

Novel Copolymers Based on Methoxythiophene-Flanked Diketopyrrolopyrrole for Wearable Resistive Sensors

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

The exposure that firefighters experience due to their occupation has recently been identified by the World Health Organization as a Group 1 carcinogen. One factor is colorless, odorless, toxic gases in “warm zones” near enough to fires where awareness and protection are lowered but the actual risks are still high. The current gas sensors available are based on metal oxides, and are bulky, inflexible, and costly to produce. By contrast, gas sensors based on conjugated polymers promise to be lightweight and flexible enough to weave directly into clothing and could be manufactured using low cost roll-to-roll printing. However, they require improvements in stability.

This work first establishes a baseline of stability for previously reported conjugated polymers. Common p-type dopant molecules are used to dope diketopyrrolopyrrole (DPP) copolymers, which are known for their stability. It was found that the longest the sensors could last was ~10 days.

Believing that the stability could be improved through increasing the energy level of the polymer’s Highest Occupied Molecular Orbital (HOMO), this thesis extends a recent report of a novel DPP-flanking group, methoxythiophene. The potential of methoxythiophene-flanking groups as a method to raise DPP polymer HOMO energy has several advantages. They are sterically small (only extending the length of the thiophene molecule by $< 2.5 \text{ \AA}$) and by using the flanking group to raise the HOMO, both the choice of solubilizing side chain and choice of comonomer remain free. A solubilizing side chain with thermally/chemically removable groups could therefore be used. The removal process could introduce stable pores, enhancing gas transport in and out of the polymer film. Likewise, a comonomer could be selected for its interaction with a target gas.

Three novel conjugated DPP-based copolymers were then synthesized, using methoxythiophene as a flanking group to the DPP unit. Two were produced through Stille coupling and one was produced through the more environmentally friendly Direct Arylation Polymerization (DAP).

As hypothesized, these copolymers show high HOMO levels, which are anticipated to grant them high stability once doped with common p-dopants. One, C8-EDOT shows conductivity stable in air over 2 months (~1%/day decrease in current) even without exogenous dopant, having been doped by trace HCl in chloroform used to coat films. The three polymers also show ultralow bandgaps, which could make them useful in Near Infrared detection or Organic Photovoltaic applications.

