}$ are employed. The boronic ester **2** was employed in the Suzuki coupling, (Scheme 2-3), which produced compound **6** in high yield, demonstrating that the Suzuki coupling can be carried out on XDOP boronate esters in high yields.



2 **6**

Scheme 2-3. Suzuki cross coupling of a ProDOP-based molecule.

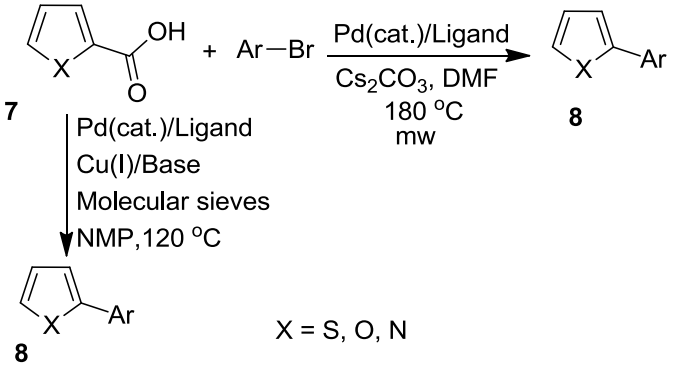
Pd-mediated Decarboxylative Cross Coupling

As was mentioned before, if the Hinsberg condensation is employed to make XDOPs—routes **A**, and **B**—then two carboxylic acids will be present in the XDOP molecule, which have to be removed by decarboxylation to produce the 2,5-unsubstituted XDOP. The 2,5-unsubstituted XDOPs can then be functionalized to react with other π-conjugated molecules to form more complex π-conjugated systems, as was shown for the Suzuki cross coupling. Another alternative route is to employ those carboxylates to generate the new π-conjugated molecules *via* palladium-mediated decarboxylative cross coupling.

The palladium-mediated decarboxylative cross coupling was recently developed by various research groups, and this methodology provides a convenient alternative to traditional cross couplings. However, this type of reaction can be only applied in a few cases when the molecular properties and structure allow it.[36,37] In the first decarboxylative coupling reported, a copper catalyzed Ullmann-like cross coupling was performed by Nilsson in 1966,[38] but remained almost unknown until few years ago. In 1997 Steglich and coworkers[39-41] and more recently Myers *et al.* in 2002,[42] Bilodeau and Forgione *et al.* in 2006,[43] Gooßen *et al.* in 2006[44] and Lee *et al.* in 2008[45] reported new effective variants of this methodology using palladium catalysts. Steglich's, Myers', Bilodeau and Forgione's reports were presented as a Heck type reaction, and Gooßen's report differed from previous reports in its use of a cooper catalyst as the transmetallating agent. Gooßen and coworkers synthesized a variety of biaryls and applied the method in the large-scale production of an intermediate of the agricultural fungicide Boscalid. Lee and coworker's report presented a one-pot synthesis of unsymmetrical diarylalkynes by a one-pot Pd-mediated Sonogashira reaction and a decarboxylative coupling, using a propiolic acid as substrate.

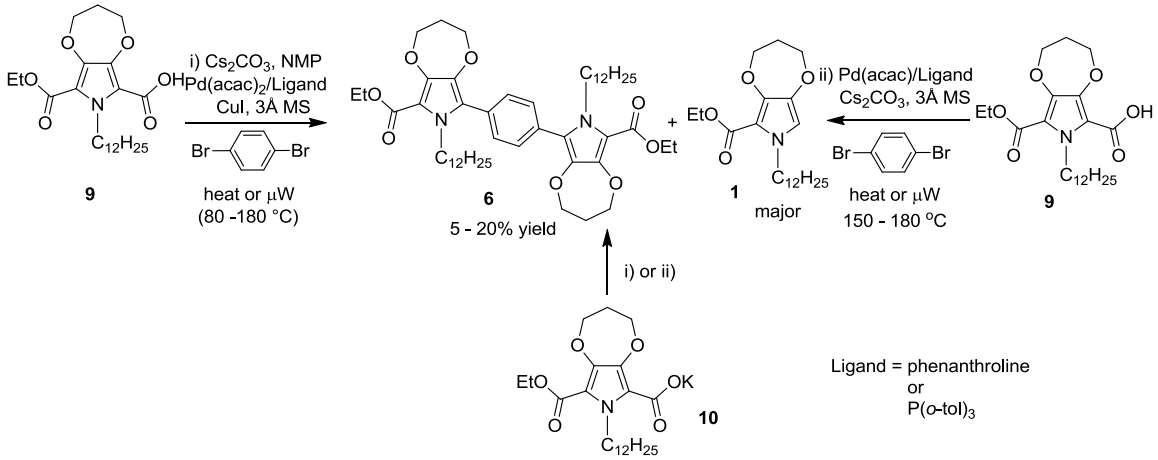
Scheme 2-4 shows the two most suitable decarboxylative cross-coupling routes for 5-member ring heteroaromatics; these two reactions were described by Gooßen *et al.*,[44] and by Bilodeau and coworkers[43] in 2006. As was mentioned before, the decarboxylation of the 3,4-dialkyldioxypyrrole dicarboxylic acids is carried out in the last step in two of the synthetic routes described in Scheme 2-1 (routes **A** and **B)**, thus, it was conceivable that this tendency of XDOPs to decarboxylate could be exploited to

produce XDOP-based materials *via* decarboxylative cross couplings by employing any of the routes presented in Scheme 2-4.



Scheme 2-4. Pd-mediated decarboxylative cross couplings according to Gooßen et al.,[44] and Bilodeau et al..[43]

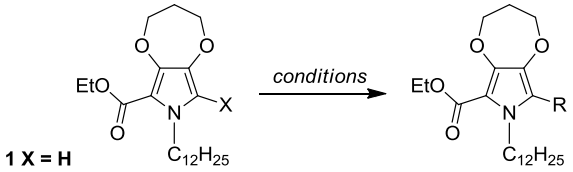
Unfortunately, both reaction conditions were ineffective for cross coupling of the 3,4-propylenedioxypyrrole (ProDOP) **9** with arylbromides, and as shown in Scheme 2-5 compound **1** was typically received as major or only product (Scheme 2-5); the desired compound **6** formed in low yield 5-20%, even when anhydrous potassium carboxylate **10** was also used to assure anhydrous conditions. Other bases were also employed (LiH, Cs_2CO_3, K_2CO_3), and reaction temperature was also manipulated; yet no improvement of reaction yields was achieved.



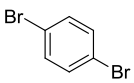
Scheme 2-5. Initial attempts to apply the Pd-mediated decarboxylative cross coupling to ProDOP-based molecules.

It was observed that if the amount of transmetallating agent (CuI/phenanthroline) was decreased—when Gooßen's reaction conditions were used—or if the temperature was decreased (150 – 180˚C)—when the Bilodeau's reaction conditions were employed—an increase in the reaction yield was achieved (25-50%). Assuming that the activity of the copper catalyst was too high, the reactivity of the copper salt was then decreased by adding KBr,[46] for Gooßen's reaction, but this did not result in any visible improvement.

Table 2-1. Various decarboxylative experiments for compounds **9**, **10**, and **1**.

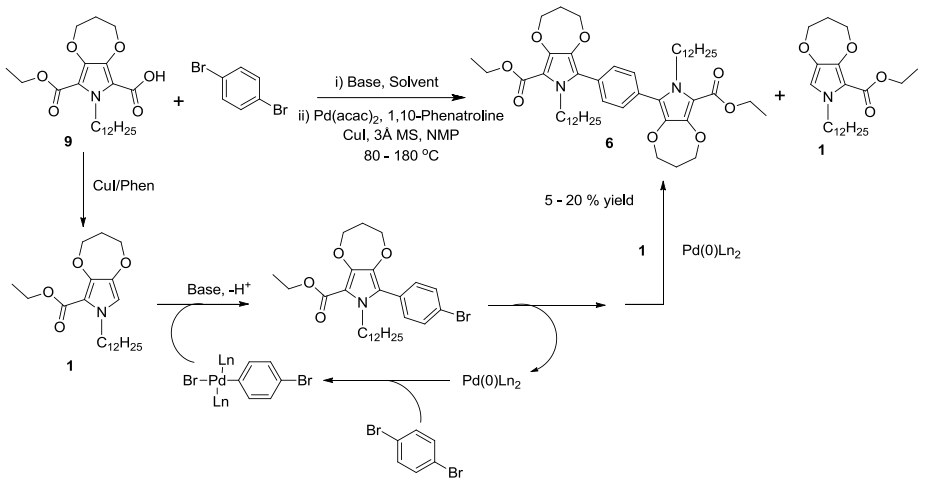


1 X = H
9 X = COOH
10 X = COOK

entry	compound	substrate	reaction conditions	product	yield (%)
1	9	none	Melt, 123˚C.	1	> 99
2	9	none	2 mol% $Pd(acac)_2$, 4 mol% P(o-tolyl)$_3$, NMP, 95°C, 24 h.	1	> 99
3	10	none	2 mol% $Pd(acac)_2$, 4 mol% P(*o*-tolyl)$_3$, NMP, 95°C, 24 h.	1	93
4	10	none	10 mol% CuI, 10 mol%, 1,10-phenantroline, 100°C, 24 h.	1	97
5	10	none	NMP, 105°C, 36 h.	none	
6	1		K_2CO_3, 2 mol% $Pd(acac)_2$, 4 mol% P(*o*-tolyl)$_3$, NMP, 95°C, 48 h.	6	21

Various experiments were carried out to understand some of the initial results. Thermogravimetric analysis (TGA) was used to measure the decarboxylation

temperature for **9** (entry 1, Table 2-1), and it was found that the decarboxylation temperature in the molten solid for this compound (**9**) was relatively low (123˚C). This temperature was in the range of the temperatures employed to run the reactions in the presence of the palladium catalyst and copper iodide, and lower than the temperatures used when no copper iodide was employed. Reactions in entries 2 and 3 (Table 2-1) showed that Pd(acac)/P(*o*-tolyl)$_3$ was able to decarboxylate **9**, and also the anhydrous potassium salt **10**, in *N*-methylpyrrolidone (NMP) producing **1** at 95˚C. CuI/phenanthroline (the transmetallating agent in the cross-coupling) produced analogous results (entry 4). The experiment in entry 5 showed that potassium salt **10** does not decompose or react under the same conditions used in entries 2-4 in the absence of palladium or copper catalysts, showing relatively stability.

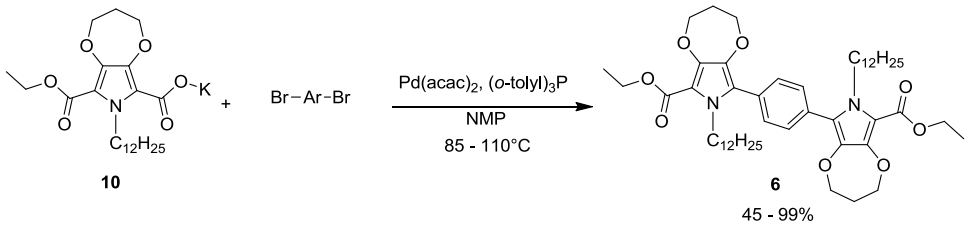


Scheme 2-6. Proposed sequential decarboxylation of **9** and direct arylation of **1** to explain the low yield in the initial attempts for the cross coupling of **9** with *p*-dibromobenzene.

Surprisingly, it was also found that Pd(acac)$_2$/(*o*-tolyl)$_3$P/K_2CO_3 produced the desired product **6** from **1** (entry 6, Table 2-1) in 21% yield at the same temperature used for the decarboxylative coupling. This latest result explained the initial results using CuI/Phen/Pd(acac)$_2$, meaning that under these conditions, the reaction yields for

9, or its carboxylate salt **10,** fit with a direct arylation mechanism[47] or a Heck type reaction[37] on compound **1**, which forms relatively fast in the reaction *via* protodecarboxylation at high temperatures or when Cu(I) is present, as shown in Scheme 2-6.

Having in mind that the copper(I) catalyst and the high temperature were causing the decomposition of the ProDOP carboxylate, the reaction was carried out without copper(I) catalyst, and the temperature was gradually increased from room temperature until product formation was observed. Product **6** is highly fluorescent under UV light, so its formation was easily confirmed by UV illumination of the reaction. This was not possible when Cu(I) was present since the copper salt quenched the fluorescence. The optimization of the reaction lead to the conclusion that the use of a phosphine ligand and Pd(acac) in NMP with temperatures between 85 to 110˚C avoids the undesired protodecarboxylation and can produce high reaction yields for the ProDOP carboxylate **10** (Scheme 2-7) *via* decarboxylative cross coupling. It is noteworthy that the reaction presented in Scheme 2-7 does not proceed under 85˚C for compound **10**.



Scheme 2-7. General decarboxylative cross-coupling using the potassium carboxylate **10**.

The structure, yield, and temperature employed for various molecules synthesized using the decarboxylative cross coupling of **10** are presented in Figure 2-1. The methodology was quite effective for several aryl dibromides that were employed, and acceptable to high yields with relatively low catalyst load (less than 2 mol%) were

obtained. Relatively low temperatures were used (85-110°C), and the optimal reaction temperature varied for each aryl dibromides. The reaction times spanned from 6 to 48 hours, and since there is no need for a copper(I) catalyst, low or no side products were observed; furthermore, the reaction was not sensitive towards the presence of water.

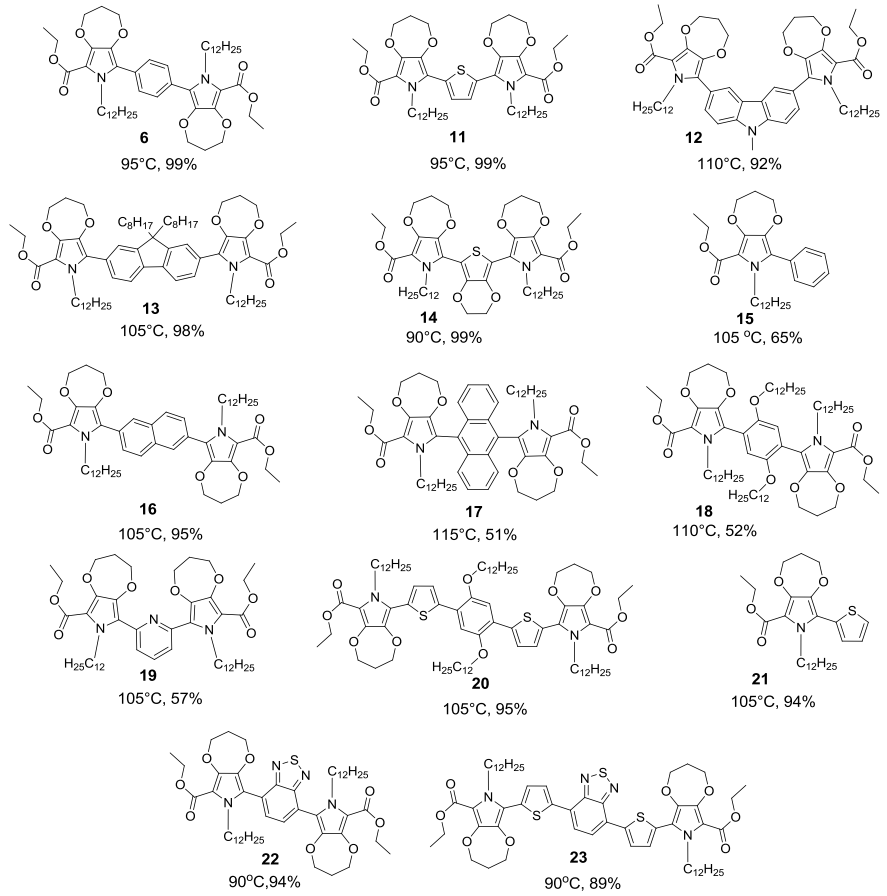


Figure 2-1. Various ProDOP-based π-conjugated molecules synthesized by Pd-mediated decarboxylative cross coupling.

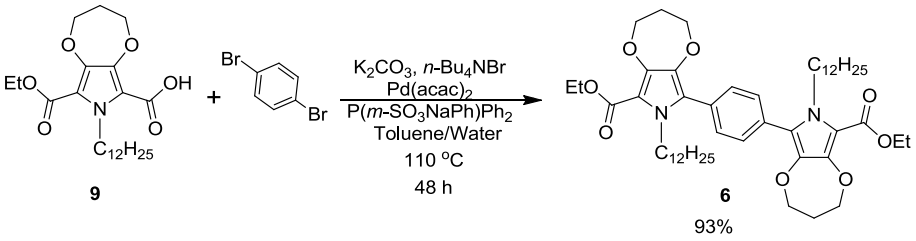
The method was also applied to produce π-conjugated oligomers containing the benzo[c][1,2,5]thiadiazole (BTD) unit (compounds **22** and **23**, Figure 2-1). The ability to incorporate this moiety was significant since inclusion of the BTD unit in a π-conjugated molecule is a practical approach to decrease the band gap of the system through an electron donor-acceptor interaction.[48] BTD is one of the most common acceptor molecules used in π-conjugated materials; unfortunately, the thiadiazole ring tends to

decompose under basic reaction conditions. Thus, initial attempts to include the BTD moiety in the ProDOP π-conjugated molecules using Pd-decarboxylative cross coupling failed since the bases K_2CO_3 and Cs_2CO_3 in *N*-methylpyrrolidone (NMP) caused decomposition of 4,7-dibromo-BTD. Switching to the milder base $KHCO_3$, however, while keeping the temperature under 90˚C and increasing dilution, allowed the reaction to proceed in high yield (94% for **22** and 89% for **23**).

Similar results were observed whether the anhydrous potassium salt **10** was pre-synthesized or formed *in situ* using potassium carbonate. It was also tested to see if the reaction could be run only with the palladium catalyst without adding a ligand. However, the yield for the tested reaction was lower—i. e. 69% yield for compound **13**. When the reaction was run with PPh_3 instead of P(*o*-tolyl)$_3$ a decrease in the reaction yield was also observed—i. e. 89% yield for compound **6**.

As previously mentioned, the reaction did not show any sensitivity towards the presence of water, so the decarboxylative cross coupling was run under similar reaction conditions to some Suzuki-Miyaura couplings (Scheme 2-8).[49-51] A toluene/water mixture was employed as solvent with sodium biphenylphosphinobenzene-3-sulfonate, PPh_2(*m*-$NaSO_3$-Ph), as ligand, and **6** and **21** were obtained in high yields (93% and 87% yield, respectively). In this case the carboxylate salt **10** was formed *in situ* from **9** using potassium carbonate (K_2CO_3) or potassium *tert*-butoxyde (*t*-BuOK), and tetrabutylammonium bromide (*n*-Bu_4NBr) was used as a phase transfer agent. These latest reaction conditions provide a good alternative for the synthesis of 3,4-dioxypyrrole derivatives without using NMP, and this result clearly demonstrated the low sensitivity of the reaction towards the presence of water. It is noteworthy that water is needed for the

reaction to proceed under these conditions since it is needed to dissolve the potassium salt. To rule out a possible product formation *via* compound **1**, the same reaction was run using **1**, and no product formation was seen. It is noteworthy that tetrahydrofuran (THF), dimethoxyethane (DME), and diethoxyethane were also tested for the aqueous reaction conditions but only toluene was found to work well.

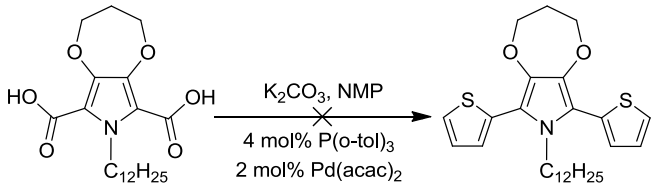


9 **6**

93%

Scheme 2-8. Pd-mediated decarboxylative cross coupling under aqueous reaction conditions.

Attempts to apply the previously optimized reaction conditions in NMP for the diacid **24** failed (Scheme 2-9). The initial thought was that the reaction required higher temperatures to proceed, but a gradual increase in the temperature from room temperature to 190°C did not produce any product formation. It was also observed that the formed potassium salt had low solubility and precipitated in the reaction even at high temperature.

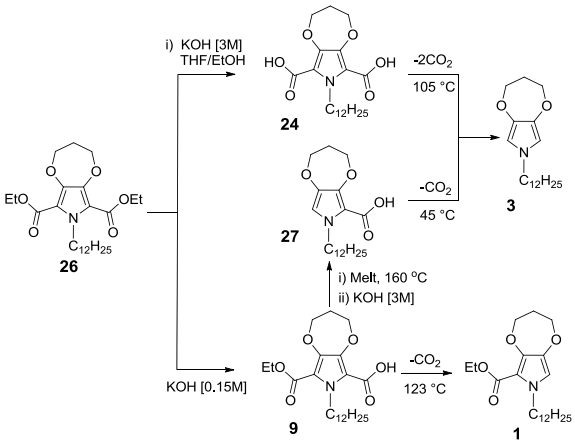


24 **25**

Scheme 2-9. Failed attempt to apply the Pd-mediated decarboxylative cross coupling to a ProDOP-dicarboxylic acid.

Due to these results, the decarboxylation temperatures of various ProDOP carboxylic acids was studied in greater detail and the results are presented in Scheme 2-10. The synthesis of these ProDOP acids were carried out by controlled

saponification of the ProDOP diester **26**, yielding the diacid **24** and mono acid **9**. To synthesize the mono acid **27**, compound **9** was decarboxylated first, and then subjected to an additional hydrolysis (as shown in Scheme 2-10), then thermogravimetric analysis (TGA) measurements were performed on the 3,4-propylenedioxypyrroles (ProDOPs) acids **24, 27** and **9**, and also on various potassium carboxylates. It is noteworthy that the temperatures presented in Scheme 2-10 correspond to the minimum required temperature for the protodecarboxylation to occur in the bulk molten compound. This data reveals that the decarboxylation temperature of the dicarboxylic ProDOP diacid **24** is lower than the temperature needed to decarboxylate the monoacid containing the ester group (**9**), and higher than the temperature needed to decarboxylate the monoacid **27**. Although it is logic not to expect the same reactivity on the respective potassium carboxylates, the TGA data provided insight into the reactivity and relative stability of each carboxylate, acids and potassium salts, with the latter decomposing around 300˚C.



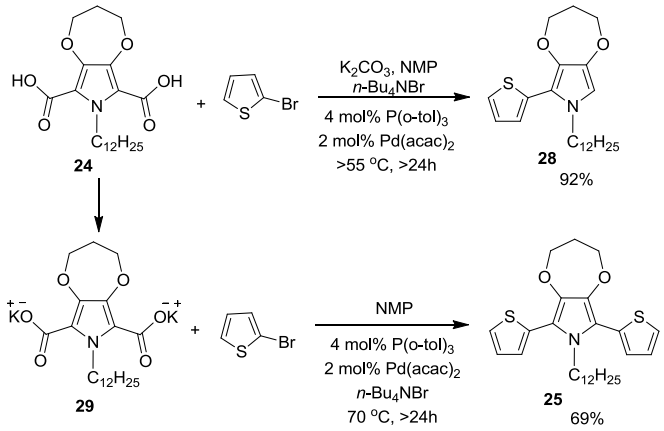
Scheme 2-10. Syntheses and decarboxylation of three different ProDOP acids.

Literature reports have shown that the appropriate temperature for the decarboxylative cross coupling not only varies with the tendency of the carboxylic acid to undergo decarboxylation, but also with other factors such as aryl halide, solvent and ligand employed,[52,53] and although the decarboxylative cross coupling reaction has

been successfully applied to various monocarboxylic acids,[37,52,54,55] there are no reports of decarboxylative cross coupling in a dicarboxylic acid.

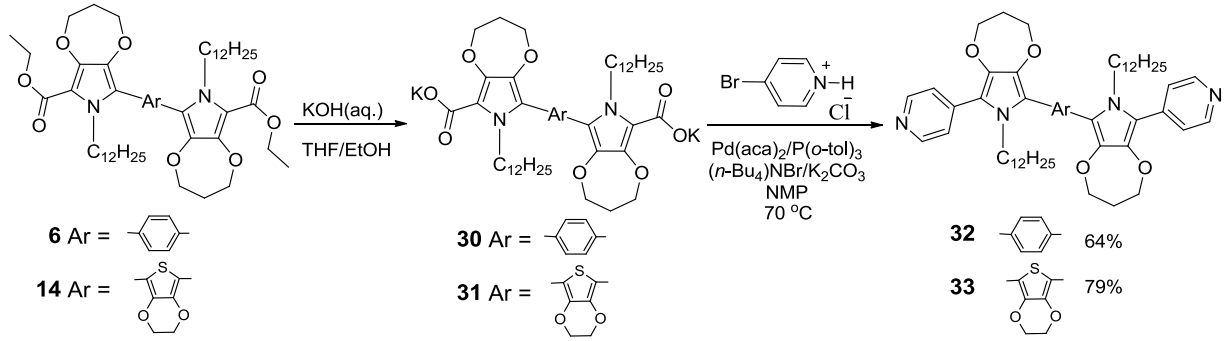
Based on the observations made for the reaction presented in Scheme 2-9—i. e. low solubility of the potassium salt formed – and assuming that the low reactivity was related to the low solubility of the potassium salt and not to the tendency of the dicarboxylate to undergo decarboxylation, the reaction was repeated, and two equivalents of tetrabutylammonium bromide were added to increase the carboxylate solubility, and the temperature was slowly increased until product formation was observed. The reaction presented on the upper part of Scheme 2-11 showed that if compound **24** is employed in combination with potassium carbonate (>3 equiv.) in the presence of tetrabutylammonium bromide, the monosubstituted ProDOP derivative **28** is synthesized in high yield (92%), and almost exclusively. Surprisingly, the formation of this compound (**28**) was observed around 55˚C—a low temperature for a decarboxylative cross coupling, but since the reaction proceeded slowly at this temperature (monitored by TLC), the temperature was then increased to 70˚C.