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Dedication

To the brilliant KLS

To JLWSML

And to the firefighters of the Cameron Peak Fire

Firefighters mission (affixed to our home) "Stay & defend". October 15, 2020

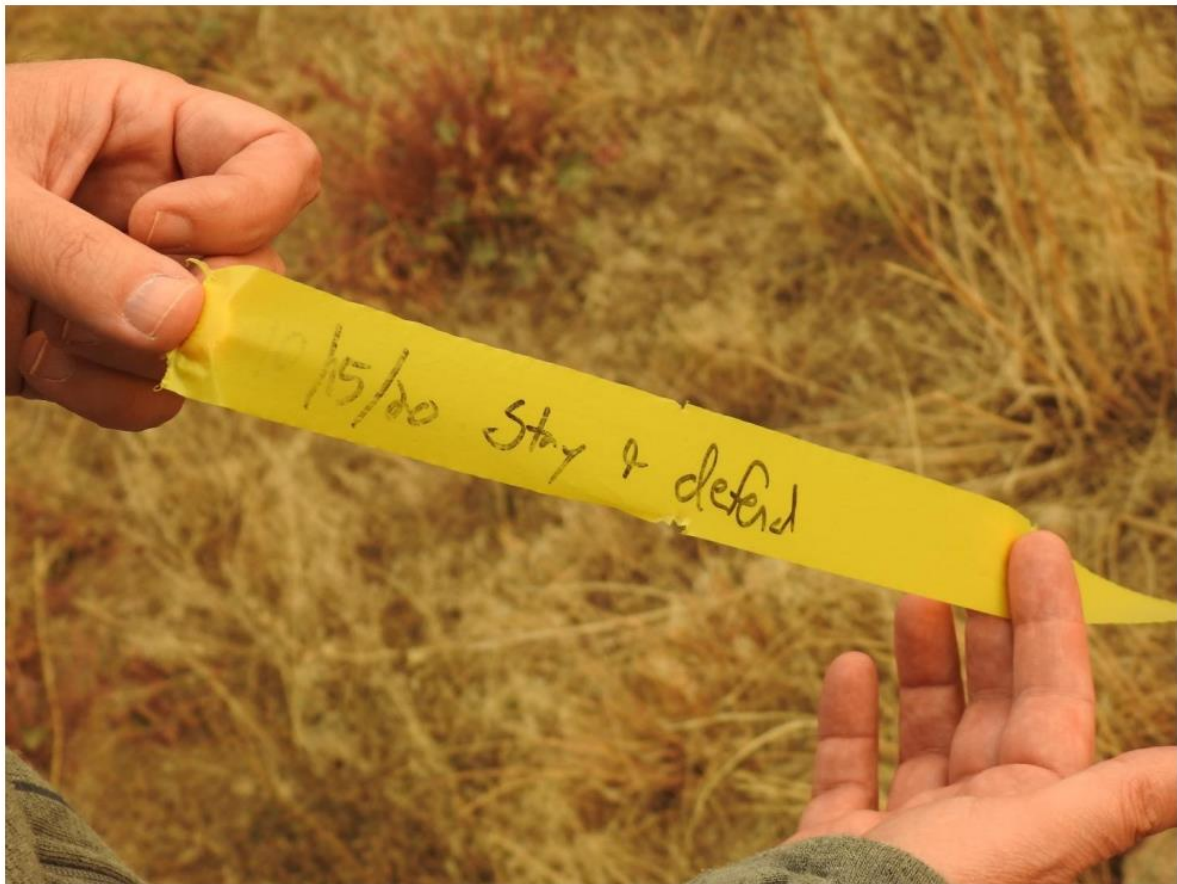


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List of Abbreviations

C8: 2-ethylhexyl bromide
C20: 2-octyl-1-dodecylbromide
CP: Conjugated polymer
CTC: Charge-Transfer Complex
CV: Cyclic Voltammetry
DAP: Direct Arylation Polymerization
DCM: Dichloromethane
DFT: Density Functional Theory
DPP: diketopyrrolopyrrole
DPP-BT: poly(thiophene-flanked DPP -co- bithiophene)
DPP-TT: poly(thiophene-flanked DPP -co- thienothiophene)
DPPPy-TT: poly(pyrrole-flanked DPP -co- thienothiophene)
EDOT: 3,4-Ethylenedioxythiophene
F4TCNQ: 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane
FeCl₃: Iron (III) chloride
FET: Field-Effect Transistor
GPC: Gel Permeation Chromatography
HOMO: Highest Occupied Molecular Orbital
LUMO: Lowest Unoccupied Molecular Orbital
Magic Blue: tris(4-bromophenyl)ammoniumyl hexachloroantimonate
MOTh: methoxythiophene
MW: Molecular Weight
NIR: Near Infrared
PDI: Polydispersity Index
RH: Relative Humidity
SCBA: Self-Contained Breathing Apparatus
TT: thienothiophene
UV-Vis: Ultraviolet-Visible Spectroscopy

List of Symbols

λ_{max} : wavelength at highest absorbance value for the sample, excluding any solvent peaks

λ_{onset} : onset wavelength of the λ_{max} absorbance peak

E_g : band gap as determined from optical (UV-Vis) measurement of λ_{onset}

HOMO_{CV} : HOMO as determined by the onset of oxidation during Cyclic Voltammetry

$\text{LUMO}_{\text{opt/CV}}$: LUMO determined by a sum of optical E_g and HOMO_{CV} from Cyclic Voltammetry

M_n : number average molecular weight

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Chapter 1: Introduction

1.1 Overview of Status Quo of Gas Sensing in Firefighting

In June 2022, the World Health Organization designated the exposure that firefighters experience due to their occupation a Group 1 carcinogen.¹ One factor is colorless, odorless, toxic gases in “warm zones.” These are areas near enough to fires where the risk of exposure is still high but awareness and protection are lowered. The final portion of an incident, after the fire is extinguished, is known as “overhaul.” This is where firefighters break down walls and look very closely for any remaining fire in hard to reach areas such as attics or ceilings and is often carried out without use of a self-contained breathing apparatus (SCBA) even though studies tracking overhaul have shown above threshold exposure to formaldehyde, carbon monoxide, and other toxic gases.² Due to the invisibility of these dangers, over time gas sensors have become more and more common in use when responding to scenes, becoming especially crucial if the emergency involves the presence of hazardous materials e.g. a chemical plant fire or chemical attack.

The increased prevalence of wildfire fighting induced by climate change also poses challenges as full SCBA personal protective equipment is rarely worn in these situations.³ Firefighters fighting wildfires need to be highly mobile, moving on foot across large distances of land for periods averaging 8-13 hours. When most SCBA units only provide about 30-60 minutes of breathing time and weigh 15 kg, it becomes apparent why the wildfire responders commonly only wear cotton bandanas, N95 masks, or often nothing.³ Without gas sensors providing real-time guidance or at least logging their exposure, the escalating incidence of wildfires from the worsening climate could worsen the health outcomes for our firefighters.

1.1.1 Limitations of Metal Oxide Gas Sensors and the Potential for Conjugated Polymer (CP) Gas Sensors

Several companies sell gas sensors specifically for firefighters and first responders. In many commercial gas sensing products, the active materials interacting with the analyte gases are vacuum-deposited metal oxides.⁴ As a result the sensing equipment is rather heavy, bulky, and expensive.

Metal oxide sensors are stable. However, they lack printability (must be produced through deposition and hence are not low cost to produce), are intrinsically not flexible, require heavy device architecture, and they require substantial power to operate as they need to be heated.⁵

A pressing goal is to produce robust, wearable toxic gas sensors for firefighters. To make them robust, they must be stable over time in air and stable at relatively high temperatures. To be wearable, the sensors must be small, lightweight, flexible, low cost, and have low energy use. Wearable gas sensors based on conjugated polymers could provide a highly effective solution, as they are printable (solutions of the polymer can be used as ink), lightweight, intrinsically flexible, low-power (they can operate at room temperature), and vastly tunable through modifications to repeat unit structure.⁶

One major issue is that sensors based on conjugated polymers are often found to not be stable.⁷⁻⁹ Stability in this case refers to the ability of the device to resist degradation—loss of sensing performance—when operated while exposed to the environment (air, moisture, light, heat, analyte gases). This is the core problem addressed in this thesis.

1.1.2 Current State of CP Gas Sensors

Since the first reported use of polypyrrole to sense ammonia in 1983, the field of conjugated polymer gas sensors has progressed significantly.¹⁰⁻¹² However, challenges with stability remain. A sensor which is perfectly stable provides the same response to an identical stimulus, even over extended lengths of time and multiple cycles of exposure to the stimulus. The less stable a sensor, the shorter its useful lifespan.

For sensing purposes, an analyte needs to interact with an active material of the sensor and change a measurable value (typically a current or voltage, or a color). Chemical sensors which use conjugated polymers as their active materials, may either a) raise the conductivity of the polymer through doping, in which case the polymer is used as a resistor and change in conductivity is used as signal, or b) it may be used in a field-effect transistor (FET) configuration. In this second configuration a gate voltage is responsible for the generation of charge carriers in the material that allow significant current to flow. The current through the device and the threshold voltage are two common choices for measurable values used to calibrate FET-based sensors, though there are other options being explored for different applications.¹³

1.2 Conjugated Polymers

Conjugated polymers are polymers in which delocalized π -electrons are spread throughout the chain. The term “conjugated” comes from Latin “con” (together) and “jugum” (yoke) implying that the electrons are all yoked together and therefore can work together to transport charge through what

without conjugation would be a highly insulating material. It is worth briefly noting that it is possible to disperse conductive particles in insulating polymers to achieve composites which could be called conducting polymers; however, those are not the topic of this thesis.

Several examples of conjugated polymers: polyacetylene, P3HT, and PEDOT are shown in Figure 1-1 below.

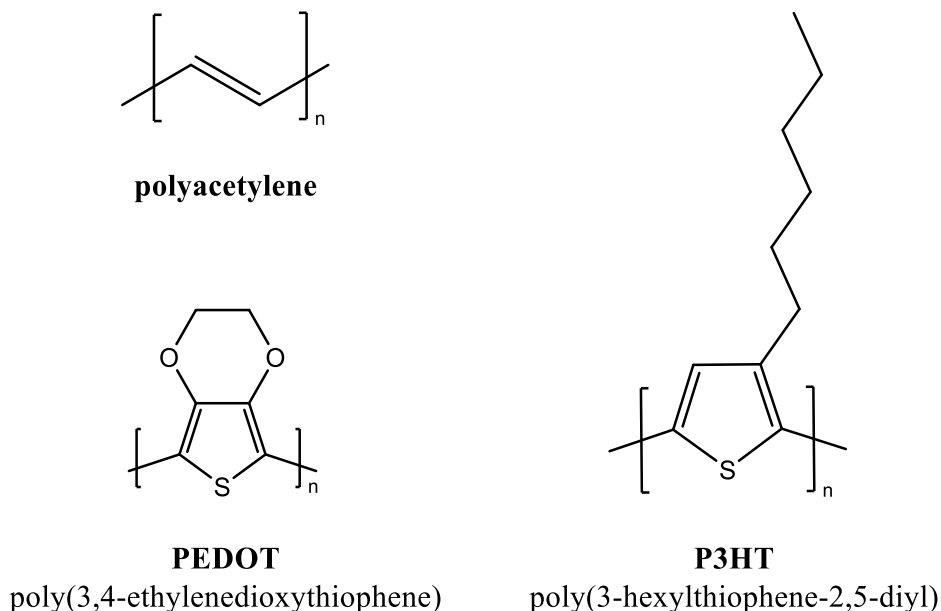


Figure 1-1: Example structures of conjugated polymers.

Electrons which are tied up in σ -bonds, i.e. spread around a hypothetical line drawing the shortest distance between two nuclei, are localized quite firmly. The electrons in π -bonds are freer to travel throughout the molecule, not quite as free as the metallic “sea of electrons” but much more than electrons in a typical insulating polymer.¹⁴ This delocalization due to the conjugation is a necessary but not sufficient condition for conductivity, as a doping process is also required in order to provide charge carriers. This topic will be further discussed in Section 1.3.

As conjugated polymers have combined the tunability, mechanical flexibility, and processability of polymers with the electronic properties of semiconductors and metals, they have drawn massive interest since their development in the late 1970s and have been used for many applications, such as organic field-effect transistors, organic photovoltaics, organic light-emitting diodes, and most relevantly, organic sensors.

Doped conjugated polymers have struggled to achieve high stability—meaning device lifetime is low. The polymer may degrade, the dopant may degrade, or the polymer-dopant complex may degrade. In this last category of degradation, a common cause is the dopant molecule either phase segregating away from the polymer but staying in the film, or the evaporation of the dopant molecule resulting in it leaving the film entirely. Interaction of the doped conjugated polymer with oxygen, moisture, and other environmental factors can promote degradation as well. In many applications the doped conjugated polymer can be protected by encapsulation. In the case of gas sensors, however, as the doped conjugated polymer is the active material, it must be in direct contact with the outside environment.

1.2.1 Diketopyrrolopyrrole-based Donor-Acceptor copolymers

Diketopyrrolopyrrole (DPP) was originally used as a resilient pigment in Ferrari sports cars, then known as “Ferrari Red.” In the framework of designing donor-acceptor polymers, the DPP unit itself is considered an electron “acceptor” and it has been copolymerized with many electron-rich “donor” comonomers. In many reports, the DPP unit has appeared flanked on either side by single phenyl rings or aromatic heterocycles such as thiophene, pyridine, and furan (see below Figure 1-2).