Based on this last result, it was assumed that potassium carbonate was not strong enough to react *in situ* with both carboxylates present in **24**, which lead to **28** *via* a mono-decarboxylative cross coupling, followed by a fast proto-decarboxylation. Hence, the potassium dicarboxylate **29** was pre-synthesized and subjected to react under similar reaction conditions (shown in the lower part of Scheme 2-11). The desired compound **25** was isolated in acceptable yield, demonstrating that the Pd-mediated cross-coupling reaction can be applied to dicarboxylic acids of the readily decarboxylable 3,4-dioxypyrrole molecules.



Scheme 2-11. Pd-mediated decarboxylative cross couplings on a ProDOP-dicarboxylic acid and a potassium ProDOP-dicarboxylate.

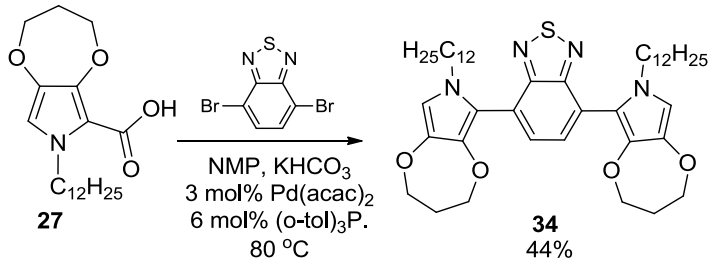
Other possibilities that were explored for the Pd-mediated decarboxylative cross coupling of ProDOPs are presented in Scheme 2-12. In this case compounds **6** and **14**, which were synthesized using the decarboxylative cross coupling and still contained a carboxylic ester, were subjected to a second hydrolysis to generate the potassium carboxylates **30** and **31**, which were then isolated, dried, and reacted with 4-bromopyridine hydrochloride to produce compound **32** and **33**; similar conditions to the ones employed for compound **29** were used.



Scheme 2-12. Pd-mediated decarboxylative cross couplings on two potassium ProDOP-dicarboxylate oligomers.

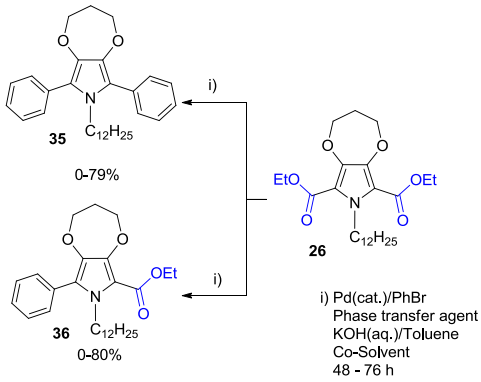
The derivatization presented in Scheme 2-12 cannot be carried out on the benzo[c][1,2,5]thiadiazole (BTD) derivatives, as was explained before, as this type of compound tends to decompose under basic conditions. Thus, it is not possible to carry

out the hydrolysis of the ester groups without affecting the BTD unit. In this case, it is possible to generate a new π-conjugated molecule by applying the decarboxylative cross coupling on the carboxylic acid **27** (Scheme 2-13); this route leads to a new system (**34**) that contains two unsubstituted positions on the 3,4-dioxypyrrole molecule that may be employed for further reaction or derivatization. The moderate yield of this latest reaction was attributed to possible side reactions such as ill-defined oligomerization. This was assumed since several side products were observed by TLC after 24 hours of reaction, which probably corresponds to oligomerization *via* direct arylation as was previously shown to occur under these reaction conditions.



Scheme 2-13. Synthesis of a BTD-based oligomer *via* decarboxylative cross coupling.

As was mentioned before, the decarboxylative cross coupling of XDOP carboxylic acids can be carried out in a water-toluene mixture, and similar yields as the non-aqueous conditions might be achieved. Having that in mind, the decarboxylative cross coupling of di-esters was also explored, and as shown in Scheme 2-14, two possible products can be obtained using this route (mono- and di-substituted dioxypyrrole). Various solvents were tried, and it was found that a mixture of solvents is required for the reaction to proceed. If only toluene/$KOH_{(aq.)}$ was employed, the reaction did not produce any product. Other solvents were also tried—THF/$KOH_{(aq.)}$, DME/$KOH_{(aq.)}$, Diethoxyethane/$KOH_{(aq.)}$, and no product formation was observed in any of these cases.



Scheme 2-14. Decarboxylative cross coupling using a ProDOP diester.

Based on various experimental observations, it was concluded that the reaction proceeds at temperatures higher that ~105°C, and only when a mixture of toluene/$KOH_{(aq.)}$ and one of the afore mentioned solvents is employed, which means that a low polarity solvent such as toluene is needed for the reaction to occur. The yield varied from 0 to 79% for the formation of the di-substituted product (**35**), and unfortunately, the reactions were not reproducible, and in many cases, the product did not form. If the concentration of the base [KOH(aq.)] was decreased, compound **36** was also produced. Typically, the reaction requires highly degassed solvents, and since the *in situ* hydrolysis of the di-ester has to occur, a homogeneous emulsion is needed. To acquire this emulsion, a co-solvent and a phase transfer agent (*n*-Bu_4NBr or aliquat-336) were employed, otherwise the reaction does not proceed. Due to the numerous failed attempts to reproduce this reaction, this route was finally discarded, and the non-aqueous conditions using NMP, or the two-step aqueous reaction conditions (hydrolysis then decarboxylative cross coupling using toluene/water) are recommended.

Experimental Section

General Information

All reagents and starting materials were purchased from commercial sources and used without further purification, unless otherwise noted. All reactions were carried

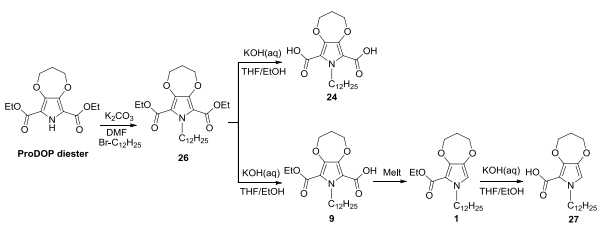
under argon atmosphere; unless otherwise mentioned. ^{1}H-NMR and ^{13}C-NMR spectra were collected on a Mercury 300 MHz or an Inova 500 MHz. High resolution mass spectrometry was performed by the spectroscopic services in the Chemistry Department of the University of Florida with a Finnigan MAT 95Q Hybrid Sector or a Bruker APEX II FTICR or Agilent 6210 TOF. FTIR measurements were performed on a Perkin-Elmer Spectrum One FTIR outfitted with a $LiTaO_3$ detector. Thermogravimetric analysis (TGA) measurements were performed with a Perkin-Elmer TGA 7 thermogravimetric analyzer

Experimental Procedures

Ethyl N-dodecyl-3,4-(propylene-1,3-dioxy)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrrole-2-carboxylate (2). The literature procedure[33] was slightly modified as follows: To a dry 25 mL round bottom flask, containing a stir bar and under argon atmosphere, and equipped with a condenser, was added $[Ir(OMe)(COD)]_2$ (5.1 mg, 0.008 mmol, 1.5 mol%), 2,2'-bipyridine (2.4 mg, 0.015 mmol, 3 mol%), and bis(pinacolato)diboron (0.1295 g, 0.510 mmol, 1.1 equiv). Compound **1** was dissolved in 3 mL of degassed heptanes and then transferred *via* syringe to the flask containing the other reagents, and the system was equipped with a bubbler. The mixture was stirred at 75°C for 24 hours. The reaction mixture was cooled down to room temperature and filtered through a short path of a mixture 4:1 of decolorizing carbon:alumina activity 3. The decolorizing-carbon:alumina mixture was flushed with 80 ml of 30% diethyl ether in hexanes to recover the entire product. After removal of the solvent the crude was subjected to high vacuum for 1h at 60°C to remove boron byproducts. The product was isolated as a colorless oil, 0.198 g (84.% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 4.41 (t, 2H, J = 7.4), 4.30 (q, 2H, J = 7.0), 4.11 (m, 4H), 2.17 (m,

2H), 1.59 (m, 2H), 1.40-1.20 (br, 33H), 0.88 (t, 3H, J = 6.4 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 161.1, 146.7, 142.6, 129.9, 113.3, 83.4, 71.7, 71.6, , 60.1, 48.0, 33.8, 32.9, 32.1, 29.9 (br), 29.8, 29.6, 29.5, 27.0, 24.9, 22.9, 14.6, 14.3. HRMS (ESI, M+H$^+$) m/z calcd. for $C_{28}H_{48}BNO_6H$ 506.3653, found 506.3696, (ESI, M+Na$^+$) m/z calcd. for $C_{28}H_{48}BNO_6Na$ 528.3472, found 528.3480.

Diethyl 5,5'-(1,4-phenylene)bis(N-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2-carboxylate) (6) via Suzuki coupling. To a 100-mL round bottom flask equipped with a condenser and containing a stir bar and under argon atmosphere was added compound **2** (0.183 g, 0.3602 mmol, 2.1 equiv.) K_2CO_3(0.320 g), *n*-Bu_4NBr(28 mg, 0.0865 mmol, 0.5 equiv), and 1,4-dibromobenzene (40.7 mg, 0.1724 mmol, 1 equiv). The system was purged with vacuum-argon 4 times and then toluene (4.5 mL, previously degassed) and deionized water (4 mL, previously degassed) were added. The mixture was stirred for 30 seconds and $Pd(PPh)_4$ (approx. 3 mg) was added. The mixture was warmed to 85-90˚C, and stirred vigorously for 18 hours. The mixture was cooled to room temperature and partitioned between water and diethyl ether, washed with water (4x), brine (1x), and dried over Na_2SO_4; an oily material was gotten which produced a white solid after treatment with MeOH. For quantification purposes, the entire crude was purified by chromatographic column (silica, neutralized with Et_3N, and ethyl ether:hexanes 1:1), producing 137 mg of a white solid in 95% yield. The compound showed the same spectroscopic characteristics as previously reported.[52]



Scheme 2-15. Synthesis of ProDOP esters and acids.

The synthesis of the ProDOP-acid derivatives 4, 6, 5, and esters **9** and **1** was carried out according to Scheme 2-15.

Diethyl N-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2,5-dicarboxylate (26). ProDOP diester (5.952 g, 21.0112 mmol, 1 equiv.), *n*-dodecylbromide (6.284 g, 25.2135 mmol, 1.2 equiv.), ground anhydrous K_2CO_3 (8.7119 g, 63.0336 mmol, 3 equiv.) and DMF (80 mL) were stirred at 95˚C. The reaction was monitored by TLC (silica, 1:2 ethyl ether:hexanes) until disappearance of the starting material (approx. 48 h). Then the solvent was removed by rotary evaporation, and the resulting crude was partitioned between water and ethyl acetate. The ethyl acetate fraction was washed with water (3x), brine (1x) and dried over anhydrous sodium sulfate. The solvent was removed by rotary evaporation and the resulting crude was purified by column chromatography (silica, 1:2 ethyl ether:hexanes); The product was isolated as a colorless oil 8.538 g (90% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 4.54 (t, 2H,J = 7.6), 4.32 (q, 4H, J = 7.1 Hz), 4.14 (t, 4H, J = 5.3 Hz), 2.21 (td, 2H, J = 5.3 Hz, J = 10.5 Hz), 1.63 (m, 2H), 1.35 (t, 6H, J = 7.1 Hz), 1.31 – 1.15 (m, br, 18H), 0.86 (t, 3H, J = 6.7 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 160.9, 142.0, 113.8, 71.8, 60.7, 46.5, 33.5, 32.2, 32.1, 29.9, 29.8, 29.8, 29.8, 29.5, 26.9, 22.9, 14.5, 14.3. FTIR (NaCl Disc) $\bar{\nu}_{max}$ (cm^{-1}): 2925.7 (s), 2854.9(m), 1713.7 (vs), 1531.0 (m), 1456.0 (m), 1435.5 (m), 1365.1 (m), 1351.3 (m), 1308.8 (m), 1249.5 (s), 1154.7 (s), 1082.3 (m), 1028.9 (m), 776.9 (w).

***N*-Dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2,5-dicarboxylic acid (24).** To a 250-mL round bottom flask containing a stir bar was added compound **26 (**1.534 g, 3.397 mmol), THF (15 mL) and ethanol (30 mL), After the solid dissolved, 30 mL of KOH [3M] was added, and argon was bubbled through the reaction mixture for 5

minutes. The flask was equipped with a condenser and the reaction mixture was heated to 75°C with strong stirring under argon for 36 hours. The organic volatiles were carefully removed in a rotary evaporator, and the aqueous solution was cooled in an ice bath, and the reaction mixture was carefully acidified by slow addition of HCl 3M. The resulting white precipitate was filtered and washed with deionized water, air-dried for about 40 minutes then placed under high vacuum overnight. The resulting solid was stirred at ~ 40°C in 25-mL of a mixture 1:25 of ethyl ether:pentanes for 5 minutes, the mixture was allowed to cool to room temperature, filtered, and washed with cold pentanes. The product was isolated as a white solid, 1.303 g (97% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 10.13 – 8.8 (br, 2H), 4.82 (t, 2H, J = 7.6 Hz), 4.32 (t, 4H, J = 4.8 Hz), 2.38 (quin, 2H, J = 4.4 Hz), 1.68 (m, 2H), 1.29 – 1.24 (m, 18H), 0.87 (t, 3H, J = 6.3 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 159.2, 139.0, 112.8, 73.6, 46.5, 33.5, 32.1, 31.8, 29.9, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 26.7, 22.9, 14.3. FTIR (KBr, pellet) $\bar{\nu}_{max}$ (cm^{-1}): 3223.6 (br, s), 2918.9 (br, s), 2850.5 (br, s), 2630.2 (br, m), 1749.2, 1669.2, 1550.9, 1438.5, 1314.7 (s), 1270.8 (s) 1169.4 (s), 1082.0 (s), 733.2 (s).

***N*-Dodecyl-5-(ethoxycarbonyl)-3,4-(propylene-1,3-dioxy)pyrrole-2-carboxylic acid (9).** To a 1000-mL round bottom flask containing a stir bar was added **26 (**10.050 g, 22.254 mmol, 1 equiv.), THF (95 mL) and ethanol (135 mL), After the solid dissolved, 150 mL of KOH 0.15 M was added, the flask was equipped with a condenser and the reaction mixture was heated to 75-80°C (slightly reflux) with strong stirring under argon. After 1 hour 25 mL more of KOH 0.15 M was added, and this was repeated again 30 minutes later (total: 200 mL of KOH 0.15 M). After 30 minutes more (2 hours total), the heating was removed. The organic volatiles were carefully removed in a rotary

evaporator, and the aqueous solution was chilled by the addition of ~100 mL of crushed ice. The reaction mixture was carefully acidified by the addition of HCl 3M. The resulting precipitate was extracted with diethyl ether (3x, 50 mL), washed with deionized water and brine, and dried over anhydrous Na_2SO_4. The diethyl ether was removed in a rotary evaporator, and the resulting viscous oil was placed under high vacuum until it solidified. The product was recrystallized from cold pentanes and dried *in vacuo* to yield 7.206 g (77%) of a white powdery solid. Based on TGA data this contains around 97% of monoacid **9** and 3% of the diacid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 10.06(br, 1H), 4.67 (t, 2H, J = 7.6 Hz), 4.34 (q, 2H, J = 7.1 Hz), 4.27 (t, 2H, J = 5.0 Hz), 4.15 (t, 2H, J = 4.9 Hz), 2.29 (quin, 2H, J = 4.9 Hz), 1.66 (m, 2H), 1.36 (t, 3H, J = 7.1 Hz), 1.30-1.20 (m, 18H), 0.86 (t, 3H, J = 5.8 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 160.47, 159.41, 140.68, 140.06, 115.48, 111.12, 73.56, 71.96, 60.99, 46.45, 33.57, 32.10, 31.96, 29.83, 29.80, 29.76, 29.52, 29.47, 26.76, 22.86, 14.48, 14.29. FTIR (KBr, pellet): $\bar{\nu}$ (cm^{-1}) = 3289.1 (br, w), 2925.3 (s), 2854.6 (m), 1742.7 (m), 1712.6 (s) 1250 (m). MS (DIP-CI, CH_4, 340°C, $M+H^+$) m/z calcd. for $C_{23}H_{38}N_2O_6$ 424.2694, found 424.2696. EA Calculated for $C_{23}H_{37}N_2O_6$: C (65.22%) H (8.81%) N (3.31%), Found: C (65.47%), H (9.20%), N (3.29%).

Ethyl N-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2-carboxylate (1). To a 100-mL round bottom flask was added compound **9 (**1.2 g, 3.1618 mmol), then the flask was equipped with an vacuum adapter and purged with argon-vacuum three times. The solid was melted at 130°C under vacuum until no bubbling was observed. The resulting oil was dissolved in DCM:hexanes 1:1 and filtered through a short path of basic alumina (or silica previously neutralized with triethylamine). The solvent was removed by rotary

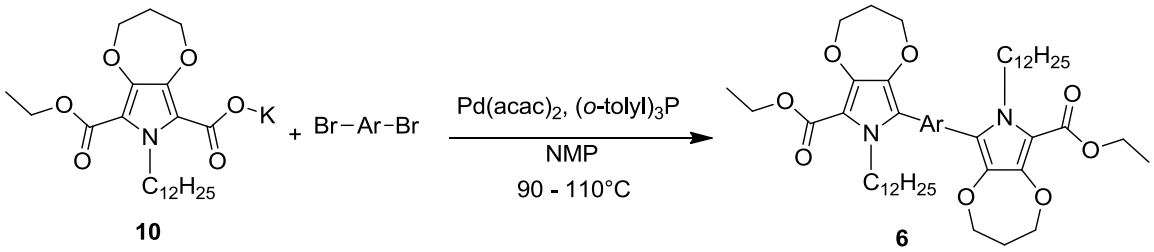
evaporation and the resulting colorless oil was subjected to high vacuum for 1 hour. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 6.39 (s, 1H), 4.27 (q, 2H, J = 7.1 Hz), 4.09 (m, 4H), 3.98 (m, 2H), 2.15 (td, 2H, J = 5.0 Hz, J = 10.2 Hz), 1.64 (m, 2H), 1.32 (t, 3H, J = 7.1 Hz), 1.23 (s, 18H), 0.86 (t, 3H, J = 6.7 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 161.2, 143.9, 137.0, 115.2, 107.9, 72.1, 72.1, 59.7, 50.0, 34.5, 32.1, 31.8, 29.8, 29.8, 29.8, 29.8, 29.5, 29.8, 26.8, 22.9, 14.7, 14.3.

***N*-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2-carboxylic acid (27)**.

Compound **1** (3.1618 mmol) was dissolved using 10 mL of THF and 20 mL of EtOH, and transferred to a 100-mL round bottom flask equipped with a stir bar and a condenser, then 15 mL of KOH [5M] was added and the mixture was degassed by bubbling argon for 10 minutes. The mixture was stirred under argon at 35 – 40˚C for 5 days. The volatiles were removed by rotary evaporation at room temperature. Deionized water (~20 mL) was added to the resulting heterogeneous solution, and then cooled to 5˚C and acidified by adding HCl [2M] dropwise (alternatively, the potassium salt can be isolated by filtration, and then dried under vacuum). The resulting solid was washed with deionized water, and dried under high vacuum. The solid was stored under argon in the freezer, 0.780 g (70% yield). The NMR showed that the product is a mixture 20:1 of compound **27** and ProDOP ester **1**. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 9.93 – 9.02 (br, 1H), 6.49 (s, 1H), 4.23 (t, 2H, J = 4.9 Hz), 4.16 (t, 2H, J = 7.2 Hz), 4.01 (t, 2H, J = 4.9), 2.24 (td, 2H, J = 5.0 Hz, J = 10.0 Hz), 1.69 (m, 2H), 1.36 – 1.17 (m, 18H), 0.87 (t, 3H, J = 6.6 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 159.6, 141.9, 135.6, 116.0, 106.6, 73.8, 72.2, 49.5, 34.4, 32.1, 31.5, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 26.7, 22.9, 14.3. FTIR (NaCl Disc) $\bar{\nu}_{max}$ (cm^{-1}): 3324.8 (br, w), 3105.4 (br, w), 2924.7, 2924.7 (vs),

2854.4 (s) 2645.5 (br, w), 1732.4 (s), 1652.3 (s), 1525.1 (m), 1456.2 (s), 1407.9 (s), 1365.2 9 (s), 1294.6 (m), 1062.9 (s), 795.7 (w).

Potassium *N*-dodecyl-5-(ethoxycarbonyl)-3,4-(propylene-1,3-dioxy)pyrrole-2-carboxylate (10). Two possible methods can be employed to make this compound. (A) To a dry 250-mL round bottom flask containing a stir bar and argon was added compound **9** (3.0030 g, 7.0902 mmol, 1 equiv.). The flask was equipped with a septum and 30 mL of anhydrous THF was added *via* cannula. After dissolution of compound **9**, a solution of potassium *t*-butoxide (0.7596 g, 7.0902 mmol, 1 equiv) in THF (100 mL) was added *via cannula*. The viscous solution was stirred for 30 minutes and then the solvent was carefully removed in a rotary evaporator, assuring anhydrous conditions. 3.270 g of sticky white solid was gotten, 100% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 4.40 (t, 2H, J = 7.3 Hz), 4.12 (q, 2H, J = 7.1 Hz), 3.94 (t, 2H, J = 4.9 Hz), 3.83 (t, 2H, J= 4.8 Hz), 2.00 (quin, 1H, J = 4.9 Hz), 1.47 (m, 2H), 1.21 (m, 18H), 0.85 (t, 3H, J = 6.5 Hz). FTIR (KBr, pellet): $\bar{\nu}$ (cm^{-1}) = 2925.8 (s), 2855.3 (m), 1701.0 (s), 1602.7 (s), 1365.8 (s), 1344.4 (s), 1249.6 (m). (B) Alternatively this compound can be made in water, using KOH, but the product has to be dried under vacuum at 50°C for three hours.



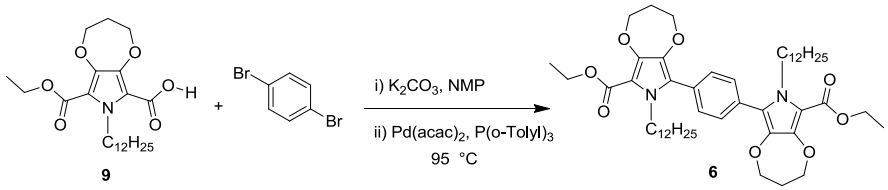
10 **6**

Scheme 2-16. General procedure 1: decarboxylative cross-coupling using the potassium carboxylate **10**.

Diethyl 5,5'-(1,4-phenylene)bis(N-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2-carboxylate) (6). In a typical procedure, to a dry 25-mL round bottom flask containing a

stir bar and argon atmosphere was added compound **10** (0.554 g, 1.200 mmol, 2.2 equiv.), 1,4-dibromobenzene (0.129 g, 0.545 mmol, 1 equiv), tri(o-tolyl)phosphine (6.6 mg, 0.022 mmol, 4 mol%) and palladium(II) acetylacetonate (3.3 mg, 0.011 mmol, 2 mol%). The flask was equipped with an air-cooled condenser then an inlet vacuum adapter is connected to the top of the condenser and the system was purged with vacuum-argon four times. N-methylpyrrolidone (1.5 mL, previously degassed) was added *via* syringe. The inlet vacuum adapter is changed to a septum and a bubbler (containing silicone oil) was connected to it. The bubbler was flushed with argon for 2 minutes by connecting an argon source through the septum. The reaction mixture was warmed to 95°C and stirred for 48 hours. The solution was then cooled down to room temperature, diluted with 40 mL of a mixture 3:2 diethyl ether:hexanes, and filtered through a short path of alumina (neutral, activity 3). The alumina was flushed with a mixture 3:2 diethyl ether:hexanes to recover the entire product. The mixture was washed with 30 mL deionized water (four times) and brine, dried over Na_2SO_4 and the organic solvent mixture (including the residual NMP) was removed in a rotary evaporator. The resulting crude solid was recrystallized from methanol yielding 0.436 g of a white solid, 96% yield. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.42 (s, 4H), 4.34 (q, 4H, J = 7.1 Hz), 4.19 (m, 8H), 4.01 (t, 4H, J = 4.0 Hz), 2.20 (m, 4H), 1.47 (m, 4H), 1.37 (t, 6H, J = 7.1 Hz), 1.32-1.12 (m, 36H), 0.86 (t, 6H, J = 6.6 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 161.4, 144.6, 135.6, 130.3, 129.4, 127.1, 108.3, 72.1, 72.0, 59.9, 46.2, 34.2, 32.1, 31.8, 29.9 (br), 29.82 (br), 29.7 (br), 29.5, 29.3, 26.7, 22.9, 14.8, 14.3. HRMS (ESI-TOF, $M+H^+$) m/z calcd. for $C_{50}H_{77}N_2O_8$ 833.5674, found 833.5693. EA calculated for

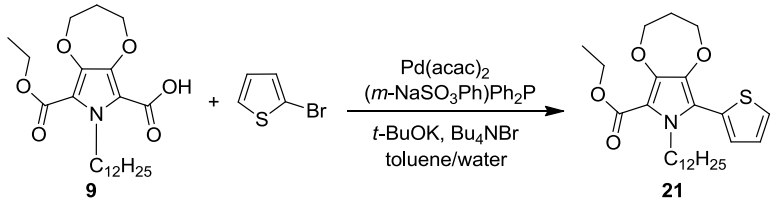
$C_{50}H_{76}N_2O_8$: C (72.08%) H (9.19%) N (3.36%). Found: C (72.02%), H (9.59%), N (3.31%).



Scheme 2-17. General procedure 2: decarboxylative cross coupling of compound **9** using potassium carbonate as base.

Diethyl 5,5'-(1,4-phenylene) bis(N-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2-carboxylate) (6). To a 25-mL round bottom flask, containing argon atmosphere and equipped with an air cooled condenser and a stir bar, was added compound **9** (0.211g, 0.457 mmol, 2.2 equiv.), 1,4-dibromobenzene (0.049g, 0.208 mmol, 1 equiv) and finely ground anhydrous potassium carbonate (0.063 g, 0.457 mmol, 2.2 equiv.). An inlet vacuum adapter was connected to the condenser and the system was purged with vacuum-argon four times, and then 1.5 mL of degassed N-methylpyrrolidone was added *via* syringe. The reaction mixture was warmed to 60°C and stirred for 45 min. Tri(o-tolyl)phosphine (2.5 mg, 0.009 mmol, 4 mol%) and palladium(II) acetylacetonate (1.3 mg, 0.004 mmol, 2 mol%) were added to the flask. The inlet vacuum adapter is changed to a septum, a bubbler (containing silicone oil) was connected to the septum and the bubbler was flushed with argon for 2 minutes by connecting an argon source to the septum. The reaction mixture was warmed to 100°C and stirred for 48 hours, then it was cooled down to room temperature, diluted with a mixture 3:2 diethyl ether:hexanes, filtered through a short path of alumina (neutral, activity 3), and the alumina was flushed with 3:2 diethyl ether:hexanes mixture to recover the entire product. The resulting mixture (solvent and crude) was washed with water (4 times), brine, and dried over

anhydrous Na_2SO_4. The solvent is removed in a rotary evaporator and the resulting crude was purified by chromatographic column on silica (previously neutralized with Et_3N) using 1:3 Et_2O:hexanes as eluent, yielding a white solid, 0.170 g, 98% yield. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.39 (s, 4H), 4.32 (q, 4H, J = 7.1 Hz), 4.17 (m, 8H), 3.99 (t, 4H, J = 4.0 Hz), 2.18 (m, 4H), 1.47 (m, 4H), 1.35 (t, 6H, J = 7.1 Hz), 1.30-1.10 (m, 36H), 0.84 (t, 6H, J = 6.6 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 161.43, 144.57, 135.61, 130.33, 129.44, 127.14, 108.26, 72.07, 71.98, 59.92, 46.17, 34.23, 32.11, 31.81, 29.87 (br), 29.82 (br), 29.71 (br), 29.54, 29.31, 26.68, 22.88, 14.76, 14.31. HRMS (ESI-TOF, $M+H^+$) m/z calcd. for $C_{50}H_{76}N_2O_8H$ 833.5674, found 833.5709.



Scheme 2-18. General procedure 3: decarboxylative cross-coupling using compound **9** in toluene/water.

Ethyl N-dodecyl-5-(thiophen-2-yl)-3,4-(propylene-1,3-dioxy)pyrrole-2-carboxylate (21). To a dry 50-mL round bottom flask containing a stir bar and argon atmosphere was added compound **9** (0.131 g, 0.309 mmol, 1 equiv.), $Pd(acac)_2$ (1.0 mg, 0.003 mmol, 2 mol%), (*m*-$NaSO_3Ph)Ph_2P$ (2.2 mg, 0.006 mmol, 4 mol%), *n*-Bu_4NBr (0.050 g, 0.155 mmol, 0.5 equiv.), K_2CO_3 (0.8 g) and aliquat-336 (a drop). The flask was equipped with a water-cooled condenser. An inlet vacuum adapter was connected to the condenser and the system was purged with vacuum-argon four times. Four mL of toluene (previously degassed), 0.04 mL of 2-bromothiophene (0.066 g, 0.402 mmol, 1.3 equiv.), and 2 mL of deionized water (previously degassed) were added. The reaction mixture was warmed up to 110°C and strongly stirred for 36h hours. The

reaction mixture was partitioned between diethyl ether and water, and the organic layer was washed with water (2 times), brine and dried over Na_2SO_4. The organic solvent was removed in a rotary evaporator and the crude was purified by chromatographic column on silica (previously neutralized with Et_3N) using 1:4 Et_2O:hexanes as eluent, yielding a pale yellow dense oil, 0.124 g, 87% yield. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.41 (dd, 1H, J=3.8 Hz, J = 3.9 Hz), 7.10 (m, 2H), 4.33 (q, 2H, J = 7.1 Hz), 4.23 (t, 2H, J = 7.7 Hz), 4.17 (t, 2H, J = 5.1 Hz), 4.02 (t, 2H, J = 5.2), 2.20 (quin, 2H, J = 5.0 Hz), 1.61 (m, 2H), 1.36 (t, 3H, J = 7.1 Hz), 1.32-1.13 (m, 18H), 0.87 (t, 3H, J = 6.7 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 161.3, 143.8, 136.2, 130.2, 128.7, 127.3, 127.1, 119.9, 108.6, 72.1, 72.0, 60.0, 46.2, 34.2, 32.1, 31.9, 29.8, 29.8, 29.7, 29.7, 29.5, 29.4, 26.7, 22.9, 14.7, 14.3. HRMS (APCI, $M+H^+$) m/z calcd. for $C_{26}H_{40}NO_4S$ 462.2673, found 462.2709. EA calculated for $C_{26}H_{39}NO_4S$: C (67.64%) H (8.51%) N (3.03%), Found: C (67.77%), H (8.64%), N (2.92%).

Diethyl 5,5'-(9-methylcarbazole-3,6-diyl)bis(N-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2-carboxylate) (12). The reaction was performed according to general procedure 1 at 110˚C and using potassium carboxylate **10** (0.554 g, 1.2 mmol, 2.2 equiv.), 3,6-dibromo-9-methylcarbazole (0.185 g, 0.545 mmol, 1 equiv), tri(*o*-tolyl)phosphine (6.6 mg, 0.022 mmol, 4 mol%), palladium(II) acetylacetonate (3.3 mg, 0.011 mmol, 2 mol%) and anhydrous N-methylpyrrolidone (1.5 mL, previously degassed). The crude was purified by chromatographic column on silica (previously neutralized with Et_3N) using 1:1 Et_2O:hexanes as eluent. A pale yellow sticky solid was gotten, 0.470g, 92% yield. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.07 (t, 2H, J = 1.0 Hz), 7.48 (d, 4H, J = 1.0 Hz), 4.35 (q, 4H, J = 7.1 Hz), 4.21 (m, 8H), 3.99 (t, 4H, J = 5.1), 3.92

(s, 3H), 2.20 (quin, 4H, J = 4.9 Hz), 1.49 (m, 4H), 1.39 (t, 6H, J = 7.1 Hz), 1.27 - 0.98 (m, 36H), 0.86 (t, 6H, J = 6.9 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 161.5, 144.6, 141.2, 135.4, 128.6, 128.6, 123.0, 122.9, 120.8, 108.7, 107.3, 72.1, 72.0, 59.8, 46.1, 34.3, 32.1, 31.8, 29.8, 29.8, 29.7, 29.7, 29.5, 29.5, 29.3, 26.7, 22.9, 14.8, 14.3. HRMS (APPI, $M+H^+$) m/z calcd. for $C_{57}H_{82}N_3O_8$ 936.6096, found 936.6103.

Diethyl 5,5'-(2,3-dihydrothieno[3,4-b][1,4]dioxine-5,7-diyl)bis(N-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2-carboxylate) (14). The reaction was performed according to general procedure 1 at 90˚C and using potassium carboxylate **10** (0.554 g, 1.2 mmol, 2.2 equiv.), 1,5-dibromoEDOT (0.164 g, 0.545 mmol, 1 equiv), tri(*o*-tolyl)phosphine (6.6 mg, 0.022 mmol, 4 mol%), palladium(II) acetylacetonate (3.3 mg, 0.011 mmol, 2 mol%) and anhydrous N-methylpyrrolidone (1.5 mL, previously degassed). The crude was purified by chromatographic column on silica (previously neutralized with Et_3N) using 1:3 Et_2O:hexanes as eluent, yielding a pale yellow sticky oil which solidified after several days under high vacuum, 0.485g, 99% yield. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 4.31 (q, 4H, J = 7.1 Hz), 4.24 (s, 4H), 4.17 (m, 8H), 4.02 (t, 4H, J = 5.08 Hz), 2.18 (quin, 4H, J = 5.0 Hz), 1.58 (m, 4H), 1.35 (t, 6H, J = 7.1 Hz), 1.28 – 1.10 (m, 36H), 0.86 (t, 6H, J = 6.7 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 161.1, 143.8, 139.5, 136.8, 116.2, 109.3, 106.0, 72.0, 64.7, 59.9, 46.6, 34.3, 32.1, 31.9, 29.8, 29.9, 29.8, 29.5, 27.0, 22.9, 14.7, 14.3. HRMS (APPI, $M+H^+$) m/z calcd. for $C_{50}H_{77}N_2O_{10}S$ 897.5293, found 897.5311.

Diethyl 5,5'-(9,9-dioctylfluorene-2,7-diyl) bis(N-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2-carboxylate) (13). The reaction was performed according to general procedure 1 at 105˚C and using potassium carboxylate **10** (0.554 g, 1.2 mmol, 2.2

equiv.), 9,9-dioctyl-2,7-dibromofluorene (0.299 g, 0.545 mmol, 1 equiv), tri(*o*-tolyl)phosphine (6.6 mg, 0.022 mmol, 4 mol%), palladium(II) acetylacetonate (3.3 mg, 0.011 mmol, 2 mol%) and anhydrous N-methylpyrrolidone (1.5 mL, previously degassed). The crude was purified by chromatographic column on silica (previously neutralized with Et_3N) using 1:3 Et_2O:hexanes as eluent. A colorless sticky oil was gotten, 0.606g, 97% yield. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.76 (d, 2H, J = 8.4 Hz), 7.35 (m, 4H), 4.34 (q, 4H, J = 7.1 Hz), 4.21 (m, 8H), 4.01 (t, 4H, J = 5.1 Hz), 2.21 (quin, 4H, J = 5.0 Hz), 1.98 (m, 4H), 1.47 (m, 4H), 1.38 (t, 6H, J = 7.1 Hz), 1.27-097 (m, 56H), 0.85 (t, 6H, J = 6.8 Hz), 0.80 (t, 6H, J = 6.9 Hz), 0.72 (m, 4H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 161.5, 151.2, 144.8, 140.6, 135.5, 129.4, 128.6, 128.4, 125.0, 120.0, 108.0, 72.0, 72.0, 59.9, 55.4, 46.3, 46.2, 46.2, 40.5, 34.3, 32.1, 32.0, 31.8, 30.3, 29.8, 29.9, 29.8, 29.8, 29.7, 29.5, 29.5, 26.8, 24.3, 22.9, 22.8, 14.8, 14.3, 14.3. HRMS (APPI, $M+H^+$) m/z calcd. for $C_{74}H_{115}N_2O_8$ 1145.8491, found 1145.8505.

Diethyl 5,5'-(naphthalene-2,6-diyl) bis(N-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2-carboxylate) (16). The reaction was performed according to general procedure 1 at 105˚C and using potassium carboxylate **10** (0.554 g, 1.2 mmol, 2.2 equiv.), 2,6-dibromonaphthalene (0.156 g, 0.545 mmol, 1 equiv), tri(*o*-tolyl)phosphine (6.6 mg, 0.022 mmol, 4 mol%) and palladium(II) acetylacetonate (3.3 mg, 0.011 mmol, 2 mol%) and anhydrous N-methylpyrrolidone (1.5 mL, previously degassed). The crude was recrystallized from MeOH yielding a yellow solid, 0.458g, 95% yield. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.92 (d, 2H, J = 8.4 Hz), 7.86 (s, 2H), 7.51 (d, 2H, J = 8.4 Hz), 4.36 (q, 4H, J = 7.1 Hz), 4.22 (m, 8H), 3.98 (t, 4H, J = 5.0 Hz), 2.20 (m, 4H), 1.51 (m, 4H), 1.39 (t, 6H, J = 7.1 Hz), 1.34–0.93 (m, 36H), 0.86 (t, 6H, J = 6.7 Hz). ^{13}C-NMR (75

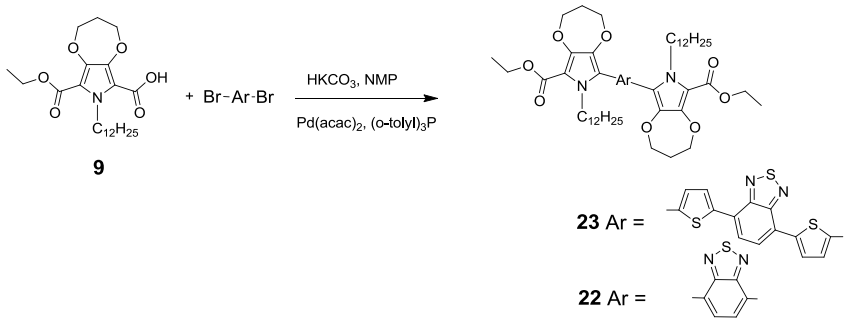
MHz, $CDCl_3$): 161.4, 144.6, 135.8, 132.7, 129.6, 128.5, 128.4, 128.0, 127.5, 108.3, 72.1, 72.0, 59.9, 46.3, 34.3, 32.1, 31.9, 29.8, 29.8, 29.6, 29.5, 29.3, 26.7, 22.9, 14.8, 14.3. HRMS (ESI, $M+Na^+$) m/z calcd. for $C_{54}H_{78}N_2O_8Na$ 905.5650, found 905.5719.

Diethyl 5,5'-(5,5'-(2,5-bis(dodecyloxy)-1,4-phenylene)bis(thiophene-5,2-diyl)) bis(N-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2-carboxylate) (20) The reaction was performed according to general procedure 1 at 105˚C and using potassium carboxylate **10** (0.252 g, 0.546 mmol, 2.2 equiv.), 5,5'-(2,5-bis(dodecyloxy)-1,4-phenylene)bis(2-bromothiophene) (0.191 g, 0.248 mmol, 1 equiv), tri(*o*-tolyl)phosphine (3.0 mg, 0.010 mmol, 4 mol%), palladium(II) acetylacetonate (1.5 mg, 0.005 mmol, 2 mol%) and anhydrous N-methylpyrrolidone (3 mL, previously degassed), differing only in that the workup was modified as follows: after the reaction was cooled down to room temperature, 50 mL of deionized water was added and the resulting solid was filtered and washed with a 1:1 mixture of water:MeOH. The solid was dissolved with ethyl acetate and filtered through a very short path of alumina (neutral, activity 3). The alumina was flushed with a mixture 2:3 ethyl acetate:hexanes to recover the entire product. The solvent was removed in vacuo and the resulting crude solid was stirred in hot EtOH, the mixture was cooled down and filtered yielding a yellow-orange solid, 0.325g, 96% yield. ^{1}H-NMR (300 MHz, C_6D_6): δ 7.63 (d, 2H, J = 3.9 Hz), 7.35 (s, 2H), 7.30 (d, 2H, J = 3.9 Hz), 4.65 (t, 4H, J = 7.4 Hz), 4.32 (q, 4H, J = 7.1 Hz), 3.85 (m, 8H), 3.74 (t, 4H, J = 5.0 Hz), 1.85 (m, 8H), 1.65 (m, 4H), 1.20-120 (m, 78H), 0.92 (m, 12H). ^{13}C-NMR (75 MHz, C_6D_6): 161.9, 150.3, 144.9, 141.4, 137.4, 131.6, 128.9, 126.1, 123.8, 121.0, 113.0, 109.9, 72.3, 72.1, 70.0, 60.0, 46.7, 34.8, 32.7, 32.7, 30.6, 30.5, 30.5, 30.5, 30.4, 30.3, 30.2, 30.2, 30.0, 27.4, 27.1, 23.5, 15.1, 14.8. EA calculated for

$C_{82}H_{128}N_2O_{10}S_2$: C (72.10%) H (9.44%) N (2.05%), Found: C (71.88%), H (9.27%), N (1.99%).

Diethyl 5,5'-(thiophene-2,5-diyl) bis(N-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2-carboxylate) (11). To a dry 25-mL round bottom flask containing a stir bar and argon atmosphere was added compound **10** (0.561 g, 1.215 mmol, 2.2 equiv.), tri(*o*-tolyl)phosphine (6.5 mg, 0.021 mmol, 4 mol%) and palladium(II) acetylacetonate (3.2 mg, 0.011 mmol, 2 mol%). The flask was equipped with an air-cooled condenser, then, the system is purged with vacuum-argon four times. Anhydrous *N*-methylpyrrolidone (1.5 mL, previously degassed) and 2,5-dibromothiophene (0.06 mL, 0.129 g, 0.532 mmol, 1 equiv.) were added *via* syringe. The vacuum adapter is changed to a septum and a bubbler was connected to it. The reaction mixture was warmed to 95°C and stirred for 36 hours, then it was cooled down to room temperature, diluted with 40 mL of a mixture 3:2 diethyl ether:hexanes, and filtered through a short path of alumina (neutral, activity 3). The alumina was washed with the mixture 3:2 diethyl ether:hexanes to recover the entire product. The mixture was washed with 30 mL deionized water (four times), brine and dried over Na_2SO_4. The solvent mixture (including the residual NMP) was removed in a rotary evaporator. The resulting solid was recrystallized from ethanol yielding 0.424 g of a pale yellow solid, 95% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.02 (s, 2H), 4.21 (m, 8H), 4.07 (t, 4H, J = 5.0 Hz), 3.94 (t, 4H, J = 5.0 Hz), 2.10 (quin, 4H, J = 5.0 Hz), 1.44 (m, 4H), 1.26 (t, 6H, J = 7.0 Hz), 1.18-1.02 (br, 36H), 0.76 (t, 6H, J = 6.6 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 161.02, 143.65, 136.00, 131.13, 128.01, 119.41, 108.68, 71.81, 59.78, 46.12, 33.94, 31.89, 31.77,

29.65, 29.61, 29.57, 29.32, 29.24, 26.59, 22.65, 14.50, 14.08. HRMS (APPI, $M+H^+$) m/z calcd. for $C_{48}H_{75}N_2O_8S$ 839.5259, found 839.5239.



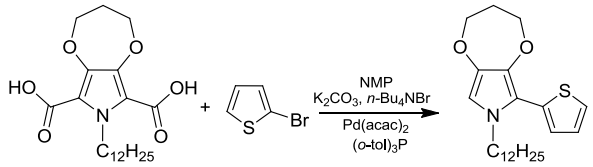
Scheme 2-19. Decarboxylative cross-coupling of ProDOP-monoacid **9** with BTD-based molecules using potassium bicarbonate.

Diethyl 5,5'-(benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(thiophene-5,2-diyl)bis(N-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2-carboxylate) (23). To a dry 25-mL round bottom flask containing a stir bar and under argon atmosphere was added compound **9** (0.060 g, 0.1417 mmol, 2.2 equiv.), and finely ground anhydrous potassium bicarbonate (0.0142 g, 0.1417 mmol, 2.2 equiv.). The flask was equipped with an air-cooled condenser; an inlet vacuum adapter was connected to the top of the condenser, and the system was purged with vacuum-argon four times, then NMP (5.5 mL, previously degassed) was added *via* syringe. The mixture was warmed to 50°C and stirred for 1 hour (vacuum was slightly applied several times to remove CO_2 and to help the neutralization process), then 4,7-bis(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole (29.5 mg, 0.0644 mmol, 1 equiv), tri(*o*-tolyl)phosphine (1.2 mg, 0.0039 mmol, 6 mol%) and palladium(II) acetylacetonate (0.6 mg, 0.0019 mmol, 3 mol%) were added. The system was then equipped with a septum and a bubbler (containing silicon oil); the reaction mixture was warmed 90 °C and stirred for 24 hours. The solvent was removed in a rotary evaporator at 80°C, then the crude was dissolved in hexanes:ethyl acetate 3:1 and filtered through a short path (~1 cm) of neutral alumina (activity 3); the alumina

was flushed with the hexanes:EtOAc mixture to recover the entire product. The solvent was removed in a rotary evaporator, and the resulting crude oil was dissolved in hexanes, washed with deionized water (3x), brine (1x), and dried over Na_2SO_4. The mixture was filtered and the solvent was removed in a rotary evaporator; the resulting sticky solid was subjected to vacuum overnight. Then, 2 mL of ethanol was added, and the mixture was slightly warmed, and diethyl ether was added until the solid dissolved. Slow evaporation of the diethyl ether produced a purple powdery solid, which was filtered, washed with ethanol, and air-dried for 2 minutes, then put under vacuum to remove the solvent traces, 60.8 mg (89% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): δ_H 8.17 (d, 2H, J = 3.9 Hz), 7.89 (s, 2H), 7.24 (d, 2H, J = 3.9 Hz), 4.35 (q, 8H, J = 7.1 Hz), 4.20 (t, 4H, J = 4.9 Hz), 4.09 (t, 4H, J = 5.1 Hz), 2.24 (m, 4H), 1.68 (m, 4H), 1.38 (t, 6H, J = 7.1 Hz), 1.19 (m, 34H), 0.84 (t, 6H, J = 6.8 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 161.3, 152.8, 144.0, 140.5, 136.5, 131.8, 129.3, 127.9, 125.9, 125.7, 119.9, 109.3, 72.2, 72.1, 60.1, 46.5, 34.2, 32.1, 32.0, 29.9, 29.8, 29.8, 29.8, 29.6, 29.4, 26.8, 22.9, 14.8, 14.3. HRMS (DART-TOF, $M+H^+$) m/z calcd. for $C_{58}H_{78}N_4O_8S_3H$ 1055.5055, found 1055.5089.

Diethyl 5,5'-(benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(N-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2-carboxylate) (22). Using compound **9** (0.1700 g, 0.4014 mmol, 2.1 equiv.), finely ground anhydrous potassium bicarbonate (0.0398 g, 0.3976 mmol, 2.08 equiv.), NMP (9 mL, previously degassed), 4,7-dibromobenzo[c][1,2,5]thiadiazole (56.2 mg, 0.1911 mmol, 1 equiv), tri(*o*-tolyl)phosphine (4.6 mg, 0.0153 mmol, 8 mol%) and palladium(II) acetylacetonate (2.3 mg, 0.0077 mmol, 4 mol%), the reaction was run for 72 hours using the same procedure as for **23**, although the workup was modified as

follows: The solvent was concentrated by rotary evaporation at 80°C to ~1 mL; then the mixture was dissolved in diethyl ether; washed with water (5x), brine (1x), and dried over Na_2SO_4 and purified by chromatographic column on silica using 1:1 diethyl ether:hexanes as eluent. The product was isolated as an orange solid (paraffin like), 0.160 g (94% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.63 (s, 2H), 4.34 (dd, 4H, J = 7.0 Hz, J = 14.1 Hz), 4.22 (br, 8H), 3.99 (m, 4H), 2.18 (m, 4H), 1.50 – 1.28 (m, 10H), 1.28 – 0.88 (m, 36H,), 0.84 (t, 6H, J = 7.1Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 161.3, 154.2, 144.3, 136.8, 131.5, 123.5, 122.6, 109.5, 72.0, 72.0, 60.0, 46.9, 34.3, 32.0, 31.8, 29.8, 29.7, 29.6, 29.6, 29.5, 29.2, 26.6, 22.8, 14.7, 14.2. HRMS (DART, M+H$^+$) m/z calcd. for $C_{50}H_{74}N_4O_8SH$ 891.5300, found 891.5295.