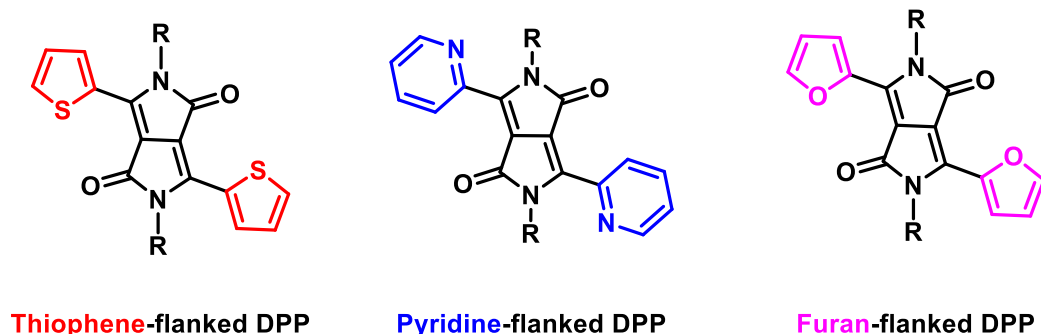


Figure 1-2: Well-studied flanking groups used to make conjugated DPP polymers.

Adding an electron-rich methoxy- group to thiophene has been a successful strategy in raising HOMO levels in polythiophenes and partly explains the dominance of PEDOT. This strategy has been relatively unexplored for DPP-based copolymers, with the first report of methoxythiophene-flanked DPP copolymers coming in 2019 from Domokos et al.¹⁵

1.3 Doping

In this work the focus is on chemiresistive sensors, in which the active material is somewhat conductive once a voltage is applied and changes conductivity upon interacting with the analyte gas. Conjugated polymers are not conductive innately, as even though there is a pathway for charge to flow, the polymers in their pristine state are neutral and have few charge carriers which are free to move along the pathways. Addition of excess charge carriers, allowing current to flow, is named “doping” in organic semiconductors just as it is in inorganic semiconductors. In organic polymeric semiconductors like conjugated polymers, typically this is either done through application of an external electric field or introduction of an exogenous compound (“dopant”) which donates or removes an electron from the polymer. Thorough details on the mechanisms and effects of doping are discussed in Section 2.2 - Background on Doping of Conjugated Polymers.

1.4 Synthesis Methods (Stille coupling and DArP)

The general reaction schemes of the two common methods of conjugated polymer synthesis used in this thesis, Stille coupling Polymerization and Direct Arylation Polymerization (DArP), are shown in Figure 1-3 below.

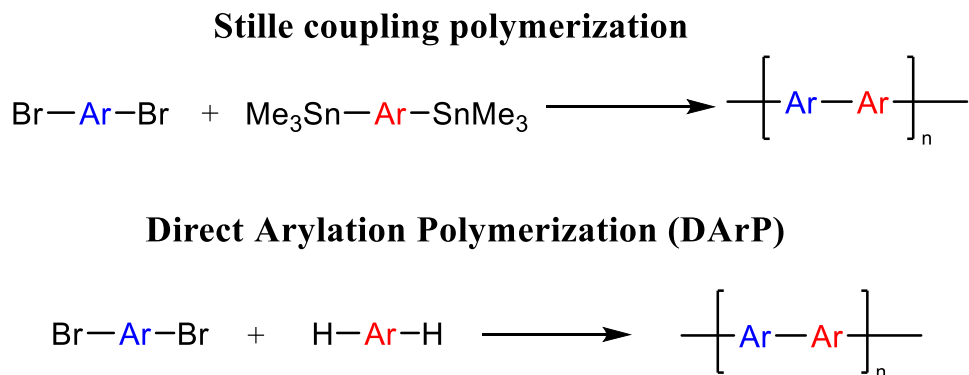


Figure 1-3: The two methods of polymerization used in this thesis, Stille coupling polymerization and Direct Arylation Polymerization (DArP).

Stille coupling has been applied to produce conjugated polymers for the past three decades, beginning from the use of a thiophene decorated with trimethyl tin by Bao et al. (1993).¹⁶ It has since shown compatibility with a wide range of monomers and is known to reliably produce high molecular weight

polymers.¹⁷ However the use of organotin, due to environmental and health concerns, has come under scrutiny in recent years and researchers have looked for alternative methods.

DArP avoids the use of organotin compounds and also has an improved atomic efficiency.¹⁸ A wide range of conditions have been studied, resulting in the establishment of five “Classes” of reaction conditions for DArP. This provides a repository of appropriate reaction conditions for testing, but in general DArP requires more trial-and-error than Stille coupling.

Both methods of polymerization employed in this work are labeled polycondensation polymerizations.^{19,20} This is opposed to a chain-growth mechanism by the fact that all “A” monomers are active to polymerize with all “B” monomers and polymer chain molecular weight is low until high conversion is reached. Specifically, the term polycondensation is most appropriate as both Stille coupling and DArP result in low molecular weight byproducts. In this work these low molecular weight side products would be Me₃Sn and HBr for Stille coupling and DArP, respectively.