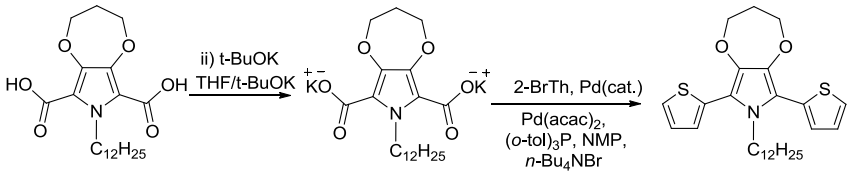


24 **28**

Scheme 2-20. Decarboxylative cross-coupling of ProDOP-diacid **24** using potassium carbonate and tetra(*n*-butyl)ammonium bromide.

***N*-Dodecyl-3,4-(propylene-1,3-dioxy)-2-(thiophen-2-yl)pyrrole (28)**. To a dry 25-mL round bottom flask containing a stir bar and under argon atmosphere was added diacid **24** (0.137 g, 0.3462 mmol, 1 equiv.), finely ground anhydrous potassium carbonate (0.144 g, 1.0386 mmol, 3 equiv.) and *n*-Bu_4NBr (0.112 g, 0.3462 mmol, 1 equiv.). The flask was equipped with an air-cooled condenser; a vacuum adapter was connected to the top of the condenser and the system was purged with vacuum-argon four times, and then *N*-methylpyrrolidone (4 mL, previously degassed) was added *via* syringe. The mixture was warmed to 70°C and stirred for 1 hour, and then 0.074 mL of 2-bromothiophene (0.124g, 0.7615 mmol, 2.2 equiv), tri(*o*-tolyl)phosphine (4.7 mg,

0.0152 mmol, 2 mol%) and palladium(II) acetylacetonate (2.3 mg, 0.0076 mmol, 1 mol%) were added. The system was then equipped with a septum and a bubbler (containing silicon oil); the reaction mixture was stirred at 70 – 75˚C for 48 hours. The mixture was cooled to room temperature and partitioned between diethyl ether and water in a separatory funnel, then washed with plenty of water (5x), brine (1x), and dried over Na_2SO_4; the solvent was removed in a rotary evaporator and the resulting crude was purified by chromatographic column on silica (previously neutralized with triethylamine) using 1:2 diethyl ether:hexanes as eluent. The product was isolated as a pale yellow oil, which was subjected to high vacuum for 6 hours and then stored under argon atmosphere, 0.124 g (92% yield).^{1}H-NMR (300 MHz, CD_2Cl_2): δ 7.34 (ddd, 1H, J = 1.3 Hz, J = 5.0 Hz, J = 15.9 Hz), 7.09 (m, 1H), 7.01 (dd, 1H, J = 1.2 Hz, J = 3.5 Hz), 6.29 (s, 1H), 3.98 (m, 4H), 3.79 (t, 2H, J = 7.4 Hz), 2.13 (m, 2H), 1.61 (td, 2H, J = 5.2 Hz, J = 10.4 Hz), 1.48 – 1.00 (m, br, 18H), 0.88 (t, 3H, J = 6.7 Hz). ^{13}C-NMR (75 MHz, D_2CCl_2): δ_C 138.9, 127.5, 127.4, 127.3, 126.5, 125.9, 125.3, 107.6, 73.1, 72.9, 48.2, 35.8, 32.5, 31.7, 30.2, 30.1, 30.0, 29.9, 29.7, 29.5, 27.1, 23.3, 14.5. HRMS (ESI-DART, $M+H^+$) m/z calcd. for $C_{23}H_{35}NO_2SH$ 390.2461, found 390.2459.



24 **29** **25**

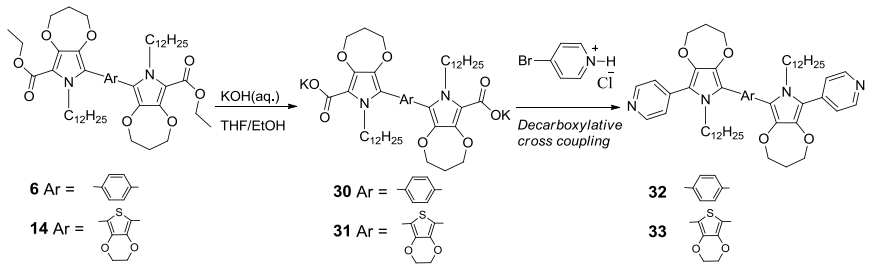
Scheme 2-21. Decarboxylative cross-coupling using the ProDOP-dicarboxylate salt **29**.

Potassium *N*-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2,5-dicarboxylate (29). This compound can be prepared by two different methods: To a dry 50-mL round bottom flask containing a stir bar and under argon atmosphere was added 0.2270 g of *t*-BuOK (2.0228 mmol, 2 equiv.). The flask was equipped with a septum and then 4 mL

of anhydrous *t*-BuOH and 15 mL of anhydrous THF were added *via* cannula. After the *t*-BuOK dissolved; a solution of compound **24** (0.4000g, 1.0114 mmol, 1 equiv.) in 10 ml of anhydrous THF was slowly added *via* cannula. The mixture was stirred for 30 minutes, and then the solvent was carefully removed in a rotary evaporator (anhydrous conditions were assured by flushing the rotary evaporator with nitrogen). A pale tan solid was gotten, which was subjected to high vacuum overnight, 0.4771 g (100% yield). FTIR (KBr, pellet) $\bar{\nu}$ (cm^{-1}): 3391.1 (br, w), 2925.8 (s), 2853.7 (s), 1618.5 (s), 1589.9 (s), 1419.5 (S), 1340.5 (s), 1132.9 (m), 1081.3 (s), 806.1 (m). Alternatively, the procedure was also carried out using deionized water (4 mL), potassium hydroxide (0.1135 g, 2.0228 mmol, 2 equiv.) and compound **24** (0.4000g, 1.0114 mmol, 1 equiv.), After removal of the water by rotary evaporation the resulting solid was dried under vacuum at 60°C for 3h.

***N*-Dodecyl-2,5-di(thiophen-2-yl)-3,4-(propylene-1,3-dioxy)pyrrole (25).** To a dry 25-mL round bottom flask containing a stir bar and under argon atmosphere was added compound **29** (0.112 g, 0.2375 mmol, 1 equiv.), *n*-Bu_4NBr (0.153 g, 0.4749 mmol, 2 equiv.), tri(*o*-tolyl)phosphine (6.4 mg, 0.021 mmol, 4 mol%), and palladium(II) acetylacetonate (3.2 mg, 0.011 mmol, 2 mol%). The flask was equipped with an air-cooled condenser, then an inlet vacuum adapter was connected to the top of the condenser and the system was purged with vacuum-argon four times, and then 0.05 mL of 2-bromothiophene (0.0852 g, 0.5224 mmol, 2.2 equiv), and anhydrous N-methylpyrrolidone (2 mL, previously degassed) were added *via* syringe. The system was then equipped with silicone oil bubbler, and the reaction mixture was warmed to 70-75°C and stirred for 36 hours. On cooling to room temperature, the mixture was

partitioned between diethyl ether and water; washed with water (5x), brine (1x), and dried over Na_2SO_4. The organic solvent mixture (including the residual NMP) was removed in a rotary evaporator. The resulting crude was purified by chromatographic column on silica (previously neutralized with Et_3N) using 1:4 Et_2O:hexanes as eluent. The product was isolated as a pale yellow paraffin-like solid, 0.078g, 69% yield. ^{1}H-NMR (300 MHz, $CDCl_3$): δ_H 7.35 (dd, 2H, J = 2.4 Hz, J = 3.8 Hz), 7.10 (m, 4H), 4.05 (t, 4H, J = 5.0 Hz), 4.00 (t, 2H, J = 7.9 Hz), 2.07 (quin, 2H, J = 5.0 Hz), 1.47 (m, 2H), 1.34-1.09 (br, m, 18H), 0.90 (t, 3H, J = 6.8 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ_C 137.3, 132.0, 127.2, 126.9, 125.5, 113.1, 72.5, 45.4, 35.0, 32.1, 31.1, 29.8, 29.7, 29.5, 29.1, 26.5, 22.9, 14.3. HRMS (ESI-TOF, M+H$^+$) m/z calcd. for $C_{27}H_{37}NO_2S_2H$ 472.2338, found 472.2357.



Scheme 2-22. Decarboxylative cross-coupling using the potassium ProDOP-dicarboxylate salts **30** and **31**.

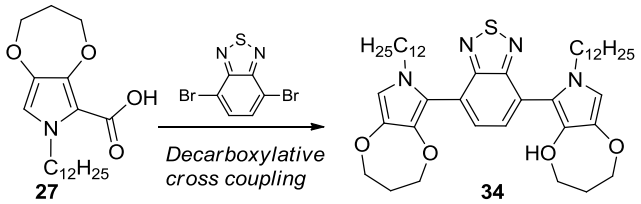
Potassium 5,5'-(1,4-phenylene)bis(*N*-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2-carboxylate) (30). To a 50-mL round bottom flask containing a stir bar was added diester **6** (0.262 g, 0.3145 mmol), THF (6 mL) and ethanol (6 mL). After the solid dissolved, 3.8 mL of [5M] KOH (19 mmol, 60 equiv.) was added, and the mixture was degassed by bubbling argon for 10 min. The flask was equipped with a condenser and the reaction mixture was heated to 55 – 60°C with strong stirring under argon for 72 hours. The reaction mixture was filtered using glass wool (to remove traces of

palladium black), and then the organic solvents (THF and ethanol) and most of the water were carefully removed in a rotary evaporator at 25 C which produced precipitation of the potassium decarboxylate salt. The resulting solid was filtered, washed with slightly basic cold water, air-dried for 5 minutes and washed with hexanes. The pale yellow solid (hydrated) was then put under vacuum (0.1 mmHg) at 115°C for 72 hours. The final product was isolated as a white solid, 0.247 g, 92% yield. ^{1}H-NMR (300 MHz, d_6-DMSO): δ_H 7.24 (s, 4H), 4.23 (t, 4H, J = 6.9 Hz), 3.82 (dd, 8H, J = 5.9 Hz, J = 9.5 Hz), 1.97 (m, 4H), 1.32 – 0.90 (br, m, 40H), 0.84 (t, 6H, J = 6.5 Hz). FTIR (KBr, pellet) $\bar{\nu}_{max}$ (cm^{-1}): 3395.5 (br, w), 2924.7 (s), 2853.5 (s), 1566.0 (s), 1447.9 (s), 1417.5 (s), 1356.9 (s), 1081 (s), 1138.1 (w), 806.3 (m).

Potassium 5,5'-(3,4-(ethylene-1,2-dioxy)thiophene-2,5-diyl)bis(N-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2-carboxylate) (31). The reaction was performed using a similar procedure as for **30**. Using 2.521 g of **14** (2.810 mmol), 54 mL of THF, 54 mL of EtOH, and 34 mL of [5M] KOH. The workup was slightly modified as follows: After removal of the volatiles, the resulting gum-like solid was filtered, washed with slightly basic cold water, and air-dried for 10 minutes. The pale yellow solid was subjected to vacuum overnight at room temperature; yielding an amber solid which was ground in a mortar, producing a fine yellow powder, 2.548 g, 99% yield. ^{1}H-NMR (300 MHz, d_6-DMSO): δ_H 4.16 (m, 8H), 3.83 (m, 8H), 1.97 (m, 4H), 1.39 – 0.09 (m, 40H), 0.84 (t, 6H, J = 6.5 Hz). ^{13}C-NMR (75 MHz, d_6-DMSO): δ_C 163.7, 138.3, 137.2, 137.2, 136.7, 120.2, 105.9, 105.9, 71.3, 71.0, 64.0, 34.6, 31.4, 31.4, 31.2, 29.1, 29.0, 29.0, 28.9, 28.6, 26.4, 22.0, 13.8. FTIR (KBr, pellet) $\bar{\nu}_{max}$ (cm^{-1}): 3392.1 (m), 2924.2 (s), 2853.7 (s), 1580.8 (s), 1510.7 (m), 1462.0 (s), 1420.6, 1420.6 (s), 1358.6 (s), 1080.6, 954.9 (w), 806.9 (w).

Synthesis of 5,5'-(1,4-phenylene)bis(*N*-dodecyl-2-(pyridin-4-yl)-3,4-(propylene-1,3-dioxy)pyrrole) (32). To a dry 50-mL round bottom flask containing a stir bar and under argon atmosphere was added compound **30** (0.233g, 0.2725 mmol, 1 equiv.), 4-bromopyridine hydrochloride (0.1113g, 0.5723 mmol, 2.1 equiv.), anhydrous K_2CO_3 (0.083 g, 0.600 mmol, 2.2 equiv.), *n*-Bu_4NBr (0.220 g, 0.6814 mmol, 2.5 equiv.), tri(*o*-tolyl)phosphine (7 mg, 0.0229 mmol, 4 mol%) and palladium(II) acetylacetonate (3.5 mg, 0.0114 mmol, 2 mol%). The flask was equipped with an air-cooled condenser then an inlet vacuum adapter was connected to the top of the condenser and the system was purged with vacuum-argon four times, then N-methylpyrrolidone (6 mL, previously degassed) was added *via* syringe. The system was then equipped with a silicon oil bubbler and the reaction mixture was warmed to 70 – 75°C and stirred for 60 hours. The reaction mixture was concentrated to ~1 mL in a rotary evaporator (at 80°C), and then it was cooled to room temperature; partitioned between diethyl ether and water, and then washed with water (5x), brine (1x), and dried over Na_2SO_4. The resulting crude was purified by chromatographic column on basic alumina using a solvent gradient from 1:0 to 0:1 Et_2O:EtOAc as eluent; yielding 0.147 g of a yellow solid, 64% yield. ^{1}H-NMR (300 MHz, $CDCl_3$): δ_H 8.60 (d, 4H, J = 5.5 Hz), 7.49 (s, 4H) 7.37 (d, 4H J = 5.5 Hz), 4.03 (dd, 8H, J = 5.0 Hz, J = 9.7 Hz), 3.78 (t, 4H, J = 7.0 Hz), 2.19 (m, 4H), 1.24 – 0.72 (br, m, 46H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ_C 149.8, 139.6, 139.1, 137.7, 129.6, 129.4, 123.9 (br), 123.0, 118.5, 72.3, 46.4, 34.8, 30.1, 29.8(br), 29.8(br), 29.6, 29.5(br), 29.5, 29.0, 26.2, 22.9, 14.3. HRMS (MALDI, sithianol matrix, $M+H^+$) m/z calcd. for $C_{54}H_{74}N_4O_4H$ 843.5783, found 843.5765.

Synthesis of 5,5'-(3,4-(ethylene-1,2-dioxy)thiophene-2,5-diyl)bis(N-dodecyl-2-(pyridin-4-yl)-3,4-(propylene-1,3-dioxy)pyrrole) (33). The reaction was performed using the same procedure as for **32**; using **31** (0.250g, 0.2725 mmol, 1 equiv.), 4-bromopyridine hydrochloride (0.1113g, 0.5723 mmol, 2.1 equiv.), anhydrous K_2CO_3 (0.083 g, 0.600 mmol, 2.2 equiv.), *n*-Bu_4NBr (0.220 g, 0.6814 mmol, 2.5 equiv.), tri(*o*-tolyl)phosphine (7 mg, 0.0229 mmol, 4 mol%), palladium(II) acetylacetonate (3.5 mg, 0.0114 mmol, 2 mol%) and 6 mL of NMP. The product was isolated as a pale orange solid, 0.195 g (79% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): δ_H 8.56 (d, 4H, J = 6.1 Hz), 7.31 (d, 4H, J = 6.2 Hz), 4.28 (s, 4H) 4.02 (m, 8H), 3.92 (t, 4H, J = 7.1 Hz), 2.16 (m, 4H), 1.40 – 0.89 (br, m, 40), 0.84 (t, 6H, J = 6.8 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ_C 149.8, 138.9, 138.6, 138.5, 138.2, 123.2, 118.4, 112.3, 106.8, 72.3, 64.8, 46.0, 34.8, 32.0, 30.6, 29.8, 29.7 (br), 29.6, 29.6, 29.5, 29.2, 26.6, 22.8, 14.2. HRMS (ESI-TOF, $[M+H]^{2+}$) m/z calcd. for $C_{54}H_{74}N_4O_6SH_2$ 454.2737, found 454.2743.



27 34

Scheme 2-23. Decarboxylative cross-coupling using the ProDOP-monoacid **27** and 4,7-dibromobenzo[c][1,2,5]thiadiazole.

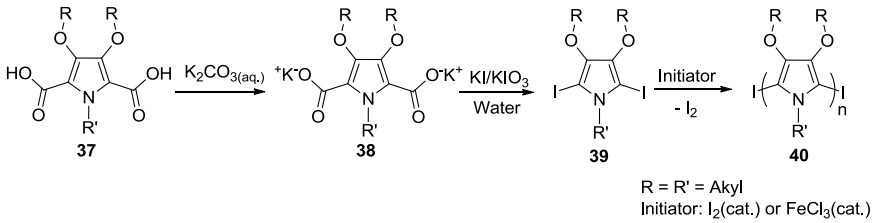
Synthesis of 4,7-bis(N-dodecyl-3,4-(propylene-1,3-dioxy)pyrrol-2-yl)benzo[c][1,2,5]thiadiazole (34). To a dry 25-mL round bottom flask containing a stir bar and under argon atmosphere was added compound **27** (0.3 g, 0.8535 mmol, 2.5 equiv.), and finely ground anhydrous potassium bicarbonate (0.089 g, 0.8877 mmol, 2.6 equiv.). The flask was equipped with an air-cooled condenser; an inlet vacuum adapter was connected to the top of the condenser and the system was purged with vacuum-

argon four times, and then NMP (15 mL, previously degassed) was added *via* syringe. The mixture was warmed to 35°C and stirred for 1 hour (vacuum was slightly applied several times to remove CO_2 and to help the neutralization process), and then 4,7-dibromobenzo[c][1,2,5]thiadiazole (0.100 g, 0.3414 mmol, 1 equiv), tri(*o*-tolyl)phosphine (6.2 mg, 0.0205 mmol, 6 mol%) and palladium(II) acetylacetonate (3.11 mg, 0.0102 mmol, 3 mol%) were added. The system was then equipped with a septum, and a bubbler (containing silicon oil), and the reaction mixture was warmed 80 – 82°C and stirred for 42 hours. The solvent was removed in a rotary evaporator at 80°C. The crude was dissolved in dichloromethane and washed with water. The dichloromethane was removed by rotary evaporation and the resulting crude was purified by chromatographic column on silica (previously neutralized with triethylamine); using a 2:1 ether:hexanes mixture as eluent; yielding 0.112 g of a bright red oil (44% yield). ^{1}H-NMR (300 MHz, DCM-d_2): δ_H 7.55 (s, 2H), 6.45 (s, 2H), 4.03 (t, 4H, J = 4.3 Hz), 3.96 (t, 4H, J = 4.8 Hz), 3.71 (t, 4H, J = 7.2 Hz), 2.13 (m, 4H), 1.67 – 0.98 (m, br, 40 H), 0.87 (t, 6H, J = 6.7 Hz). ^{13}C-NMR (75 MHz, DCM-d_2): δ_C 54.9, 139.4, 138.0, 131.1, 123.8, 115.7, 108.0, 73.1, 73.0, 48.9, 35.9, 32.5, 31.6, 30.2, 30.2, 30.1, 30.0, 29.9, 29.7, 27.1, 23.3, 14.5. HRMS (APCI, $[M+H]^+$) m/z calcd. for $C_{44}H_{66}N_4O_4SH$ 747.4878, found 747.4876.

CHAPTER 3
SYNTHESIS OF DIOXYPYRROLE-BASED POLYMERS *VIA* DEHALOGENATION POLYCONDENSATION

Dehalogenation Polycondensation

As was mentioned previously, 2,5-dihalo-3,4-dioxypyrroles (dihalo-XDOPs) tend to decompose or to oligomerize;[32] consequently, to take advantage of this type of chemical behavior, Walczak *et al.* explored this feature to generate polymers from diiodo-XDOPs. [23,56] The deiodination polycondensation resulted a convenient methodology to synthesize XDOP-based materials, and the method was successfully applied to the synthesis of homopolymers[23] and both block and random copolymers.[56] A description of the method is shown in Scheme 3-1. The method is a three-step synthesis, starting from the XDOP diacid **37** and requiring the isolation and purification of the intermediate **39**. This diiodo compound can be polymerized in bulk or using a suitable solvent.

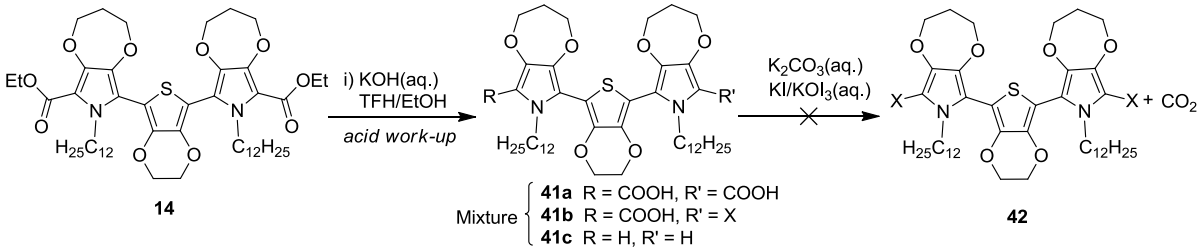


Scheme 3-1. Synthesis and polymerization of 2,5-diodo-3,4-dioxypyrroles previously reported by Walczak et al..[23]

The research carried out by Walczak showed that the deiodination polycondensation effectively generates high molecular weight polymers and can be scaled up without the use of metals, oxidants, solvents, or other additives. Additionally, the methodology is aqueous compatible and tolerant to many functionalities, allowing the synthesis of various types of XDOP polymers. The research presented here describes a modified version of the deiodination polycondensation method.[23] This new

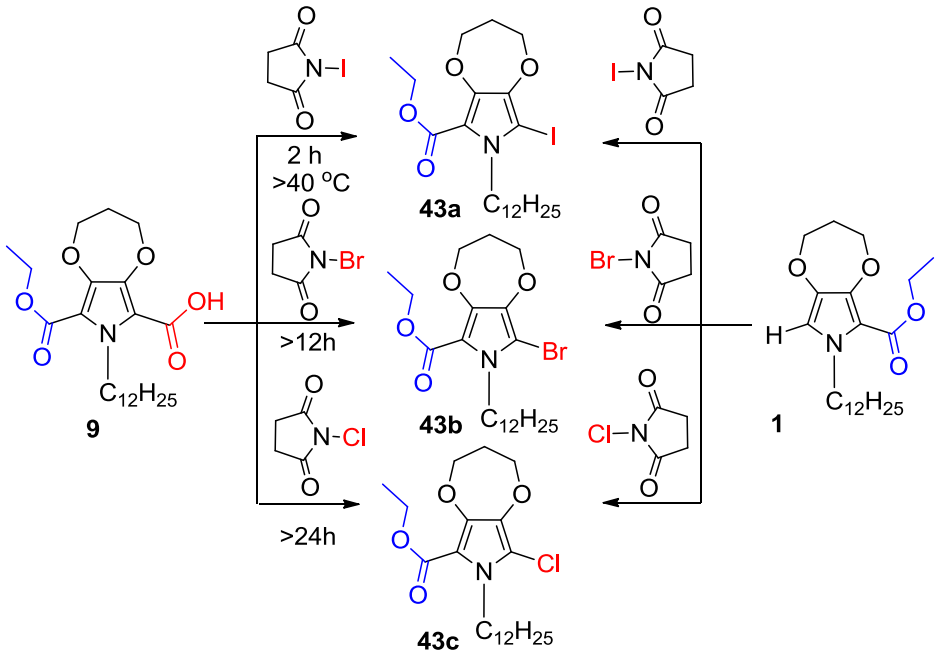
methodology can not only be applied to the polymerization of the XDOP monomers that were previously reported by Walczak *et al.*,[23] but also to new XDOP-based monomers that cannot be polymerized efficiently by the original approach.