1.5 Characterization Methods

1.5.1 Chemical Structure of Monomers and Intermediates

¹H NMR was used to analyze the small molecule intermediates toward making monomers, as well as the monomers themselves. This is in order to a) provide positive identification that the target compound was synthesized and b) ensure that the purity is sufficient for the next step of synthesis. ¹H NMR of the polymers was also measured, although it is unusual for conjugated polymers to fully dissolve to the molecular level in room temperature solvents. Therefore, it was especially critical to ensure purity of the monomer before using it for polymerization.

1.5.2 Physical Properties (GPC, TGA)

Gel Permeation Chromatography (GPC) allows polymers to travel through a column packed with a porous material. The more the polymers interact with the column packing, the longer it takes them to reach the detector at the end. GPC is a form of Size Exclusion Chromatography because polymers of larger size are excluded from the pores in the packing. This leads to them having a very short retention time. Polystyrene standards of known molecular weight, retention time, and detector response can then be used to estimate the molecular weight of an unknown polymer. This assumes that molecular weight and molecule size are proportional, which is justified if both polymers are fully

dissolved and form random coils. In practice, conjugated polymers are rarely fully dissolved in room temperature solvents and so High-Temperature GPC (HT-GPC) is typically employed. This can involve using mobile phases like trichlorobenzene which can be heated to 150 °C in an effort to promote polymer dissolution. In conjugated polymers where one comonomer is electron donating and another is electron withdrawing (called “Donor-Acceptor” type), the π - π stacking between chains is especially intense and this pulls chains together so tightly that solvent molecules have trouble penetrating.

TGA works by heating a sample in a nitrogen atmosphere and recording the weight loss of the sample. It measures the decomposition of a material with respect to temperature which provides an indication of a material’s thermal stability. This is a critical factor for firefighter gear.

1.5.3 Optoelectronic Properties (UV-Vis, CV)

UV-Vis spectroscopy probes how a solution or film interacts with light of a range of energies. The sample is irradiated with light of low energy scanning to high energy, and it is used to determine the onset of absorption, peak absorption, and also the optical bandgap E_g . Note that the term “UV-Vis” will be used throughout this thesis as a shorthand to refer to light absorption measurements even though several of the spectra extend into the IR region and beyond.

To perform Cyclic Voltammetry (CV), an electrode is coated with a polymer sample, introduced into an electrolyte, and then an external power supply is used to scan from low voltage to high. At certain voltage values, the sample may undergo oxidation (loss of electrons) or reduction (gain of electrons). By recording the values at which these processes begin, the HOMO and LUMO levels are determined. Specifically, the onset of oxidation is used to calculate the HOMO level. In practice, most reported optoelectronic properties for conjugated polymers measure E_g from UV-Vis, HOMO from CV, and subsequently add the two values together in order to calculate the LUMO level.

1.6 Thesis Structure and Objectives

The objective of the thesis is to drive forward the development of robust, wearable gas sensors for firefighters through the development of stable doped conjugated polymers.

Chapter 2 describes doping a series of DPP-copolymers (DPP-BT, DPP-TT, and DPPP_y-TT) with common p-type dopants in order to produce conductive polymers. These could have been used as

chemiresistive gas sensors if the polymer-dopant complex were stable. The development of the method for doping, and the UV-Vis and conductivity results are presented along with stability data.

Chapter 3 describes the synthesis of three novel conjugated DPP copolymers with high HOMO levels and ultralow bandgaps, which are anticipated to improve on the stability of the polymer-dopant combinations reported in Chapter 2.

In Chapter 4, major results of the thesis are summarized and direction for future work is suggested in order to enable robust, wearable gas sensors for firefighters.

Chapter 2: P-type doping of thiophene-flanked DPP-based copolymers

2.1 Introduction

In order to make resistive gas sensors, conjugated polymers must be doped sufficiently to reach $\sim 10^{-4}$ S/cm and retain this conductivity for long enough to be useful. There are literature reports of doped DPP copolymers, but these are done in a nitrogen environment. To make robust, wearable sensors for firefighters, the sensors will need to be stable outside a glovebox.

In this Chapter, baselines for stability in air are established by studying three DPP copolymers doped with two common dopants. Conductivity levels (S/cm) measured in air are determined and the number of days that the conductivity persists is tracked while the samples are stored in air.

In order for conductive polymers to be useful in devices such as resistor-based chemical sensors (“chemiresistive” sensors), it is important that they have conductivity which is measurable and stable over time. For this reason, in this chapter it is investigated whether three conjugated DPP copolymers under study were dopable with two common p-dopants, and how stable the conductivity was over time and changes in the environment.

2.2 Background on Doping of Conjugated Polymers

A network of π -bonds allows electrons to delocalize along conjugated polymer chain backbones, giving them significant mobility μ . However, in order for the material to achieve significant conductivity, they need charge carriers to travel along this pathway. The equation for conductivity σ indicates the missing factor n which is charge carrier density (q is simply the elementary charge):

$$\sigma = nq\mu$$

Thus, the aim of doping in conjugated polymers is to increase the number of charge carriers n . In p-type doped polymers where electron “holes” are the majority charge carrier, this is achieved by the use of oxidizing molecules which typically have low-lying LUMO levels which can remove and accept the high energy electrons of the polymer’s HOMO electrons.