Attempts to extend the deiodination polycondensation method to produce regioregular copolymers from discrete oligomers, such as the 3,4-propylendioxypyrrole (ProDOP) derivative **14** shown in Scheme 3-2, failed. The partial decarboxylation, high reactivity and low solubility in aqueous base of **41a** hindered its utilization for the iododecarboxylation using triiodide. The partial loss of the carboxylic functionalities occurred during the hydrolysis of **14** and was confirmed by proton NMR, which showed that the reaction crude is approximately a mixture 24:6:1 of diacid **41a**, monoacid **41b** and non-substituted dioxypyrrole oligomer **41c**. The partial decarboxylation occurred even if the hydrolysis was carried out at relatively low temperature (<40˚C).



Scheme 3-2. Polymerization attempt for a ProDOP-based oligomer using the triiodide route.

Due to the problems applying the Walczak method to this new XDOP system, it was convenient to search for an alternative source of electrophilic iodide, and as shown in Scheme 3-3, compounds **1** and **9** were employed as trial molecules. Conveniently, it was found that the *N*-halosuccinimides can produce the halo compound *via* electrophilic halogenation on the 3,4-dioxypyrrole **1**, and also by halo-decarboxylation of the carboxylic acid **9**.



Scheme 3-3. Halodecarboxylation and halogenation of two 3,4-propylenedioxypyrroles using *N*-halosuccinimides.

In order to obtain information about the degree of conversion of the halo-decarboxylation, the iododecarboxylation reaction using *N*-iodosuccinimide (NIS) was run in an NMR tube and the ^{1}H-NMR signal was monitored throughout the reaction (Figure 3-1). The ^{1}H-NMR experiment showed that the iododecarboxylation took place in less than 2 hours, and full conversion was observed. The monitoring of the reaction was carried out using the α-methylene of the $C_{12}H_{25}$ chain, and it was possible to observe that the reaction proceeded to high conversion with no byproducts present, apart from the *N*-*H*-succinimide and a small amount of the diodo-ProDOP (δ_H 4.6 ppm) which formed from the diacid-ProDOP that was present in the starting material. The halodecarboxylation occurred considerably slower for the other *N*-halosuccinimides – *N*-bromosuccinimide (NBS) and *N*-chlorosuccinimide (NCS) – requiring longer reaction times, and in these cases full conversion was not observed. Various byproducts were

visible in the TLC, with one of the byproducts being identified as the dimerization product.

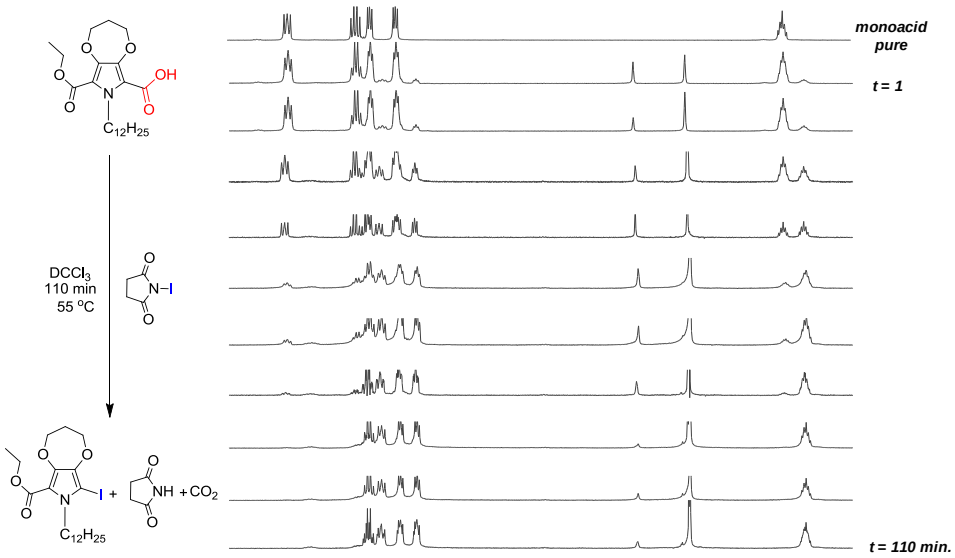
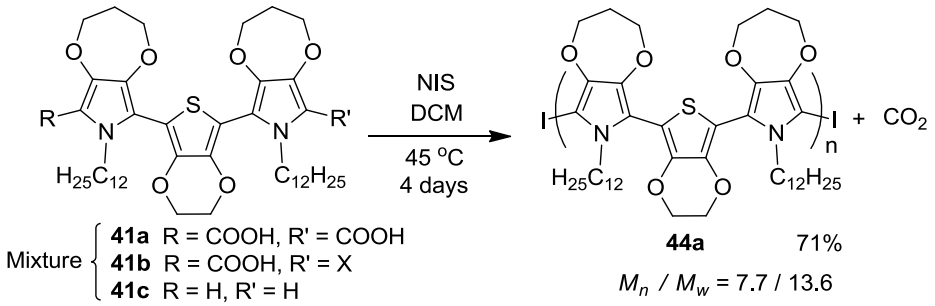


Figure 3-1. Proton-NMR monitoring of the degree of conversion of a ProDOP monoacid using NIS in $DCCl_3$. t = 1: reaction mixture ~1 minute after reactants were added to the NMR tube at 25˚C. t = 110: the same reaction run for 110 minutes at 55˚C.

A test reaction using NIS and the oligomeric mixture **41a-c** was carried out, and as shown in Scheme 3-4, acceptable molecular weights were obtained in a 4-day reaction.

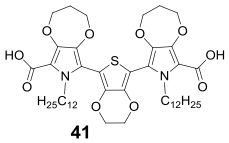
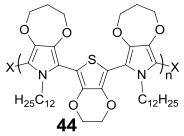
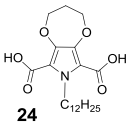
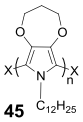
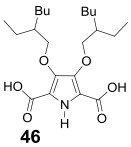
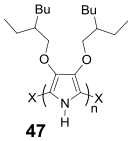


Scheme 3-4. In situ halo-decarboxylation and dehalo-polycondensation of the oligomeric mixture **41a-c**.

The same reaction was carried out using NBS and NCS for three different ProDOP carboxylic acids, and the results are shown in Table 3-1. Although, some of the reactions presented in Table 3-1 produced acceptable molecular weights, these molecular weights can be considered too low to produce the desired electronic

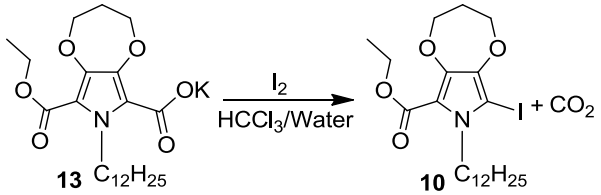
properties; therefore, it was necessary to explore other alternatives for this type of polymerization.

Table 3-1. Polymerization of various ProDOP-dicarboxylic acids via dehalogenation polycondensation using *N*-halosuccinimides.

entry	monomer[a]	*X-source*	polymer	M_n / M_w (kDa)	Yield (%)[a]
1	 **41**	NIS NBS NCS	 **44**	44a X = I: 7.7 / 13.6 44b X = Br: 6.3 / 8.9 44c X = Cl: 5.0 / 6.3	71[b] 83[b] 39[b]
2	 **24**	NIS NBS NCS	 **45**	45a X = I: 6.9 / 17.4 45b X = Br: 0.9 / 1.1 45c X = Cl: 1.1 / 1.5	60 76 79
3	 **46**	NIS	 **47**	47 X = I: 3.7 / 5.2	31

[a]The yields were calculated using the equation reported previously,[23] and based on the potassium salt for entry 1. [b]The crude mixture was used for the polymerization after acidic work-up of the respective potassium salt.

It was also found that the potassium ProDOP carboxylates can be also employed directly for the halo-decarboxylation in combination with iodine. A model reaction was carried out, and it proceeded in less than one hour when run at 60˚C (monitored by TLC), shown in Scheme 3-5.

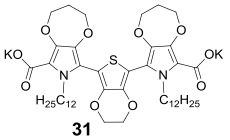
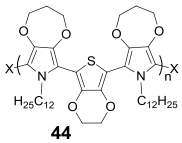
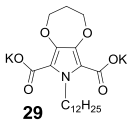
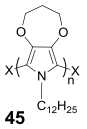
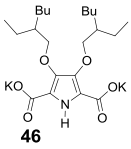
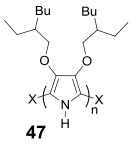


Scheme 3-5. Halo-decarboxylation of the potassium ProDOP-carboxylate **13** using iodine.

Evaluation of this reaction for the synthesis of ProDOP-based polymers showed higher molecular weights than the *N*-halosuccinimides, and the results are presented in Table 3-2. Bromine was also evaluated for the polymerization of ProDOP carboxylates,

but the method did not yield any promising result, and only oligomeric materials were received (Table 3-2). NIS in combination with the potassium ProDOP-dicarboxylate produced similar molecular weights as when the ProDOP-diacid was employed (Table 3-2, entry 1).

Table 3-2. Polymerization of various ProDOP-dicarboxylic acids via dehalogenation polycondensation using various halogen sources.

entry	monomer[a]	X-source	polymer	M_n / M_w (kDa)	Yield (%)[a]
1	 **31**	I_2 Br_2 NIS	 **44**	44a X = I: 22.9 / 58.1 44b X = Br: 1.3 / 1.9 44a X = I: 6.2 / 10.0	67 66 20[b]
2	 **29**	I_2 Br_2	 **45**	45a X = I: 15.9 / 35.7 45b X = Br: 0.9 / 1.9	55 48
3	 **46**	I_2	 **47**	47 X = I: 2.1 / 2.8	36

[a]The yields were calculated using the equation reported previously,[23] and based on the potassium salts. [b]The polymer did not precipitate in methanol, so after removal of the solvent *in vacuo*, the resulting crude was washed with water and methanol, and then dried under vacuum.

The lower molecular weights when NIS was employed, instead of I_2, may be attributed to the reaction of the *N*-*H*-succinimide with the polymer end groups, which produces end-capping of the polymer and causing the reaction to stop. The polymerizations presented in Tables 3-1 and 3-2 can be run at relatively low temperatures (40 – 60˚C), and the polymerization using NIS required longer reaction times (>4 days) than iodine (~48h). Additionally, due to the low solubility of the potassium carboxylates, water was required for the reaction to proceed when I_2 was

employed. DCM or chloroform is a suitable solvent for this polymerization, since these solvents can dissolve both the polymer and the starting materials. THF was also tested as solvent for the synthesis of **45a** using NIS and similar results were observed (M_n = 6.2kDa M_w = 10.4kDa) as when DCM or chloroform was employed.

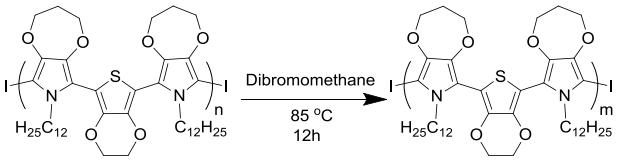
This method did not generate high molecular weights for *N*-*H*-XDOPs (entry 3, in Table 3-1 and Table 3-2), but it is logic to anticipate that the methodology can efficiently create polymers based on *N*-alkyl-3,4-dioxypyrroles, and it can be also applied to different types of XDOP monomers. Compared with the $FeCl_3$ oxidative polymerization, it is expected that the reaction displays higher functionality tolerance and lower sensitivity toward presence of water.

After the reaction was stopped, the polymer needs to be de-doped by addition of hydrazine; this is necessary since the reaction produces a polymer in its doped form. It is worthy to note that since I_2, Br_2 and Cl_2 are released during the reaction, side reaction can occurs, such as halogenation, on the non-substituted positions of aromatic rings if non-substituted aromatic systems are employed.

In most cases, the dehalopolycondensation started spontaneously, but if it did not occur, the polymerization reactions were initiated with UV-light by irradiating the reaction vessel for one minute using a standard TLC UV-lamp—i.e. if *N*-halosuccinimides were employed. The use of UV-light for a few minutes (1 – 3 min.) catalyzes the initial condensation of the monomer which releases iodine, and which in turn oxidizes the oligomers that have just formed, apparently initiating a chain-growth polycondensation reaction; thus, the reaction seems to proceed by a combination of

step and chain growth polycondensation mechanism.[57] Other feasible initiators can be an iodine crystal or a catalytic amount of $FeCl_3$.

Increasing the number of equivalents of NIS did not lead to polymers with higher molecular weights. Additionally, if less than two equivalents of NIS was used a decrease in the molecular weight (M_n = 4.9kDa, M_w = 7.7kDa for **45a**) was observed, also yielding a polymer with a dark appearance. Since typically poly-XDOPs are colorless, this could mean that polymer decomposition occurred, or impurities due to side reactions were present in the polymeric material. The end groups for these polymers are assumed to be halogens; thus, all the molecules described in Table 1 can perform as macromers or pre-polymers. These end groups can be further employed to produce higher molecular weight polymers or to make an additional derivatization on the polymeric chain. The reaction shown in Scheme 3-6 not only proves that the polymer end groups are still active but also shows that polymer **44a** can behave as a macromer. The pre-polymer **44a**, presented in Scheme 3-6, was prepared using NIS in DCM, purified by precipitation in MeOH after reduction with hydrazine, and stored under argon for several months. The post-polymerization reaction was carried out in dibromomethane, which has a higher boiling point than DCM, and the molecular weight increase was evident, improving from M_n = 7kDa to M_n = 11kDa.



Scheme 3-6. Post-polymerization of the polymer **44a** in dibromomethane.

Solution doping was carried on the polymer **44a**, and as expected this polymeric material displayed interesting electrochromic properties. Under solution doping the

ProDOP-EDOT-ProDOP polymer (**44a**, Figure 3-2) goes from highly transmissive in the neutral state, passing through faint blue-black, to pale yellow (partially transmissive in the visible region) in the oxidized state. Cyclic voltammetry on ITO also showed that the polymer **44a** has a low oxidation potential as expected for this electron rich system. Unfortunately, the polymer delaminated from the ITO slide upon electrochemical oxidation due to the high solubility of the oxidized polymer in propylene carbonate or acetonitrile.

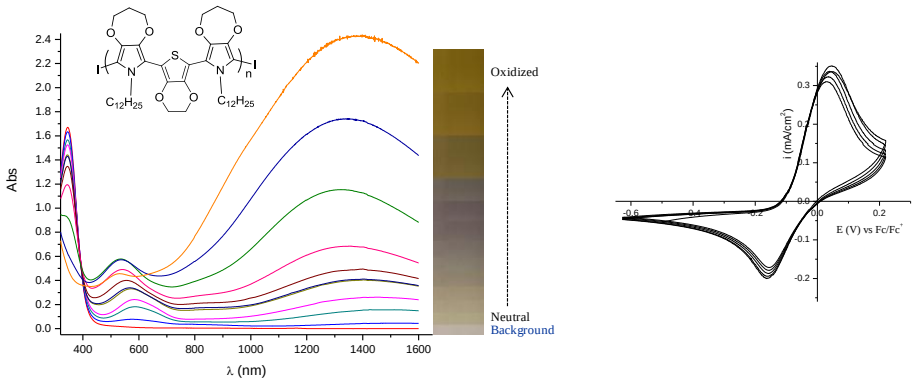


Figure 3-2. a) Solution doping of polymer **44a**, Using $NOPF_6$ [3mM] in DCM, and b) CVs of the same polymer spray-cast onto ITO-coated glass from solution (3 mg/mL) in toluene, 0.1M $LiBF_4$ / PC, vs = 50mV/s.

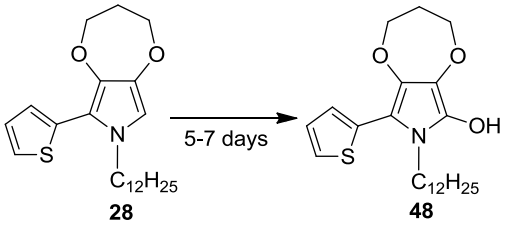
In general, the deiodination polycondensation using iodosuccinimide or iodine proved to be a convenient and efficient polymerization method for the synthesis of ProDOP-based polymers and oligomers. It was demonstrated that the method can generate polymers with relatively high molecular weights, and it is logical to think that the method can be applied to synthesize a variety of XDOP-based materials under relatively mild reaction conditions.

General Stability of 3,4-Dioxypyroles

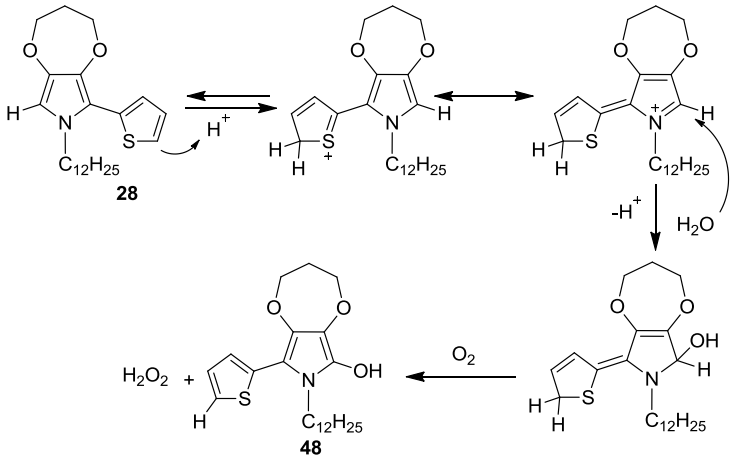
It is possible to tune the dioxypyrrole properties by *N*- and *O*- substitution, but in general, due to their electron rich nature, XDOPs produce polymers with high electronic

band gaps and low oxidation potentials;[24] however, these same desirable properties can render XDOP monomer syntheses difficult and time consuming and, thus, non-2,5-substituted XDOPs must be handled carefully – typically, under acid- and oxygen-free conditions, since they can decompose during reaction workup, purification, or storage.

An example of the reactivity of 3,4-dioxypyrroles is presented in Scheme 3-7. The oligomer **28**, which was made by decarboxylative cross coupling, decomposed after one week of storage under argon. Apparently, water, oxygen and acid traces (from chloroform decomposition, which was used to run the NMR) were able to produce this oxidation, *via* the mechanism proposed in Scheme 3-8. It is worthy to note that other plausible mechanisms may be also possible.



Scheme 3-7. Unexpected oxidation of a ProDOP-based molecule.



Scheme 3-8. Proposed mechanism for the oxidation of a ProDOP-based molecule.

For most reactions presented in the studies in this dissertation, a 3,4-dioxypyrrole containing a propylene bridge was employed (3,4-propylenedioxypyrrole, ProDOP).

The propylene bridge is preferred since the presence of the dioxepine ring offers higher stability toward oxidation to the pyrrole ring than the ethylenedioxy (EDOP)-analog and the open chain substituents such as methoxy or hexyloxy. The relatively higher stability comes from the torsion generated in the seven member ring, which decreases the electron donation from the oxygen atoms into the pyrrole ring, thus decreasing the electron density of the heterocyclic ring. In addition, ProDOPs also possess higher solubility than their EDOP analogs which is attributed to the lower symmetry of the dioxepine ring, which decreases the possibility of π-stacking.

Experimental Section

General Information

All reagents and starting materials were purchased from known commercial sources and used without further purification, unless otherwise noted. All reactions were carried out under argon atmosphere unless otherwise mentioned. ^{1}H-NMR and ^{13}C-NMR spectra were collected on a Mercury 300 or Inova 500. Elemental analyses were carried out by the CHN elementary analysis service in the Chemistry Department of the University of Florida. FTIR measurements were carried out on a Perkin-Elmer Spectrum One FTIR outfitted with a $LiTaO_3$ detector. Gel permeation chromatography (GPC) was performed using a Waters GPCV2000 liquid chromatography system with an internal differential refractive index detector (DRI), at 40 °C, and using two Waters Styragel HR-5E columns (10 μm PD, 7.8 mm i.d., 300 mm length). THF was employed as the mobile phase at a flow rate of 1.0 mL/min. Injections were made at 0.05 – 0.08% w/v sample concentration. Retention times were calibrated against narrow molecular weight polystyrene standards.

Experimental Procedures

Monomer syntheses: Dioxypyrrole potassium salts and diacids were synthesized from their respective diesters as was previously described in Chapter 2.

Synthesis of 5,5'-(3,4-(ethylene-1,2-dioxy)thiophene-2,5-diyl)bis(N-dodecyl-3,4-(propylene-1,3-dioxy)pyrrole-2-carboxylic acid) (41). Compound **31** (0.133 g, 0.1449 mmol, 1 equiv.), 10 mL of water, and 20 mL of DCM were added to a 100-mL separatory funnel, the mixture was shaken, and then 20 mL of [0.5M] HCl was added until most of the diacid was regenerated, the DCM layer was collected and the remaining aqueous layer was treated with 20 mL more of DCM and 10 mL of [0.5M] HCl. The DCM fractions were washed with deionized water (3x), and then dried using sodium sulfate. The DCM was removed *in vacuo*, and the resulting sticky solid was put under vacuum for 2 hours. The product was obtained as a mixture of approximately 24:6:1 of diacid **41a**, monoacid **41b** and non-substituted dioxypyrrole oligomer **41c**. The product was used without further purification. ^{1}H-NMR (300 MHz, $DCCl_3$): δ_H 9.77 (br, 2H), 6.33 (s, 0.22H), 6.31 (s, 0.08H), 4.26 (m, 12H), 4.05 (m, 4H), 3.71 (m, 1.44H), 2.26 (m, 4H), 2.13 (m, 0.75H), 1.62 (m, 5.47), 1.45 – 1.19 (br, m, ~ 40H), 0.86 (t, 6H, J = 6.6). ^{13}C-NMR (75 MHz, $DCCl_3$): δ_C 159.7, 141.9, 139.9, 135.4, 117.3, 107.7, 105.5, 73.8, 72.2, 64.8, 46.4, 34.3, 32.1, 31.7, 29.9, 29.8, 29.6, 29.5, 26.9, 22.9, 14.3.

General polymerization method Using *N*-halosuccinimides. Polymer 44a. The crude diacid **41** (0.122 g, 0.1449 mmol, 1 equiv.) and 2 mL DCM (or chloroform) were added to a 25-mL round bottom flask, containing argon and equipped with a stir bar and a condenser. The flask was cooled to -20 °C, and then *N*-iodosuccinimide (0.069 g, 0.3043 mmol, 2.1 equiv., freshly recrystallized from dioxane) was added in one portion. The reaction mixture was stirred for 10 minutes, slowly warmed to 60 °C

and stirred for 4 days. The reaction mixture was cooled to room temperature and carefully reduced with cold hydrazine monohydrate. The resulting mixture was poured in methanol (120 mL) and stirred for 30 minutes (or until the polymer precipitated); the resulting solid was collected by vacuum filtration and washed with methanol, then it was dissolved in 2 mL of THF and precipitated into MeOH, filtered (osmotics, 20-μm nylon membrane), and dried under vacuum. A pale yellow solid, 80 mg, was received, 71% yield. M_n = 7675, M_w = 13599. ^{1}H-NMR (300 MHz, $DCCl_3$): δ_H 4.22 – 3.40 (m, 16H), 2.18 (s, br, 2H), 2.09 (s, br, 2H), 1.70 – 1.00 (m, br,40H), 0.86 (m, 6H). ^{13}C-NMR (125 MHz, $DCCl_3$): δ_C 138.5(br), 137.9 (br), 137.2 (br), 112.6, 109.2 (br), 107.0, 72.3 (br), 64.7 (br), 45.7 (br), 35.3 (br), 32.2, 31.4, 31.0, 29.9 (br), 29.7, 29.6 (br), 28.9, 27.2 (br), 26.9, 26.8, 22.9, 14.3. Elemental Analysis calculated for $C_{44}H_{66}N_2O_6S$: C (70.36%), H (8.86%), N (3.73%), Found: C (70.32%), H (8.96%), N (3.52%).

Polymer 44b using *N*-bromosuccinimide. The reaction was carried out using the same procedure as for polymer **44a**, 83% yield. M_n = 6300, M_w = 8898. ^{1}H-NMR (300 MHz, $DCCl_3$): δ_H 4.22 – 3.40 (m, 16H), 2.18 (s, br, 2H), 2.09 (s, br, 2H), 1.70 – 1.00 (m, br,40H), 0.86 (m, 6H). ^{13}C-NMR (125 MHz, $DCCl_3$): 138.5 (br), 137.9 (br), 115.9 (br), 109.0 (br), 72.3, 64.7, 45.7, 35.3, 32.2, 31.0, 30.5, 29.9, 29.6, 29.2, 29.1, 28.9, 27.2, 27.1, 27.0, 22.9, 14.3.

Polymer 44c using *N*-chlorosuccinimide. The reaction was carried out using the same procedure as for polymer **44a**, 39% yield. M_n = 4978, M_w = 6291. ^{1}H-NMR (300 MHz, $DCCl_3$): δ_H 4.22 – 3.40 (m, 16H), 2.18 (s, br, 2H), 2.09 (s, br, 2H), 1.70 – 1.00 (m, br,40H), 0.86 (m, 6H). ^{13}C-NMR (125 MHz, $DCCl_3$): 138.3 (br), 137.9 (br),

137.2 (br), 119.8 (br), 109.1 (br), 109.0 (br), 72.3, 64.7, 45.7, 35.3, 32.2, 31.0, 30.7, 29.9, 29.7, 29.6, 29.1, 29.0, 27.3, 22.9, 14.3.