It is also possible to see the effects of doping clearly through UV-Vis measurements. For the class of conjugated polymers under discussion, typically the primary absorption signal found between ~ 800 - 900 nm decreases in intensity while higher wavelength signal >1000 nm increases. Below in Figure 2-1 is an example from Kim et al. (2021), showing DPP-BT being 2-step doped by FeCl_3 .

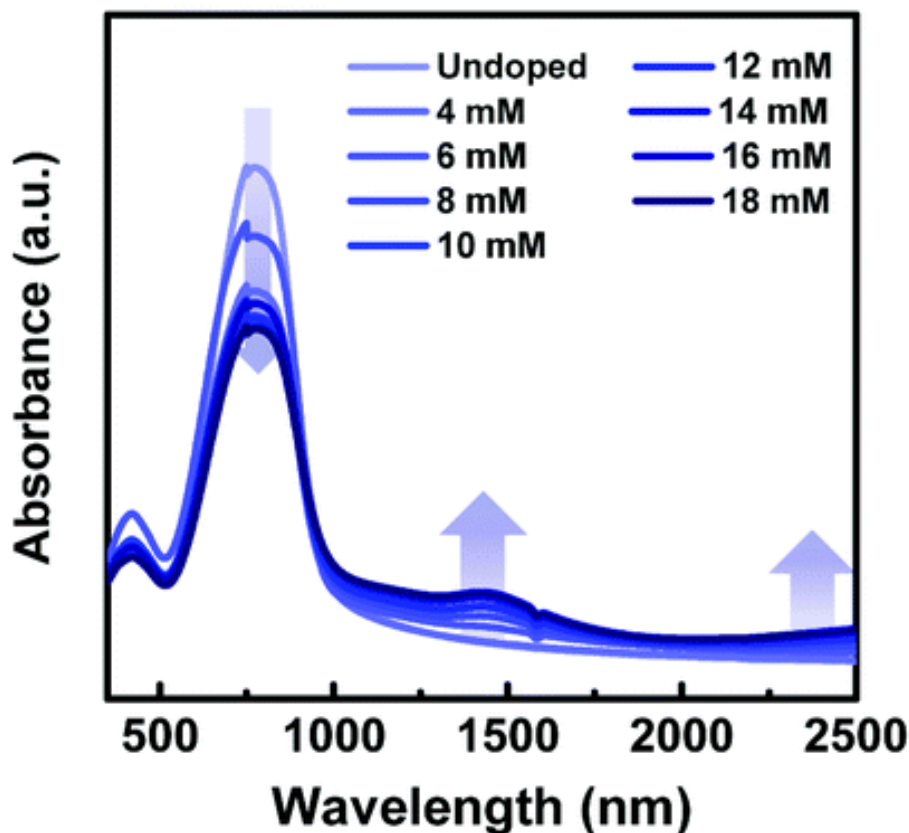


Figure 2-1: Example UV-Vis spectra of DPP-BT undoped and also after doping with a various concentrations of FeCl_3 dissolved in acetonitrile; light blue arrows indicate two characteristic changes of conjugated polymer absorption spectra upon doping: 1) a decrease in main peak intensity and 2) an increase in higher wavelength (>1000 nm) absorption, attributed to (bi)polaron signal. Modified figure from Kim et al. (2021).²¹

There are two main mechanisms thought to be behind the process of doping. These two mechanisms bear some resemblance to the difference between ionic bonds (similar to integer charge doping mechanism) and covalent bonds (similar to charge-transfer complex).

The first is more straightforward and is indicated in the previous paragraph: an integer number of electrons are “removed” from the polymer and transferred to the dopant molecule. This requires there to be an energetic driving force for the electrons to transfer, e.g. the LUMO of the dopant could be lower in energy than the HOMO of polymer, so stability would be increased by the transfer of electrons from polymer to dopant.

In the second mechanism, there is not simply an integer number of electrons transferred from one species to another, but instead rather than the polymer donating HOMO electrons to the dopant's LUMO level, the polymer and the dopant molecule hybridize their orbitals to make entirely new orbitals. This second mechanism is known as “charge-transfer complex formation” and is driven by the creation of new charge-transfer complex (CTC) frontier energy levels e.g. HOMO_{CTC} and LUMO_{CTC} orbitals. There are several reported cases where p-type doping has occurred even in polymer-dopant systems where the LUMO of the dopant is much higher than the HOMO of the polymer, which can be explained by formation of a CTC rather than ion-pair formation. Three of these cases are discussed in detail in an extensive review paper on doping of organic semiconductors by Scaccabarozzi et al. (2022).²² The review also concludes that given the field's developing understand of the processes, predicting whether a particular dopant will work or not and by which mechanism it will dope is still difficult.

With regard to the processes used by experimenters to dope conjugated polymers, there are primarily two categories: 1-step or “blend” doping and 2-step or “sequential” doping. In 1-step doping, solutions of polymer and dopant are blended, and a doped film is coated directly from the blend. In 2-step doping, a polymer solution is used to coat a polymer film. In the second step, a dopant solution is allowed to contact the dried polymer film in order for dopant to diffuse into the polymer film. While both methods have their advantages, in this thesis blend doping is primarily employed because it allows for specific and precise dopant:polymer ratios (see next paragraph). Additionally, as the end-goal is mass production, it would be convenient from a manufacturing perspective to directly coat sensors from a single solution.