Polymer 45a using *N*-iodosuccinimide. The reaction was carried out using the same procedure as for polymer **44a**, 60% yield. M_n = 13980, M_w = 16781. ^{1}H-NMR (300 MHz, $DCCl_3$): δ_H 4.38 – 3.20 (m, br, 6H), 2.15 (s, br, 2H), 1.74 – 0.95 (m, br, 20H), 0.86 (s, br, 3H). ^{13}C-NMR (125 MHz, $DCCl_3$): 139.0, 109.1, 72.2, 46.1, 35.3, 32.2, 30.8, 30.1, 30.0, 29.9, 29.7, 29.6, 27.1, 22.9, 14.3. Elemental Analysis calculated for $C_{19}H_{31}NO_2$: C (74.71%), H (10.63%), N (4.21%), Found: C (74.58%), H (10.73%), N (4.34%).

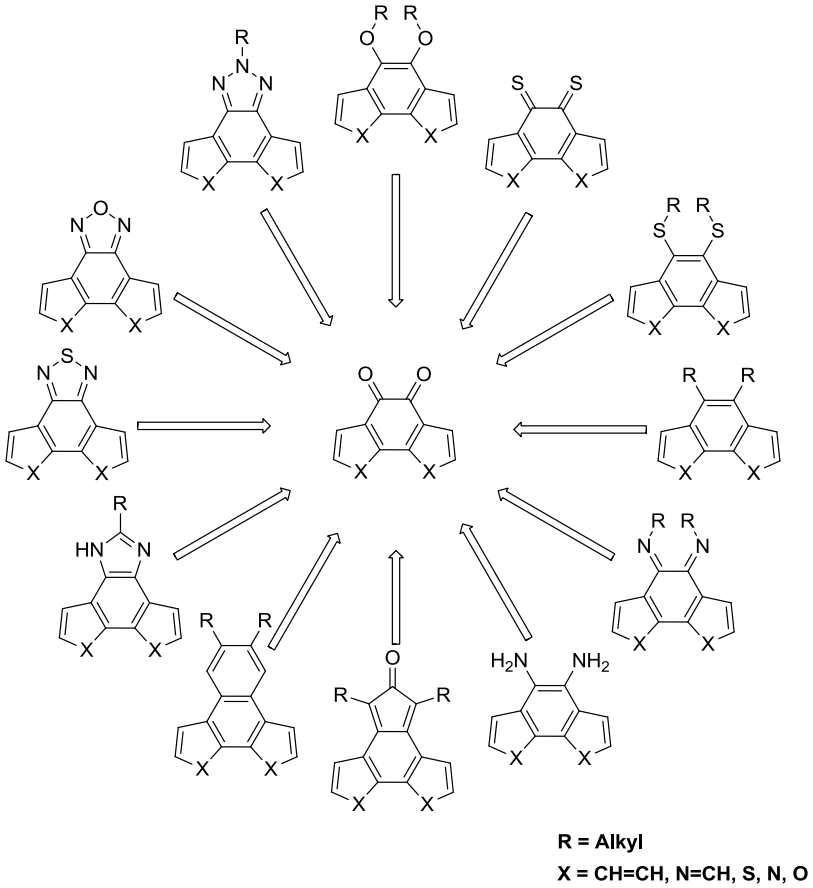
Polymer 47 using *N*-iodosuccinimide. Reaction was carried out using the same procedure as for polymer **44a**, but the work up was modified as follows: after careful reduction with cold hydrazine monohydrate, the reaction mixture was added dropwise to 75 mL of MeOH in an Erlenmeyer flask. The mixture was stirred for 20 minutes, and then decanted. The sticky oil that remained in the Erlenmeyer flask was washed with 40 mL of MeOH, then dissolved with THF and transferred to a vial, the solvent was removed *in vacuo* and the product was stored under argon. The product was received as a brown-black sticky solid, 31% yield. M_n = 3646, M_w = 5222. ^{1}H-NMR (300 MHz, $DCCl_3$): δ_H 9.68 – 8.60 (s, br, 1H), 4.37 – 3.57 (m, 4H), 2.04 – 1.09 (m, 18), 0.84 (m, 12). ^{13}C-NMR (125 MHz, $DCCl_3$): δ_C 131.1, 129.0, 40.3, 30.4, 29.2, 23.6 (br), 23.3, 14.3, 11.0. FTIR (NaCl, disc) $\bar{\nu}_{max}$ (cm^{-1}): 3436.8 (w), 2958.0 (s), 2929.6 (s), 2873.6 (s), 2856.5 (s), 1717.5 (w), 1605.4 (m, br), 1464.4 (s, br), 1379.2 (s), 1343.8 (m), 1194.7 (m), 1112.1 (s), 1051.0 (s), 772.1 (w), 728.0 (w).

General polymerization method using iodine. **Polymer 45a**. The ProDOP potassium salt **29** (0.200 g, 0.4240 mmol, 1.0 equiv.), iodine (0.226 g, 0.8905 mmol, 2.0 equiv), and 2 mL of DCM were added to a 25-mL round bottom flask, containing argon and equipped with a stir bar and a condenser. The condenser was equipped with a septum and a silicon oil bubbler was connected to it. The reaction mixture was stirred at room temperature for 10 minutes, and then 2 mL of deionized water was added. The reaction was warmed up to 60˚C, and stirred for 48 hours. The reaction mixture was allowed to cool to room temperature and reduced by careful addition of 2 mL of cold hydrazine monohydrate. The entire crude was added into 75 mL of methanol and stirred for 15 minutes (or until the polymer precipitated). The resulting solid was collected by filtration (osmotics, 20 μm nylon membrane), dissolved in 2 mL of THF and precipitated in 75 mL of MeOH. The solid was collected by filtration (osmotics, 20 μm nylon membrane) and subjected to Soxhlet extraction using MeOH for 16 hours. The resulting solid was dissolved with dichloromethane (if the solution turned dark it was then reduced with various drops hydrazine monohydrate), concentrated to approximately 2 mL and precipitated into 50 mL of methanol. The resulting solid was collected by filtration (osmotics, 20 μm nylon membrane), and dried under vacuum. The product was obtained as a pale yellow solid, 0.072 g, 55% yield. M_n = 15909, M_w = 35718. ^{1}H-NMR (300 MHz, $DCCl_3$): δ_H 4.30 – 3.20 (m, br, 6H), 2.14 (s, br, 2H), 1.70 – 0.90 (m, br, 20H), 0.85 (s, br, 3H). ^{13}C-NMR (125 MHz, $DCCl_3$): δ_C 138.3 (br), 109.1 (br), 108.6 (br), 72.2, 72.1, 45.7, 35.4, 32.2, 31.3, 30.8, 30.0, 29.6, 27.4, 27.1, 22.9, 14.3. Elemental Analysis calculated for $C_{19}H_{31}NO_2$: C (74.71%), H (10.63%), N (4.21%), Found: C (74.71%), H (10.23%), N (4.59%).

Polymer 44a using iodine. The reaction was carried out using the same procedure as for polymer **45a**, 66% yield. M_n = 22875, M_w = 58099. ^{1}H-NMR (300 MHz, $DCCl_3$): δ_H 4.5 – 3.48 (m, br, 16H), 2.19 (s, br, 2H), 2.09 (s, br, 2H), 1.68 – 1.00 (m, br, 40), 0.86 (t, 6H, J = 6.9 Hz). ^{13}C-NMR (125 MHz, $DCCl_3$): δ_C 138.5, 138.0, 137.2, 109.2, 109.0, 107.0, 77.2, 72.3, 64.7, 45.6, 35.3, 32.1, 31.0, 30.5, 29.9, 29.9, 29.6, 29.6, 14.3. Elemental Analysis calculated for $C_{44}H_{66}N_2O_6S$: C (70.36%), H (8.86%), N (3.73%). Found: C (70.99%), H (9.28%), N (3.13%).

CHAPTER 4
FUSED-AROMATIC DIKETONES AS PRECURSORS FOR THE SYNTHESES OF CONJUGATED MATERIALS

Aromatic diketones are practical starting materials that can serve as synthons to generate a wide variety of monomers for the synthesis of π-conjugated oligomers and polymers. As shown in Scheme 4-1, these molecules can be converted into other molecules with different properties and characteristics (e. g. electron donors or electron acceptors), and most of these transformations can be done in one or two steps, demonstrating the versatility of these intermediates. In this chapter, the syntheses of various diketones (X = S, CH=CH, N=CH), and some of their derivatives will be described.



Scheme 4-1. Various molecules that can be synthesized from fused-aromatic diketones.

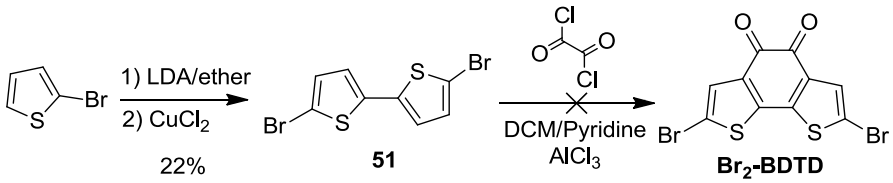
The band gap (E_g)—the energy difference between HOMO and LUMO—is the key factor that establishes the electronic and conducting properties of π-conjugated polymers. The donor-acceptor approach has become one of the most powerful strategies for band gap engineering in π-conjugated polymers, therefore, to access new donor and acceptor molecules is highly convenient since it can lead to new π-conjugated systems with a wide range of band gaps. The donor-acceptor motif produces a decrease in the electronic E_g of the π-conjugated polymer. Such a decrease of the electronic E_g results from the orbital interaction of the two monomeric units (donor and acceptor), which also generates a decrease of the bond length alternation in the π-conjugated polymer. Herein will be described the syntheses of various fused-aromatic diketones, and how these fused-aromatic diketones can be turned into different donor and acceptor molecules.

Syntheses of Fused-Aromatic Diketones

Synthesis of Benzo[1,2-b:6,5-b']dithiophene-4,5-dione (BDTD)

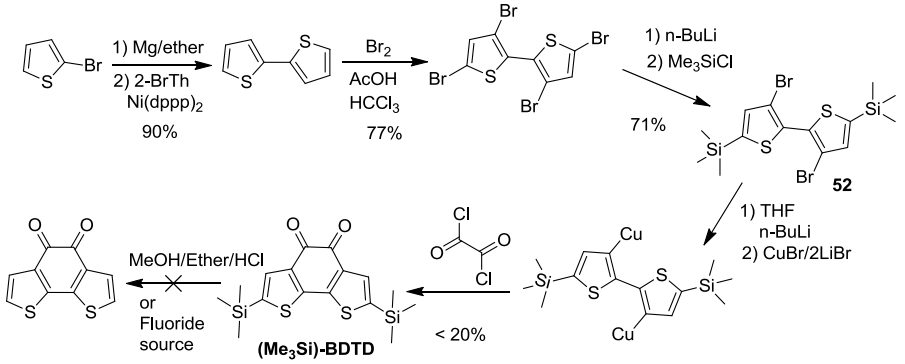
The most interesting diketone of the series presented in Scheme 1 is when X = S, benzo[1,2-b:6,5-b']dithiophene-4,5-dione (BDTD). The importance of this molecule is due to various factors: on the one hand, there is a wide range of properties offered by the thiophene-based materials,[17] and on other hand, the system lends itself to facile post derivatization that can be carried out on the thiophene rings (i. e. halogenation, borylation, stannylation,…, etc) and on the carbonyl groups. The synthesis of BDTD is also one of the most challenging of these syntheses, and the research presented in this section will show the efforts to synthesize this molecule, and its utilization as precursors for some of the molecules presented in Scheme 4-1 by different synthetic approaches.

The initial approach to make the Br_2-BDTD is presented in Scheme 4-2. This approach failed since the compound **51** did not react using Friedel-Crafts acylation. An alternative approach is presented in Scheme 4-3. This route uses the readily available 2-bromothiophene as the starting material, and was based on previously reported literature procedures[58-61] to produce the intermediate **52**.



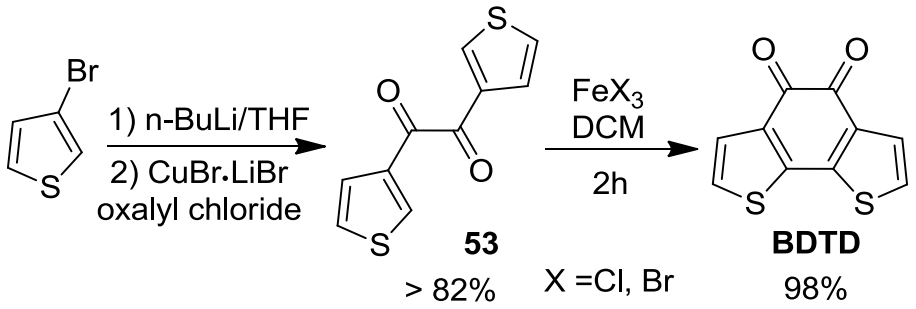
Scheme 4-2. Failed synthesis of Br_2-BDTD *via* Friedel-Crafts acylation.

Unfortunately, this route (Scheme 4-3) contains a considerable number of synthetic steps, and some of these steps produced low yields and required column purification, making the synthesis expensive and non-suitable for a large scale production of the desired product. Additionally, as shown in the final step in Scheme 4-3, the deprotection of the silyl compound (Me_3Si)-BDTD couldn't be accomplished with standard deprotection methods (fluoride source or dilute acid), and only concentrated HCl could produce the cleavage of the trimethylsilyl groups in the (Me_3Si)-BDTD. However, concentrated HCl also causes the product to decompose, decreasing the overall reaction yield.



Scheme 4-3. Alternative route towards BDTD.

Due to the aforementioned results, a new synthetic route was devised; this route and its results are shown in Scheme 4-4. This synthetic path is highly convenient; since the reaction can be carried out in only two steps, in high yields and requiring no column purification; additionally, it also uses the inexpensive and readily available 3-bromothiophene as starting material.

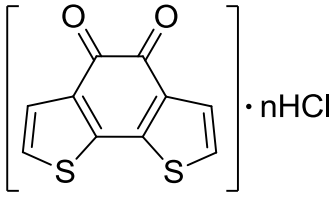


Scheme 4-4. Two-step synthesis of BDTD

This synthetic route (Scheme 4-4) was initially discarded for two main reasons, namely: the synthesis of the intermediate **53** could be quite challenging, and, it was also believed that the oxidative polymerization of BDTD, using $FeCl_3$, could occur. Fortunately, BDTD did not polymerize, and the synthetic path resulted in an excellent alternative to produce this molecule (BDTD). The synthesis of the diketone **53**, which is the key intermediate, was carried out using a modified literature procedure,[62] then after **53** was isolated, it was subjected to oxidative ring closing using iron trichloride in DCM. In order to optimize the oxidative ring closing conditions, the reaction was run several times under different conditions—i. e. different concentrations and temperatures, 25, 35 and 40˚C, in dichlomethane (DCM)—and monitored by TLC for several hours (1 – 24 h), which lead to the conclusion that the reaction must be carried out at room temperature for at least two hours, using three or more equivalents of $FeCl_3$ or $FeBr_3$ to achieve high conversion. Higher temperatures and longer reaction times seemed to lead to partial

chlorination (or bromination) of the final product, which was confirmed by high resolution mass spectrometry (HRMS), and if less than 2.5 equivalents of iron chloride was employed, it requires up to 24 hours of reaction, and full conversion was not observed.

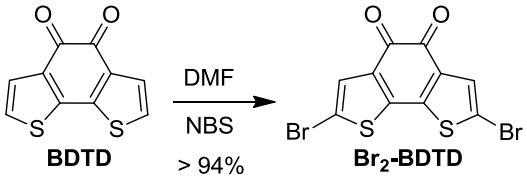
It can be hypothesized that the polymerization of BDTD did not occur due to the low solubility of the reaction product. Once **53** ring-closes, the product seems to form an adduct with HCl (compound **54**, Figure 4-1), which precipitated in the reaction as a green solid. This adduct dissociates upon addition of water, and then the product can be isolated as a fluffy black-purple solid (red in DCM). The same adduct can be generated by bubbling HCl gas to a dispersion of BDTD in DCM. Additional evidence of the aforementioned adduct is the fact that no or small amounts of HCl gas is released during the reaction, meaning that somehow the hydrochloric acid is being trapped by the reaction system.



54

Figure 4-1. Proposed BDTD·HCl adduct, n = 1 – 2.

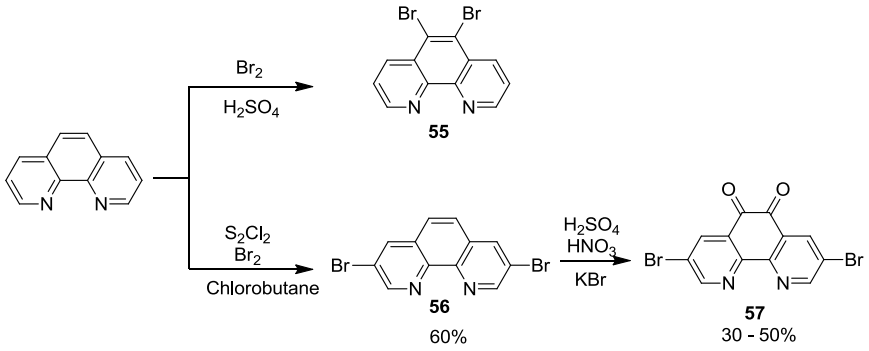
As was mentioned previously, $FeBr_3$ was also employed as oxidant. The main purpose of using this oxidant was to produce the ring closing of **53** and further bromination of BDTD in one pot. The bromination took place, but unfortunately several byproducts were also observed, producing a low yield for Br_2-BDTD and a mixture of polybrominated products and oligomers of BDTD. Since this latest approach failed, BDTD was isolated and purified, and then the bromination was carried out using *N*-bromosuccinimide in *N*,*N*-dimethylformamide (DMF) in high yield (Scheme 4-5).



Scheme 4-5. Bromination of BDTD.

Synthesis of 3,8-Dibromo-1,10-phenanthroline-5,6-dione and 2,7-Dibromophenanthrene-9,10-dione

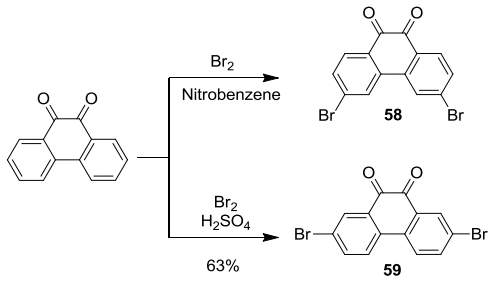
The 3,8-dibromo-1,10-phenanthroline-5,6-dione (**57**) is an interesting molecule, due to the electron deficient feature of the two pyridinic rings, which makes it a potential candidate for the synthesis of electron acceptor molecules. Since the 1,10-phenanthroline-5,6-dione is an electron deficient system, bromination will take place slowly and under harsh conditions, leading to a mono- and di-brominated mixture of products. Thus, to circumvent this problem, the route presented in Scheme 4-6 was devised**.** Given that typical bromination of 1,10-phenatroline leads to 5,6-dibromo-1,10-phenanthroline (**55**), the reaction was carried out in the presence of sulfur monochloride (S_2Cl_2) and using 1-chlorobutane as solvent, and this way the 3,8-dibromo-1,10-phenanthroline (**56**) was produced instead.[63] After isolation and purification, **56** can be converted into **57** by oxidation with H_2SO_4/HNO_3 and KBr.[64,65] It is noteworthy that it is important to place the two bromo atoms on the 3- and 8-positions of the phenanthroline-5,6-dione **57** to produce a continuous π-conjugated system.



Scheme 4-6. Synthesis of 3,8-dibromo-1,10-phenanthroline-5,6-dione (**57**)

Synthesis of 2,7-Dibromophenanthrene-9,10-dione

As was mentioned for the 3,8-dibromo-1,10-phenanthroline-5,6-dione (**57**), it is important to maintain a continuous conjugation of the π-system in phenanthrene-based diketones; therefore 2,7-dibromophenanthrene-9,10-diones (**59**) are more useful than 3,6-dibromophenanthrene-9,10-diones (**58**) for some applications. Most common brominating reaction conditions for phenanthrene-9,10-dione (nitrobenzene/Br_2/organic peroxide)[66] produce 3,6- substitution (compound **58**) shown in Scheme 4-7, but by using the same reaction conditions employed for fluorenone (H_2SO_4/Br_2),[67,68] it is possible to generate the 2,7-substituted phenanthrenedione (**59**) in acceptable yields.

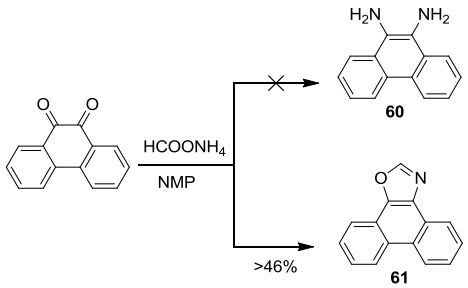


Scheme 4-7. Synthesis of 2,7-dibromophenanthrene-9,10-dione (**59**)

Synthesis of Acceptor Molecules

Synthesis of Phenanthro[9,10-d]oxazole

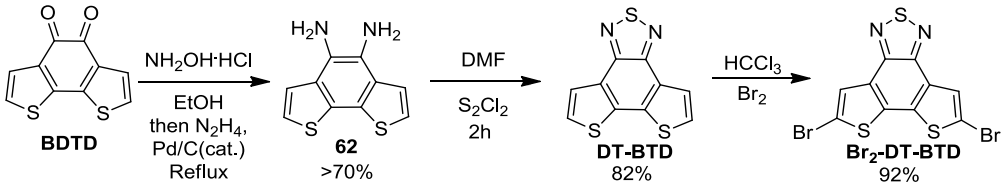
The synthesis of this compound was found in an attempt to make the phenanthrene-9,10-diamine (**60**) using the Leuckart reaction (Scheme 4-8).[69] Expecting to get the diamino-compound **60**, ammonium formate was employed as the ammonium source and the reducing agent in *N*-methylpyrrolidone (NMP). Instead of the expected product (**60**), the reaction yielded the oxazole derivative **61**. This resulted in an interesting method for the synthesis of fused-benzoxazoles, and although, the reaction was not applied to other diketones, it is logical to think that it can be applied to produce analogue molecules from other fused-diketones.



Scheme 4-8. Unexpected synthesis of phenanthro[9,10-d]oxazole (**61**)

Synthesis of Dithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-c][1,2,5]thiadiazole (DT-BTD) and Dithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-c]furazan (DTBF)

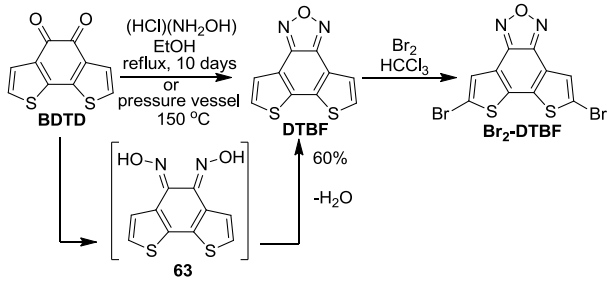
In order to make the diamino compound **62**, BDTD was reacted with hydroxylamine hydrochloride to produce the respective dioxime, which was then reduced with hydrazine, with Pd on carbon as the catalyst, in a one pot reaction (Scheme 4-9). The diamine **62** was isolated and reacted with sulfur monochloride in DMF leading to the desired electron acceptor molecule DT-BTD, this molecule was subjected to bromination, producing the compound Br_2-DT-BTD in high yield.



Scheme 4-9. Synthesis of Br_2-DT-BTD.