The dopant concentration naturally plays a large role in the extent of doping. This work adopts the nomenclature of the closest work Liang et al. (2018) of using mol% with respect to aromatic rings.²³ Below is an example calculation for reference:

$$\begin{aligned}
 7.4 \times 10^{-3} \text{ g DPP-BT} &\times \frac{1 \text{ mol repeat unit}}{1023.65 \text{ g}} \times \frac{6 \text{ mol aromatic rings}}{1 \text{ mol repeat unit}} = 43.4 \text{ umol aromatic rings} \\
 0.140 \text{ ml FeCl}_3 \text{ solution} &\times \frac{46.3 \times 10^{-3} \text{ g FeCl}_3}{9.2 \text{ mL FeCl}_3 \text{ solution}} \times \frac{1 \text{ mol FeCl}_3}{162.2 \text{ g FeCl}_3} = 4.34 \text{ umol FeCl}_3 \\
 \frac{4.34 \text{ umol FeCl}_3}{43.4 \text{ umol aromatic rings}} &= \frac{10 \text{ mol FeCl}_3}{100 \text{ mol aromatic rings}} = \boxed{10 \text{ mol}\%}
 \end{aligned}$$

2.3 Polymers and Dopants Structures and HOMO/LUMO

In this Section, the polymers used are introduced along with their HOMO energy levels, and the dopants used and their LUMO energy levels. The three polymers will be referred to as DPP-BT, DPP-TT, and DPPPpy-TT while the three dopants will be referred to as FeCl₃, F4TCNQ, and Magic Blue. Structures of all six are shown below in Figure 2-2 along with HOMO/LUMO levels in Table 2-1. DPP-BT and DPP-TT have HOMO levels near -5.2-5.3 eV while the HOMO level of DPPPpy-TT is much lower at -5.7 eV. Even though DPPPpy-TT's low HOMO energy may prove to be difficult to dope by the p-type (oxidative) dopants, the Lewis-base character of the DPP-flanking pyridine rings could allow it to interact with FeCl₃, a Lewis-acid.²⁴