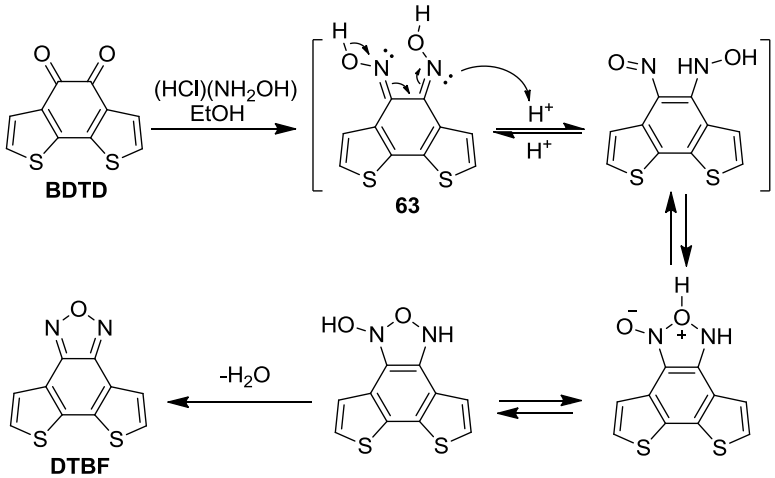
The conversion of BDTD into the dioxime was monitored by thin layer chromatography (TLC), and besides the expected dioxime **63**, shown in Scheme 4-10, the formation of a strong fluorescent compound was observed on the TLC plate, and the intensity of that fluorescent compound increased over time; hence, the reaction was run longer (10 days) than normal (~24 hours) and DTBF was isolated in 62% yield. This compound was brominated using the same reaction conditions as for DT-BTD to produce Br_2-DTBF. In order to decrease the reaction time, the reaction was carried in a

glass pressure vessel at 140°C, and high conversion (~60%) was achieved in less than 72 hours.



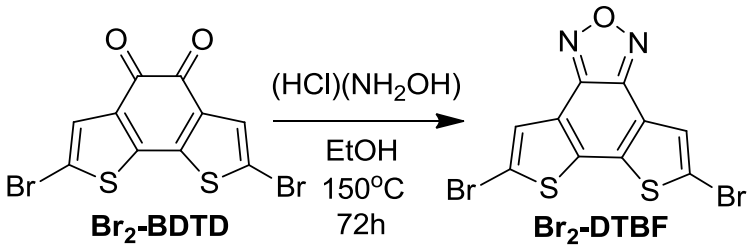
Scheme 4-10. Synthesis of Br_2-DTBF.

This reaction presumably occurred through the mechanism shown in Scheme 4-11. The dioxime **63** only formed when hydroxylamine hydrochloride was employed, which means that the acid plays an important role in the mechanism, not only in the formation of the dioxime but also in the tautomerization and further dehydration to form DTBF**.** The tautomerization is favored due to the aromatization of the central phenyl ring. It is noteworthy that if only hydroxylamine was used, it seemed to lead to an unstable compound, presumably the 5-nitrosobenzo[1,2-b:6,5-b']dithiophen-4-ol and/or 5-aminobenzo[1,2-b:6,5-b']dithiophen-4-ol, and this is the reason why hydroxylamine hydrochloride ($ClNH_3OH$) was employed instead.



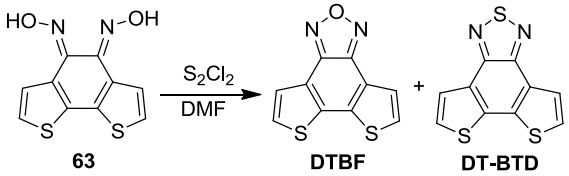
Scheme 4-11. Proposed mechanistic path for formation of DTBF.

The same reaction can be run on Br_2-BDTD to produce the furazan derivative Br_2-DTBF, Scheme 4-12, and this reaction path does not require column purification, but the quality of the final product (Br_2-DTBF) is lower. This assumption—lower purity product—was based on the fact that the color of the Br_2-DTBF made by this method (brown) differs from the one made by the route presented on Scheme 4-10 (bright yellow). Due to the low solubility of Br_2-DTBF, removal of impurities can be difficult.



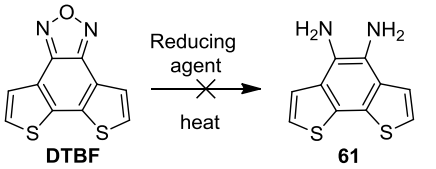
Scheme 4-12. Synthesis of Br_2-DTBF from Br_2-BDTD.

Alternatively, it was also found that treatment of **63** or other dioximes with S_2Cl_2 in DMF leads to a mixture of two compounds – furazan and thiadiazole derivatives, shown in Scheme 4-13 – and these results fit with a previous literature report.[70]



Scheme 4-13. Synthesis of DTBF and DT-BDT from the dioxime **63**.

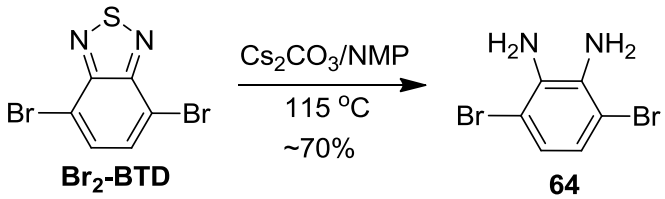
The reduction of DTBF was attempted by various methods in order to obtain an alternative route towards the diamino compound **62**. As shown in Scheme 4-14, the stability of the furazan ring towards reducing agents is quite high, and all the attempted conditions failed. These results showed that the ring opening of the furazan moiety will require stronger reducing agents, but stronger reducing conditions could not be applied to Br_2-DTBF, since such reaction conditions will cleave the bromo atoms, making the route not practical.



Reducing Conditions:
- Cs_2CO_3/NMP/water 120 ^oC
- EtOH/ $NaBH_4$
- THF/EtOH, $NaBH_4$
- THF/EtOH, $Na_2S_2O_4$(aq.)/ pH 13
- THF/EtOH, $NaBH_4$/$(NH_4)_2SO_4$
- THF/EtOH, $NaBH_4$/NH_4/SO_4/Mg(powder)
- EtOH/N_2H_4, Pd/C

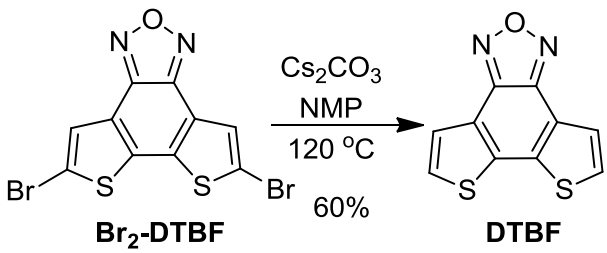
Scheme 4-14. Failed reduction of DTBF under various relatively mild reaction conditions.

The first reducing conditions that were tried for the reduction of DTBF (Cs_2CO_3, NMP) were found during the studies made for the decarboxylative cross coupling of 3,4-dioxypyrroles with Br_2-BTD (Chapter 2 of this dissertation). Optimization of the reaction conditions showed that the reduction of Br_2-BTD could be done in *N*-methylpyrrolidone (NMP) using cesium carbonate and traces of water, as shown in Scheme 4-15.



Scheme 4-15. Reduction of Br_2-BTD, using cesium carbonate in NMP.

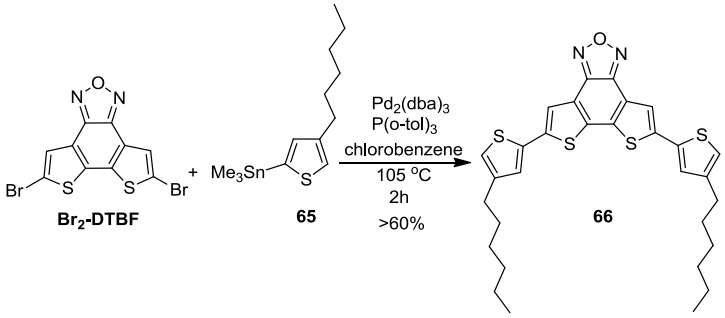
Unfortunately, when these reaction conditions were applied to Br_2-DTBF, cleavage of the bromo atoms occurred, as shown in Scheme 4-16, and no reduction of the furazan ring was observed.



Scheme 4-16. Unexpected cleavage of Br_2-DTBF, using cesium carbonate in NMP.

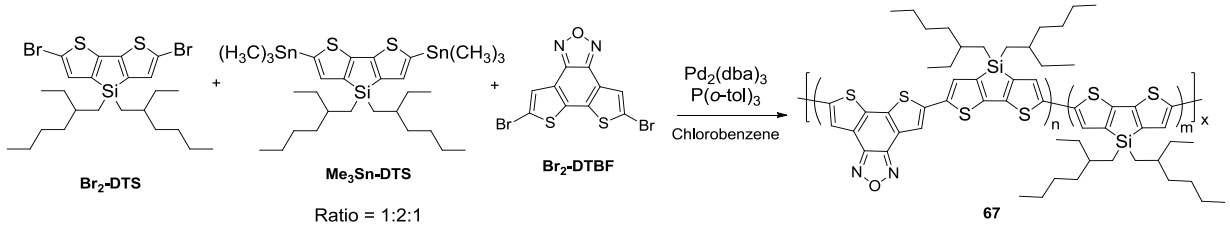
Reactivity of Br_2-DTBF in the Stille Coupling

A model reaction was carry out to test the reactivity of Br_2-DTBF in the Stille cross coupling. As shown in Scheme 4-17, the reaction proceeded quickly and in high yields, proving that the DTBF unit can be easily included into a π-conjugated system by using this or other suitable organometallic cross couplings.



Scheme 4-17. Model Stille reaction for Br_2-DTBF.

In addition, a Stille co-polymerization was carried out on Br_2-DTBF, and, to overcome the low solubility that can result from the lack of solubilizing groups in the DTBF unit, a random approach was adopted. A ratio 1:2:1 of Br_2-DTS:Me_3Sn-DTS:Br_2-DTBF was employed (Scheme 4-18), resulting in a final polymer containing six solubilizing chains in the donor moiety per each acceptor DTBF unit, which increases the polymer solubility, and, by extension, its processibility.



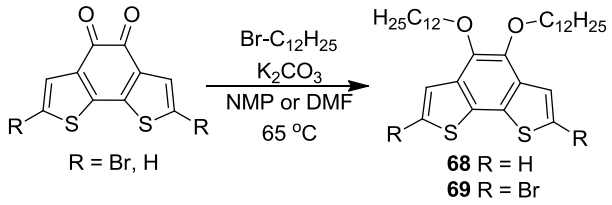
Scheme 4-18. Random Stille co-polymerization for Br_2-DTS, $(Me_3Sn)_2$-DTS and Br_2-DTBF.

The reaction presented in Scheme 4-18 proceeded in high yield, and the incorporation of the DTBF unit occurred to a high extent (i. e. based on the elemental analysis of the final polymer). The final polymer had a limited solubility in common

solvents, such as THF, DCM, and chloroform, but the material still could be processed from chlorobenzene or *o*-dichlorobenzene.

Reductive Etherification of Aromatizable Diketones

Typically, to carry out the etherification of aromatic diketones, it is necessary to first carry out the reduction of the diketone, and then the etherification of the resulting product in a two-step method. The reaction conditions presented in this section demonstrate that the reaction can be accomplished in only one step by using a suitable solvent/base combination, which allows the simultaneous reduction and etherification of diketones without needing Zn(0) or other metals; thus, the conditions may be applied to various halo-diketones as well as to unsubstituted diketones (shown in Scheme 4-19). This reaction uses similar conditions applied to reduce Br_2-BTD—shown in a previous reaction scheme (Scheme 4-5). The reaction produced acceptable yields (50 – 70%) when Br-$C_{12}H_{25}$ was employed, and these reaction yields are comparable to the literature reports using Zn(0) in the two-step route,[71] where the resulting donor molecules can be employed in a number of polymer syntheses.



Scheme 4-19. Reductive etherification of aromatizable diketones

Experimental Section

General Information

All reagents and starting materials were purchased from commercial sources and used without further purification, unless otherwise noted. All reactions were carried under argon atmosphere, and using oven-dried glassware unless otherwise mentioned.

^{1}H-NMR and ^{13}C-NMR spectra were collected on a Mercury 300 MHz or an Inova 500 MHz. High resolution mass spectrometry was performed by the spectroscopic services in the Chemistry Department of the University of Florida with a Finnigan MAT 95Q Hybrid Sector or a Bruker APEX II FTICR or Agilent 6210 TOF. FTIR measurements were performed on a Perkin-Elmer Spectrum One FTIR outfitted with a $LiTaO_3$ detector. Thermogravimetric analysis (TGA) measurements were performed with a Perkin-Elmer TGA 7 thermogravimetric analyzer

Experimental Procedures

Synthesis of 1,2-di(thiophen-3-yl)ethane-1,2-dione (53). The literature procedure[62] was modified. A solution of 3-lithiumthiophene, labeled as Solution A, was prepared as follows: 100 mL of 2.5 molar *n*-butyllithium (0.250 mol) in hexanes was added *via* cannula to 250 mL of anhydrous THF, previously cooled to -78°C. The mixture was stirred for 10 minutes, and then 23.4 mL of 3-bromothiophene (40.758 g, 0.250 mol) was added dropwise. The mixture was stirred for ~150 minutes, keeping the temperature at -78°C. Meanwhile, Solution B was prepared as follows: In a 3000-mL round bottom flask (equipped with stir bar and a septum), containing 1750 mL of anhydrous THF, was added LiBr (21.713 g, 0.250 mol, 1 equiv.) and CuBr (35.863 g, 0.250 mol, 1 equiv.), the CuBr and LiBr mixture was stirred until all the salts dissolved, then this mixture was cooled to -40°C or to lower temperatures. Solution C: 9.66 mL of oxalyl chloride (14.280 g, 0.1125 mol, 0.45 equiv.) was dissolved in 250 mL of anhydrous THF in a 500-mL round bottom flask (previously equipped with a septum) and cooled to -40°C or to lower temperatures. Solution A was added *via* cannula to Solution B, and the mixture was strongly stirred for ~5 minutes; then the Solution C was slowly added *via* cannula. The mixture was kept in the cold bath for 2 hours, allowed to

warm up to room temperature, and quenched with 100 mL of saturated $NH_4Cl_{(aq.)}$. The THF was removed by rotary evaporation, and ~400 mL of ethyl acetate was added to the resulting mixture, which was then transferred to a separatory funnel and washed with saturated NH_4Cl(aq.) (3x, 150 mL), water (2x, 100 mL), and brine (1x, 100mL). Hexanes (300 mL) was added to the organic mixture, and the mixture was dried with Na_2SO_4, and then filtered trough a short path of silica (the silica was flushed with hexanes:diethyl ether 1:1 to recover the entire product). The organic solvents were completely removed by rotary evaporation, and then the resulting yellow solid was strongly stirred in ~80 mL of a mixture 1:10 of diethyl ether:pentanes (or 1:10 diethyl ether:hexanes), until all the solid chunks turned into a small powder. The resulting fine solid was filtered in a Buchner funnel, washed with cold pentanes, and then air-dried. The organic solvent of the remaining filtrate was removed by rotary evaporation and the procedure (diethyl ether:pentanes treatment) was repeated with the resulting solid, but using smaller amounts of the solvent mixture (this procedure was repeated three times total). The resulting solids were collected and subjected to vacuum to remove solvent traces. Alternatively, the solid can be purified by column chromatography (silica, and 1:3 of diethyl ether:hexanes). A pale yellow solid was isolated, 18.147 g, 72.6% yield. ^{1}H-NMR (500 MHz, CD_2Cl_2): δ_H 8.43 – 8.30 (m, 2H), 7.78 – 7.66 (m, 2H), 7.48 – 7.35 (m, 2H). ^{13}C-NMR (125 MHz, CD_2Cl_2): δ_C 185.9, 137.8, 137.6, 127.7, 127.1. HRMS (ESI-TOF, M+Na^+) m/z calcd. for $C_{10}H_6O_2S_2$ 244.9701, found 244.9696.

Benzo[1,2-b:6,5-b']dithiophene-4,5-dione (BDTD). To a 500-mL Erlenmeyer flask, equipped with a stir bar and an inlet adapter and containing 250 mL of DCM, was added anhydrous $FeCl_3$ (19.465 g, 120 mmol, 3 equiv.). The mixture was stirred for a

few seconds, and then the diketone **53** (8.8914 g, 40 mmol, 1 equiv.) was added in one portion. A silicon-oil bubbler was connected to the inlet adapter, and the reaction mixture was stirred for 2 h at room temperature. The mixture was quenched with ~100 mL of chilled water and stirred for 5 minutes more. Afterwards, DCM was removed by rotary evaporation. The resulting solid was filtered and washed with plenty of deionized water and stirred in 200 mL of water until a fine powder was formed. The solution was then filtered and washed with plenty water. The resulting solid was air-dried for 10 minutes and then washed with 200 mL of diethyl ether and dried under vacuum. The resulting solid can be recrystallized from acetonitrile or purified as follows: the black solid was added to ~200 mL of DCM, stirred for 10 minutes, and then 100 mL of silica was added. The mixture was stirred until the solid was dispersed on the silica, and then the entire mixture was transferred to a chromatographic column containing a short path of silica. The column was then flushed with a mixture of diethyl ether:DCM [1:3] until all the black-purple solid was recovered; the solvent can be roto-evaporated and recycled into the column, a green stain remains on the silica after the product is recovered. After removal of the organic solvent, the resulting solid was stirred in hot ether for 15 minutes, vacuum-filtered, and then air-dried. The resulting black solid was dried under vacuum, 8.627 g, 97.8% yield. ^{1}H-NMR (500 MHz, CD_2Cl_2): δ_H 7.47 (d, 2H, J = 5.2 Hz), 7.26 (d, 2H, J = 5.2 Hz). ^{13}C-NMR (125 MHz, CD_2Cl_2): δ_C 175.3, 144.5, 135.9, 128.1, 126.5. HRMS (DART, $M+H^+$) m/z calcd. for $C_{10}H_4N_2O_2$ 220.9726, found 220.9726.

Synthesis of 2,7-dibromobenzo[1,2-b:6,5-b']dithiophene-4,5-dione (Br_2-BDTD). To a 250-mL round-bottom flask, equipped with a stir bar and an air-cooled condenser, was added BDTD (2.2027 g, 10 mmol, 1 equiv), NBS (3.738 g, 21 mmol, 2.1

equiv.), and DMF (100 mL). The mixture was heated to 65 – 70°C, and stirred for 24 hours. The DMF was removed by rotary evaporation at 45°C. The resulting solid was washed with hot water, filtered, and air-dried. The resulting solid was stirred in 60 mL of boiling acetonitrile for 15 minutes. The mixture was allowed to cool to room temperature, and then it was placed in a refrigerator overnight. The resulting crystals were collected by vacuum filtration, washed with acetonitrile, air-dried, and put under vacuum for >2 hours to remove solvent traces. A dark purple microcrystalline solid was received, 3.621 g, 96% yield. ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H 7.46 (s, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C 172.8, 143.8, 135.6, 130.2, 114.8. HRMS (ESI-TOF, $(M+Na)^+$) m/z calcd. for $C_{10}H_2O_2S_2Br_2$: 400.7734, found *m/z* 400.7751.

Synthesis of 3,8-Dibromo-1,10-phenanthroline (56). The synthesis was carried out according to the literature procedure.[63]

Synthesis of 3,8-Dibromo-1,10-phenanthroline-5,6-dione (57). The synthesis was carried out according to the literature procedure for analogous compounds.[64,65] To a 50-mL round-bottom flask was added 3,8-dibromo-1,10-phenanthroline (**56**) (0.218 g, 0.6450 mmol, 1 equiv.), and KBr (0.768 g, 6.450 mmol, 10 equiv.). The flask was cooled to 0 °C, and concentrated sulfuric acid (2.4 mL) was added dropwise, and then, concentrated nitric acid (1.2 mL) was added. The flask was equipped with a condenser and the resulting mixture was heated for 2 h at 80 °C. The mixture was cooled to room temperature, and poured slowly into 200 mL of chilled water. The resulting yellow solid was collected by filtration, and air-dried. The solid was dissolved with ethyl acetate and the resulting solution was dried over Na_2SO_4. The ethyl acetate was removed by rotary evaporation, and the resulting solid was washed with diethyl ether. A bright yellow solid

was obtained, 74 mg, 31% yield. ^{1}H-NMR (300 MHz, $CDCl_3$): δ_H 9.12 (s, 2H), 8.58 (s, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ_C 177.3, 157.8, 150.6, 139.7, 128.6, 123.8.

Synthesis of 2,7-Dibromophenanthrene-9,10-dione (59). The reaction was modified from the literature procedure.[67,68] Phenanthrene-9,10-dione (12 g, 57.6341 mmol,1 equiv) was suspended in 500 mL of concentrated sulfuric acid (in a 1000-mL round-bottom flask, or in a 1000-mL Erlenmeyer flask). NBS (9.350 g, 52.5 mmol, 2.1 equiv) was added in one portion, and then the flask was equipped with a large stir bar or a mechanical stirrer. The mixture was stirred at room temperature for 3 hours. The mixture was poured into 600 mL of ice/water and stirred for 5 minutes, and then the resulting solid was vacuum filtered in a fritted funnel, washed with water, $K_2CO_{3(sat.)}$, water (plenty), and air-dried for several hours. The resulting orange solid was dissolved in 600 mL of amine-free DMF (hot), allowed to cool to room temperature. After 6-7 hours the resulting crystals were collected by filtration, and washed with diethyl ether. The remaining DMF solution was roto-evaporated until more solid precipitated (~150 mL), then the DMF solution was heated to dissolve the solid again. The mixture was allowed to cool to recover more product as orange crystals. The resulting solids were collected together and stirred in hot toluene (>200 mL). The heterogeneous mixture was allowed to cool to room temperature, and the resulting solid was vacuum-filtered and washed with toluene, then place under vacuum overnight; alternatively the solid can be recrystallized from DMSO. An orange solid was recovered, 13.2 g, 62.6% yield. ^{1}H-NMR (300 MHz, DMSO-d_6, 120°C): δ_H 8.19 (d, 2H, J = 8.6 Hz), 8.10 (d, 2H, J = 1.9 Hz), 7.94 (dd, 2H, J = 1.8 Hz, J = 8.5 Hz). ^{13}C-NMR (75 MHz, DMSO, 90°C): δ_C 176.7, 137.2, 133.2, 130.7, 127.9, 126.3, 122.3.

Phenanthro[9,10-d]oxazole (61). Phenanthrene-9,10-dione (0.560 g, 2.6896 mmol, 1 equiv.), ammonium formate (1.018 g, 16.1376 mmol, 6 equiv.), and 30 mL of NMP were added to a 100-mL Erlenmeyer flask. The flask was equipped with an air-cooled condenser and the mixture was warmed to 105 – 110°C, and stirred for ~3h. Then the temperature was increased to 165°C, and the stirring was continued for 12 hours more. The reaction mixture was allowed to cool to ~60°C and filtered (to remove insoluble byproducts). The resulting NMP solution was cooled to room temperature and poured into water (75 mL), and then the resulting solid was collected by filtration, washed with water and air-dried. The resulting beige solid was put under high vacuum. 0.245g, 46% yield. ^{1}H-NMR (300 MHz, $CDCl_3$): δ_H 8.72 (t, 2H, J = 7.5 Hz), 8.55 (d, 1H, J = 7.6 Hz), 8.34 – 8.20 (m, 2H), 7.85 – 7.60 (m, 4H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ_C 151.5, 129.7, 129.1, 127.8, 127.6, 126.9, 126.5, 126.3, 123.9, 123.6, 123.0, 121.2. HRMS (APCI, $M+H^+$) m/z calcd. for $C_{15}H_9NO$ 220.0757, found 220.0763.

Benzo[1,2-b:6,5-b']dithiophene-4,5-diamine (62). To a 250-mL round-bottom flask, containing a stir bar, and under argon atmosphere, was added BDTD (2 g, 9.0799 mmol, 1 equiv.), hydroxylamine hydrochloride (1.577 g, 2.5 equiv.), and 200 proof ethanol (100 mL). The flask was equipped with a condenser and the mixture was warmed to 75 – 80°C, and stirred for 20 hours. The reaction mixture was cooled to room temperature, and 200 mg of 10% of Pd on activated carbon (Pd/C) was added. An addition funnel containing a solution of hydrazine monohydrate (15 mL of $N_2H_4 \cdot H_2O$ in 25 mL of EtOH) was placed on top of the condenser. The reaction mixture was warmed up to 65 °C, and then the hydrazine solution was added dropwise for ~1h. The reaction temperature was increased to 85 °C, and then the mixture was stirred for 48

hours. The mixture was allowed to cool to ~60 °C and filtered (by gravity filtration, and the filter was washed with ethanol to recover the entire product). The solvent was removed by rotary evaporation, and the resulting solid was dispersed in water, filtered, washed with plenty water and cold ethanol. The resulting yellow solid was air-dried for 1 minute, placed under vacuum, and stored under argon. In the event that the product had dissolved when washing with ethanol, it was recovered by removing the organic solvent from the filtrate and by repeating the filtration procedure. A bright yellow solid was isolated, 1.409 g, 70.4% yield. ^{1}H-NMR (300 MHz, CD_2Cl_2): δ_H 7.35 (q, 4H, J = 5.5 Hz), 3.85 – 3.52 (s, br, 4H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ_C 130.8, 125.9, 125.6, 124.1, 120.9. HRMS (APCI, [M + H^+]) m/z calcd. for $C_{10}H_{11}N_2S_2$ 221.0202, found 221.0200.

Synthesis of Dithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-c][1,2,5]thiadiazole (DT-BTD). To a 25-mL round-bottom flask, equipped with a stir bar, a septum and a bubbler, and containing argon atmosphere, was added DMF (2 mL) and sulfur monochloride (0.6 mL, 0.9801 g, 7.2624 mmol, 4 equiv.). The flask was cooled to 0°C, then the mixture was stirred, and the diamino compound **62** (previously dissolved in 2 mL of anhydrous DMF) was added dropwise *via* syringe. The mixture was allowed to warm to room temperature and stirred for 2 hours. The reaction mixture was quenched with 15 mL of water, stirred for 5 minutes, vacuum-filtered, and air-dried for 5 minutes. The resulting sticky solid was extracted with dichloromethane (DCM) by grinding it with a spatula. The resulting DCM solution was filtered to remove sulfur byproduct. Then silica (~40 mL) was added to the DCM solution, and then the DCM was removed by rotary evaporation. The resulting silica was transferred to a filtration funnel (vacuum) containing a short path of silica, then sand was placed on top of the silica. The silica

was flushed with hot hexanes (~250 mL). TLC was taken frequently from the hexanes fractions to confirm that all the sulfur byproduct had been eluted, and then a new filtration flask was placed under the funnel. The silica was flushed with a mixture 2:1 DCM:hexanes until all the yellow product had come out. The solvent was removed by rotary evaporation and the resulting solid was recrystallized from hot ethanol (~50 mL). The fine yellow needles were collected by filtration, washed with ethanol, air-dried, and put under vacuum, 0.370g, 82% yield. ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H 8.00 (d, 2H, J = 5.3 Hz), 7.51 (d, 2H, J = 5.3Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C 150.8, 135.8, 129.3, 125.3, 124.4. HRMS (APCI, $M+H^+$) m/z calcd. for $C_{10}H_4N_2S_3$ 248.9609, found 248.9616.

Synthesis of 5,8-dibromodithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-c][1,2,5]thiadiazole (Br_2-DT-BTD). To a 250-mL round-bottom flask, equipped with a stir bar and a condenser was added DT-BTD (0.380 g, 1.2402 mmol, 1 equiv), chloroform (100 mL), and bromine (0.14 mL, 0.436 g, 2.7284 mmol, 2.2 equiv.). The reaction mixture was warmed to 80 – 85°C, and stirred for 12 hours. The reaction mixture was cooled to room temperature, and the resulting solid was filtered, washed with chloroform, air-dried, and put under vacuum to remove solvent traces. A bright yellow solid was recovered, 0.460 g, 91.3% yield. ^{1}H-NMR (500 MHz, chlorobenzene-d_5, 95°C): δ 7.85 (s, 2H). ^{13}C-NMR (125 MHz, chlorobenzene-d_5, 95°C): δ_C 149.4, 135.4, 129.7, 126.4, 114.2.

Dithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-c]furazan (DTBF). To a 150-mL glass pressure vessel, equipped with a stir bar, was added the diketone BDTD (0.778g, 3.5321 mmol, 1 equiv), hydroxylamine hydrochloride (0.614g, 8.8302 mmol, 2.5 equiv.),

and 70 mL of ethanol (200 proof). The vessel was equipped with its respective Teflon cap, and the mixture was stirred at 85°C for 24 hours. The temperature was then increased to 140°C, and the reaction mixture was stirred for 60 hours. The mixture was cooled to room temperature and transferred to a round bottom flask. The solvent was removed by rotary evaporation, and the resulting solid was washed with water. The solid was then purified by column chromatography (silica, 1:5 ethyl acetate:hexanes). The resulting solid was stirred in a mixture of hot diethyl ether:hexanes 1:1 for 10 minutes. The mixture was cooled to room temperature, filtered, washed with the ethyl ether:hexanes (1:1 mixture), and air-dried. The remaining filtrate was roto-evaporated, and the procedure was repeated with the remaining solid (two times). The solids were collected and dried under vacuum. A yellow solid was received, 0.488 g (60% yield). Alternatively, this compound can be made in a 100-mL round-bottom flask, equipped with a condenser, at 85°C for 10 days. ^{1}H-NMR (300 MHz, $CDCl_3$): δ_H 7.91 (d, 2H, J = 5.3 Hz), 7.56 (d, 2H, J = 5.3 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ_C 146.0, 137.3, 126.5, 124.3, 122.7. HRMS (EI, M^+) m/z calcd. for $C_{10}H_4N_2OS_2$ 231.9765, found 231.9762.

Synthesis of 5,8-dibromodithieno[3',2':3,4;2'',3'':5,6]benzo[1,2-c]furazan (Br_2-DTBF). The reaction was carried using the same procedure as for Br_2-DT-BTD. A bright yellow solid was received, >65% yield. ^{1}H-NMR (300 MHz, chlorobenzene-d_5, 90°C): δ 7.62 (s, 2H). ^{13}C-NMR (75 MHz, chlorobenzene-d_5, 90°C): δ_C 144.7, 136.9, 126.8, 123.1, 115.2.

Synthesis of Br_2-DTBF from Br_2-BDTD. The reaction was carried out using the same procedure as for DTBF, using 1.6545 mmol of Br_2-BDTD. The work up was modified as follows: the reaction was cooled to room temperature, and the solvent

removed by rotary evaporation. The resulting solid was filtered and washed with water and acetone. The resulting solid was air-dried, and stirred in 100 mL of hot tetrahydrofuran (THF), and filtered when still hot. The remaining residue was treated again with 100 mL of hot THF. The THF filtrates were roto-evaporated, and the resulting solid was stirred in acetone (~15 mL) for 30 min, filtered, washed with acetone, and air-dried. A pale brown solid was received in 61.5% yield.

Synthesis 5,8-bis(4-hexylthiophen-2-yl)-DTBF (66). To a 25-mL Schlenk flask, containing a stir bar and argon atmosphere, was added (4-hexylthiophen-2-yl)trimethylstannane (51 mg, 0.1538 mmol, 3 equiv.), Br_2-DTBF (20 mg, 0.0513 mmol, 1 equiv.), $Pd_2(dba)_3$ (0.5 mg), and P(*o*-tol)$_3$ (0.5 mg). The flask was purged with vacuum-argon three times, and 1.5 mL of chlorobenzene (previously degassed) was added. The mixture was warmed to 105 °C, and stirred for 12 hours. The reaction mixture was cooled to room temperature, and plenty methanol was added until the product precipitated. The resulting solid was filtered, washed with methanol, air-dried, dissolved with DCM and filtered through a short path of silica. The DCM was removed by rotary evaporation and the resulting solid was washed with methanol, and dried under vacuum, affording 17.2 mg of an orange solid (>60% yield). ^{1}H-NMR (300 MHz, $CDCl_3$): δ_H 7.83 (s, 2H), 7.14 (s, 2H), 6.93 (s, 2H), 2.61 (t, 4H, J = 7.6 Hz), 1.70 – 1.61 (m, 4H), 1.43 – 1.25 (m, br, 12H), 0.91 (t, 6H, J = 6.4 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$): δ_C 145.7, 144.8, 138.9, 135.5, 134.9, 126.9, 123.1, 121.2, 119.2, 31.9, 30.6, 30.5, 29.2, 22.8, 14.3. HRMS (APCI, $[M+H]^+$) m/z calcd. for $C_{30}H_{32}N_2OS_4$ 565.1470, found 565.1483.

Synthesis of polymer 67. The synthesis was carried out using the same procedure as for **66**, in a scale of 0.13 mmol of Br_2-DTBF, using a ratio 1:2:1 of Br_2-DTS:$(Me_3Sn)_2$-DTS:Br_2-DTBF, and $Pd_2(dba)_3$ (1 mol%), P(*o*-tol)$_3$ (3 mol%), and chlorobenzene (7 mL). The reaction was run for 7 days at 115 °C, then, 5 mL of chlorobenzene, and a scoop of diethylammonium diethyldithiocarbamate were added. The mixture was stirred for 15 minutes and added dropwise into 300 mL of MeOH. The resulting solid was filtered (osmotics, nylon membrane, 20 μm), and washed with acetone. The resulting solid was transferred to a cellulose thimble and purified by Soxhlet extraction, using MeOH (12 hours), acetone (12h), hexanes (6h), DCM (6h), and chlorobenzene. The resulting chlorobenzene solution was concentrated to ~15 mL and then precipitated dropwise into 200 mL of methanol. The resulting solid was filtered (osmotics, nylon membrane, 20 μm), air-dried for 5 minutes, and dried under vacuum overnight. Elemental analysis calculated for $C_{82}H_{110}N_2OS_8Si_3$: C (66.52%), H (7.49%), N (1.89%). Found: C (65.08%), H (7.8%), N (1.43%).

Synthesis of 2,7-dibromo-4,5-bis(dodecyloxy)benzo[1,2-b:6,5-b']dithiophene (69). To a 25-mL round-bottom flask, equipped with a stir bar and an air-cooled condenser, was added Br_2-BTDT (0.150 g, 0.3968 mmol, 1 equiv.), dodecylbromide (0.297 g, 1.1903, 3 equiv.), K_2CO_3 (0.219, 1.5872 mmol, 4 equiv.), and anhydrous *N,N*-dimethylformamide (5 mL). The reaction mixture was stirred at 65°C for 24 hours, cooled to room temperature, and poured into 50 mL of water. The resulting solid was filtered, washed with water, and purified by column chromatography (silica, 1:8 hexanes:diethyl ether). A white solid was received, 0.174 g, 61% yield. ^{1}H-NMR (500 MHz, $CDCl_3$): δ_H 7.44 (s, 2H), 4.12 (t, 4H, J = 6.7 Hz), 1.83 – 1.75 (m, 4H), 1.52 – 1.46

(m, 4H), 1.40 – 1.20 (m, 32H), 0.89 (t, 6H, J = 6.9 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$): δ_C 143.0, 134.4, 129.2, 124.9, 113.0, 74.6, 32.2, 30.6, 29.92, 29.87, 29.8, 29.7, 29.6, 26.3, 22.9, 14.3.

CHAPTER 5
PERSPECTIVE AND OUTLOOK

Synthetic methodologies played a vital role in the development and understanding of π-conjugated polymers, and this is understandable, given the fact that the new synthetic developments had led to numerous ways to produce new π-conjugated polymers not only with the desired physical and electronic properties but also with high processability. When the synthetic metals revolution started in the mid-seventies, few synthetic tools were available to carry out such a task, but nowadays, polymer scientists possess new tool sets that allow us to construct new polymeric materials, with improved purities and higher molecular weights. Currently, it is possible to synthesize almost any imaginable molecule, allowing us to correlate our experimental data with our theoretical knowledge. Unfortunately, in many cases, scientists forget that their role as scientific researchers is to explore, and to understand the different phenomena that the universe put in front of them, and in this way to develop new solutions for the common good. Now π-conjugated polymer research has evolved more into a competition than into a science, and the lack of originality seems to be a widespread trend in our field. The work presented herein has shown how emerging synthetic methodologies can be applied to produce new organic materials, and provided a new toolset to develop 3,4-dioxypyrrole-based π-conjugated materials (Chapters 1 and 2). Additionally, it has been shown how the same monomeric unit can be slightly modified to generate a variety of new molecules with different properties—i. e. the donors and acceptors shown in Chapter 4.

Their electron rich nature and tunability are the two features that make 3,4-dioxypyrroles (XDOPs) attractive for applications in organic electronics, and due to this

electron rich nature XDOPs can produce polymers able to combine high electronic band gaps with low oxidation potentials. Also due to their electron rich nature however, XDOPs must be handled carefully, since they can easily decompose during reaction workup, purification, or storage.

It is clear now that 3,4-dioxypyrroles have been underutilized , and this is logical, given the fact that, so far, we have had a limited amount of tools to include this moiety into a π-conjugated material. While the monomer synthesis has probably been the most limiting factor in the progress of XDOP and PXDOP research, the work presented herein attempts to complement the available toolset of synthetic methodologies and allows for the derivatization of XDOPs and the synthesis of PXDOPs.

The studies of the decarboxylative cross coupling on 3,4-dioxypyrroles shown in Chapter 2 demonstrated the versatility of this methodology for molecules with a tendency to undergo decarboxylation. It is well known that molecules such as 3,4-dioxytiophenes and 3,4-dioxyfurans can also undergo decarboxylation, therefore, it is understandable to envision that the decarboxylative cross coupling methodology may be expanded to these molecules too. The decarboxylation temperature for 3,4-dioxytiophenes and 3,4-dioxyfurans are higher than for 3,4-dioxypyrroles, so future work will require model reactions to determine if the methodology is suitable for these molecules.

Chapter 4 has shown how aromatic diketones can be derivatized to produce various acceptor and donor molecules, giving us access to a new molecular kit that can be combined with a wide variety of other available molecules. These new fused systems may lead to new materials with higher electron and hole mobilities and unique

electronic band gaps, three important elements in a π-conjugated polymer. It is also clear that the solubility of the polymers generated from these molecules may be relatively low. Therefore, in order to surpass this problem, various approaches need to be employed, for example, using a random-reaction approach, as shown in Scheme 4-18, or using effective solubilizing groups in the donor molecule, or by synthesizing the same molecules containing various solubilizing groups in the aromatic rings.

LIST OF REFERENCES

(1) Letheby, H. *J. Chem. Soc., Trans.* **1862**, *15*, 161 – 163.

(2) Inzelt, G. In *Conducting Polymers*; Springer Berlin Heidelberg: 2008, p 265 – 269.

(3) McNeill, R.; Siudak, R.; Wardlaw, J. H.; Weiss, D. E. *Aust. J. Chem.* **1963**, *16*, 1056 – 1075.

(4) Bolto, B. A.; Weiss, D. E. *Aust. J. Chem.* **1963**, *16*, 1076 – 1089.

(5) Bolto, B. A.; McNeill, R.; Weiss, D. E. *Aust. J. Chem.* **1963**, *16*, 1090 – 1103.

(6) Dall'Olio, A.; Dascola, G.; Varacca, V.; Bocchi, V. *C. R. Acad. Sci., Paris, Ser. C* **1968**, *267*, 433 – 5.

(7) Natta, G. *J. Polym. Sci.* **1955**, *16*, 143 – 54.

(8) Natta, G.; Mazzanti, G. *Tetrahedron* **1960**, *8*, 86 – 100.

(9) The Nobel Prize in Chemistry 1963. http://nobelprize.org/nobel_prizes/chemistry/laureates/1963/ (accessed: Oct 11, 2011).

(10) Natta, G.; Mazzanti, G.; Corradini, P. *Atti accad. nazl. Lincei Rend. Classe sci. fis. mat. e nat.* **1958**, *25*, 3 – 12.

(11) Shirakawa, H.; Ikeda, S. Film and fibers of acetylene high-molecular-weight polymer. JP patent, 1970-34406, April 22, 1973.

(12) Meshcheryakov, S. V.; Shvachkin, Y. A. *Khim. Khim. Tekhnol., Tezisy Kraev. Nauchno-Tekh. Konf. Molodykh Uch., Aspir. Spets.-Khim. Kubani, 2nd* **1973**, *2*, 206 – 7.

(13) Ito, T.; Shirakawa, H.; Ikeda, S. *J. Pol. Sci.: Pol. Chem. Ed.* **1974**, *12*, 11 – 20.

(14) Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J. *J. Chem. Soc. Chem. Comm.* **1977**, 578 – 580.

(15) The Nobel Prize in Chemistry 2000. http://nobelprize.org/nobel_prizes/chemistry/laureates/2000/ (Accessed: Oct 11, 2011).

(16) Skotheim, T. A.; Reynolds, J. R. *Handbook of Conducting Polymers: Processing and Applications*; Third ed.; CRC Press LLC, Boca Raton, FL, 2007.

(17) Skotheim, T. A.; Reynolds, J. R. *Handbook of Conducting Polymers: Conjugated Polymers, Theory, Synthesis, Properties, and Characterization*; Third ed.; CRC Press LLC, Boca Raton, FL, 2007.

(18) Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R. *Handbook of Conducting Polymers*; 2nd ed.; Marcel Dekker: New York, 1998.

(19) (a) Peierls, R. E. *More surprises in theoretical physics*; Princeton University Press: Princeton, N.J., 1991; p 106. (b) Peierls, R. E., *Quantum Theory of Solids*; Oxford Univ. Press: N.Y., 1955; p 229.

(20) Salzner, U.; Lagowski, J. B.; Pickup, P. G.; Poirier, R. A. Synth. Met. 1998, 96, 177 – 189.

(21) Brédas, J. L.; Chance, R. R.; Silbey, R. *Phys. Rev. B* **1982**, *26*, 5843.

(22) Heeger, A. J.; Kivelson, S.; Schrieffer, J. R.; Su, W. P. *Rev. Mod. Phys.* **1988**, *60*, 781.

(23) Walczak, R. M.; Leonard, J. K.; Reynolds, J. R. *Macromolecules* **2008**, *41*, 691 – 700.

(24) Walczak, R. M.; Reynolds, J. R. *Adv. Mater.* **2006**, *18*, 1121 – 1131.

(25) Ateh, D. D.; Navsaria, H. A.; Vadgama, P. *J. R. Soc. Interface* **2006**, *3*, 741 – 752.

(26) Schottland, P.; Zong, K.; Gaupp, C. L.; Thompson, B. C.; Thomas, C. A.; Giurgiu, I.; Hickman, R.; Abboud, K. A.; Reynolds, J. R. *Macromolecules* **2000**, *33*, 7051 – 7061.

(27) Sonmez, G.; Schwendeman, I.; Schottland, P.; Zong, K.; Reynolds, J. R. *Macromolecules* **2003**, *36*, 639 – 647.

(28) Thomas, C. A.; Zong, K.; Schottland, P.; Reynolds, J. R. *Adv. Mater.* **2000**, *12*, 222 – 225.

(29) Walczak, R. M.; Jung, J.-H.; Cowart, J. S.; Reynolds, J. R. *Macromolecules* **2007**, *40*, 7777 – 7785.

(30) Merz, A.; Schropp, R.; Dötterl, E. *Synthesis* **1995**, *1995*, 795 – 800.

(31) Merz, A.; Meyer, T. *Synthesis* **1999**, *1999*, 94 – 99.

(32) Merz, A.; Kronberger, J.; Dunsch, L.; Neudeck, A.; Petr, A.; Parkanyi, L. *Angew. Chem. Int. Ed.* **1999**, *38*, 1442 – 1446.

(33) Ishiyama, T.; Takagi, J.; Yonekawa, Y.; Hartwig, J., F. ; Miyaura, N. *Adv. Synth. Catal.* **2003**, *345*, 1103 – 1106.

(34) Dhanabalan, A.; Knol, J.; Hummelen, J. C.; Janssen, R. A. J. *Synth. Met.* **2001**, 119, 519 – 522.

(35) Jana, G. H.; Jain, S.; Arora, S. K.; Sinha, N. Bioorg. Med. *Chem. Lett.* **2005**, 15, 3592 – 3595.

(36) Baudoin, O. *Angew. Chem. Int. Ed* **2007**, *46*, 1373 – 1375.

(37) Gooßen, L. J.; Rodríguez, N.; Gooßen, K. *Angew. Chem. Int. Ed.* **2008**, *47*, 3100 – 3120.

(38) Nilsson, M. *Acta Chem. Scand.* **1966**, *20*, 423 – 426.

(39) Heim, A.; Terpin, A.; Steglich, W. *Angew. Chem.* **1997**, *109*, 158 – 159.

(40) Heim, A.; Terpin, A.; Steglich, W. *Angew. Chem. Int. Ed.* **1997**, *36*, 155 – 156.

(41) Peschko, C.; Winklhofer, C.; Steglich, W. *Chem. Eur. J.* **2000**, *6*, 1147 – 1152.

(42) Myers, A. G.; Tanaka, D.; Mannion, M. R. *J. Am. Chem. Soc.* **2002**, *124*, 11250 – 11251.

(43) Forgione, P.; Brochu, M.-C.; St-Onge, M.; Thesen, K. H.; Bailey, M. D.; Bilodeau, F. *J. Am. Chem. Soc.* **2006**, *128*, 11350 – 11351.

(44) Gooßen, L. J.; Deng, G.; Levy, L. M. *Science* **2006**, *313*, 662 – 664.

(45) Moon, J.; Jeong, M.; Nam, H.; Ju, J.; Moon, J. H.; Jung, H. M.; Lee, S. *Org. Lett.* **2008**, *10*, 945 – 948.

(46) Gooßen, L. J.; Thiel, W. R.; Rodríguez, N.; Linder, C.; Melzer, B. *Adv. Synth. Catal.* **2007**, *349*, 2241 – 2246.

(47) Miura, M.; Nomura, M. In *Cross-Coupling Reactions*; Springer Berlin / Heidelberg: 2002; Vol. 219, p 211 – 241.

(48) Beaujuge, P. M.; Reynolds, J. R. *Chem. Rev.* **2010**, *110*, 268 – 320.

(49) Miyaura, N.; Suzuki, A. *Chem. Commun.* **1979**, *19*, 866 – 867.

(50) Miyaura, N.; Yamada, K.; Suzuki, A. *Tetrahedron Lett.* **1979**, *20*, 3437 – 3440.

(51) Kotha, S.; Lahiri, K.; Kashinath, D. *Tetrahedron* **2002**, *58*, 9633 – 9695.

(52) Arroyave, F. A.; Reynolds, J. R. *Org. Lett.* **2010**, *12*, 1328 – 1331.

(53) Shang, R.; Xu, Q.; Jiang, Y.-Y.; Wang, Y.; Liu, L. *Org. Lett.* **2010**, *12*, 1000 – 1003.

(54) Gooßen, L., J. ; Lange, P., P. ; Rodríguez, N.; Linder, C. *Chem. Eur. J.* **2010**, *16*, 3906 – 3909.

(55) Bilodeau, F.; Brochu, M.-C.; Guimond, N.; Thesen, K. H.; Forgione, P. *J. Org. Chem.* **2010**, *75*, 1550 – 1560.

(56) Reynolds, J. R.; Walczak, R. M. Catalyst free polymerization of 3,4-alkylenedioxypyrrole and 3,4-alkylenedioxyfuran. U.S. patent, 20070270571, 2007, 2007.

(57) Walczak, R. M. Synthetic methodology as a basis for conducting polymer design. Ph. D. Dissertation, University of Florida, Gainesville, FL, 2006.

(58) Khor, E.; Ng, S. C.; Li, H. C.; Chai, S. *Heterocycles* **1991**, *32*, 1805 – 12.

(59) Nicolas, Y.; Blanchard, P.; Roncali, J.; Allain, M.; Mercier, N.; Deman, A.-L.; Tardy, J. *Org. Lett.* **2005**, *7*, 3513 – 3516.

(60) Usta, H.; Lu, G.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 9034 – 9035.

(61) Hou, J.; Chen, H.-Y.; Zhang, S.; Li, G.; Yang, Y. *J. Am. Chem. Soc.* **2008**, *130*, 16144 – 16145.

(62) Babudri, F.; Fiandanese, V.; Marchese, G.; Punzi, A. *Tetrahedron Lett.* **1995**, *36*, 7305 – 7308.

(63) Saitoh, Y.; Koizumi, T.-a.; Osakada, K.; Yamamoto, T. *Can. J. Chem.* 1997, 75, 1336 – 1339.

(64) Dickeson, J. E.; Summers, L. A. *Aust. J. Chem.* **1970**, *23*, 1023 – 7.

(65) Yamada, M.; Tanaka, Y.; Yoshimoto, Y.; Kuroda, S.; Shimao, I. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1006 – 11.

(66) Bhatt, M. V. *Tetrahedron* **1964**, *20*, 803 – 821.

(67) Dewhurst, F.; Shah, P. K. J. *J. Chem. Soc. C* **1969**, 1503 – 1504.

(68) Hanif, M.; Lu, P.; Li, M.; Zheng, Y.; Xie, Z.; Ma, Y.; Li, D.; Li, J. *Polym. Int.* **2007**, *56*, 1507 – 1513.

(69) Leuckart, R. *Ber. Dtsch. Chem. Ges.* **1885**, *18*, 2341 – 2344.

(70) Weinstock, L. M.; Davis, P.; Handelsman, B.; Tull, R. J. *J. Org. Chem.* **1967**, *32*, 2823 – 2829.

(71) Phillips, K. E. S.; Katz, T. J.; Jockusch, S.; Lovinger, A. J.; Turro, N. J. *J. Am. Chem. Soc.* **2001**, *123*, 11899 – 11907.

BIOGRAPHICAL SKETCH

Frank A. Arroyave was born in Sevilla (Valle), Colombia, in 1976. He graduated with his B.S. in Chemistry from Universidad del Valle at Cali in 2004, where he worked in the research group of professor Rodrigo Abonia, in the area of heterocyclic chemistry. In fall 2006, he began graduate school at the University of Florida in Gainesville, Florida, in the department of chemistry, where he joined the group of professor John Reynolds and focused his studies on organic and polymer chemistry.