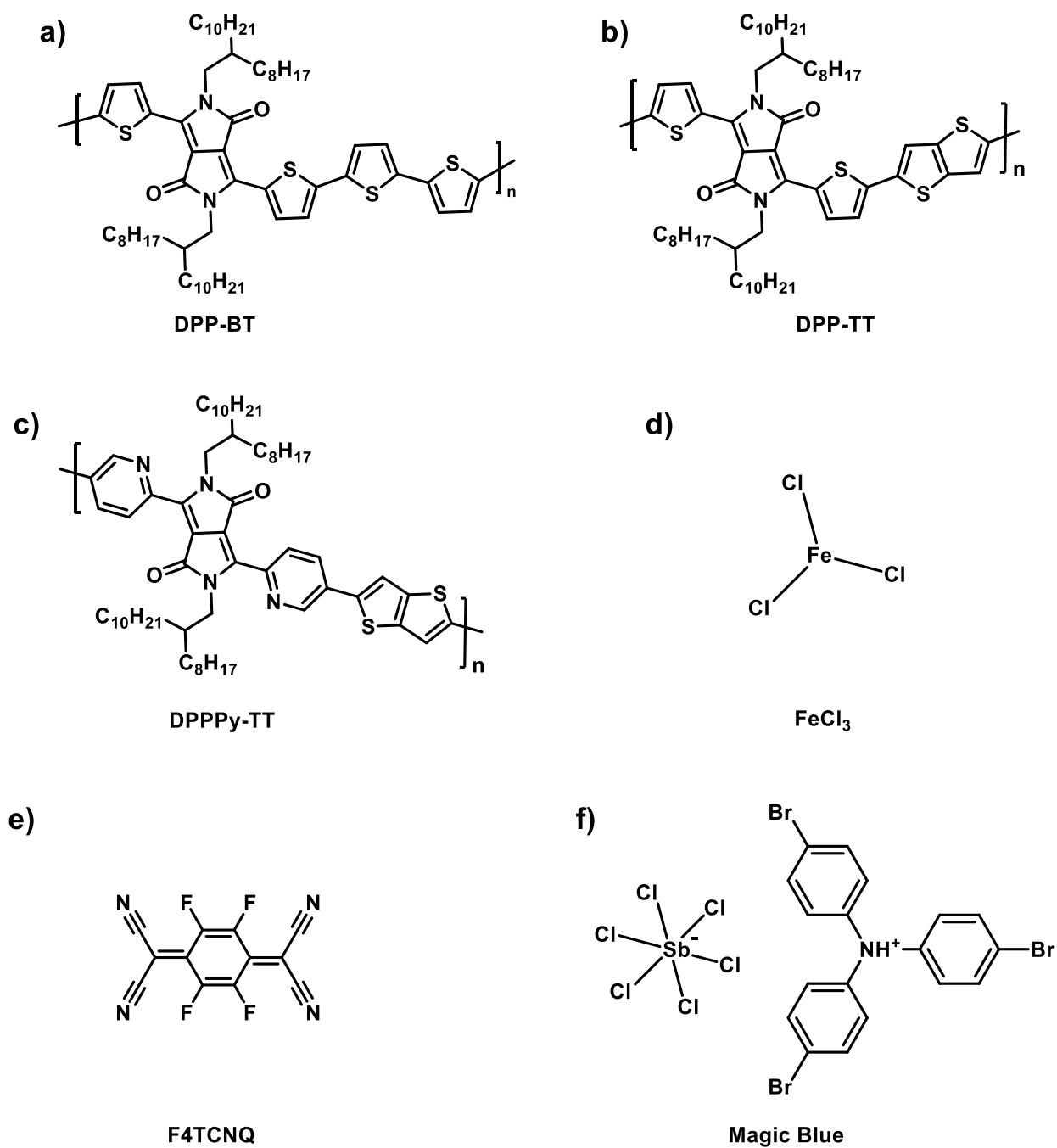


Figure 2-2: Chemical structures of polymers a) DPP-BT, b) DPP-TT, c) DPPPpy-TT, and dopants d) Iron(III) chloride “FeCl₃”, e) 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane “F4TCNQ”, and f) tris(4-bromophenyl)ammoniumyl hexachloroantimonate “Magic Blue”.

Table 2-1: Polymer and Dopant HOMO/LUMO

Polymer or Dopant	HOMO for polymer [eV]	LUMO for dopant [eV]
DPP-BT	-5.3 ²⁵	
DPP-TT	-5.25 ²⁶	
DPPPy-TT	-5.7 ²⁷	
FeCl ₃		-4.6 ²³
F4TCNQ		-5.24 ^{23,28}
Magic Blue		-5.8 ²⁸

2.4 Development of Doping method

The blend-doping method employed in this study used Liang et al. (2018) as a starting point.²³ However, to achieve successful blend-doping, details of the method required trial-and-error and adaptation. It was found that anhydrous chloroform could not be used as FeCl₃ does not dissolve if the solvent was perfectly anhydrous (or if it did, it dissolved at a concentration below 1 mg/ml). Using non-anhydrous chloroform led to stable solutions of FeCl₃. The relevance of water to the function of the FeCl₃ dopant would grow even further as the study progressed.

Following the literature procedure, the blend-doping was conducted in a nitrogen glovebox. The procedure used in this study requires an overnight stirring of the polymer and dopant in solution with heating (40 °C) and performing this in nitrogen is more cautious, as there may be cases where the presence of air poses a stability issue for polymer/dopant/doped polymer.

For the organic dopant F4TCNQ, it was desired to use the same doping method that was used for FeCl₃. Initially, acetonitrile was used to dissolve F4TCNQ, as it is a good solvent. However, even when using a small amount of dopant solution (0.05 ml acetonitrile) vs. the polymer solution (0.2 ml chloroform) the resulting mixture upon addition of the acetonitrile solution to the chloroform solution F4TCNQ looked paste-like rather than homogeneous. This did not improve during the overnight

stirring on 40 °C hotplate. Then when it came to the drop coating, the mixture of the two solvents led to coating issues where the acetonitrile, which has about half the vapor pressure of chloroform at room temperature, evaporated more slowly and this two-solvent solution led to film defects including a pool of material in the center of the film as well as thicker material deposition around the edge, see Figure 2-3a.

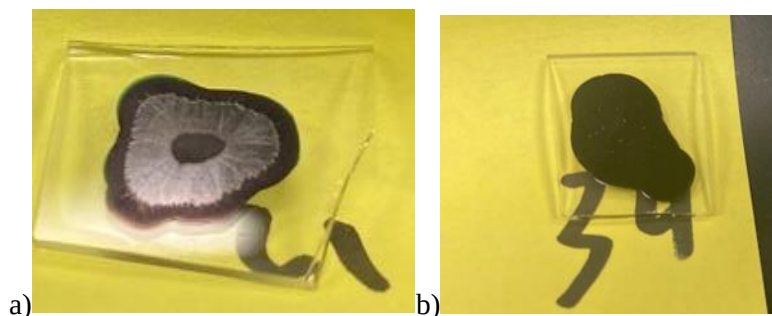


Figure 2-3: Samples of DPP-BT doped with 10 mol% F4TCNQ where in a) the blend doped solution was made up of polymer-dissolved-in-chloroform and F4TCNQ-dissolved-in-anhydrous-acetonitrile and in b) no acetonitrile was used, instead it was added “dry,” leading to a much more uniform film.

However, as it is known that the solubility of F4TCNQ in chloroform is relatively low (~ 0.5 mg/ml according to Li, Zhang, Holm et al. 2015²⁹) and it would be challenging to find a solvent which dissolves both the polymers under study and F4TCNQ, it was decided to proceed by simply adding the F4TCNQ “dry” i.e. without any solvent. The hope was that as the F4TCNQ is “consumed” from its pure state to bind to the polymer forming a polymer-dopant complex, additional free F4TCNQ would dissolve and thus avoiding blending solvents that do not like each other.

A polymer solution of concentration 15 mg/ml was used because it was found that when using a 5 mg/ml solution, the attempts to drop coat films were unable to reliably wet the glass substrate. This result might be explained by the surface tension of the liquid and/or its viscosity being different enough in the 5 mg/ml case vs. 15 mg/ml case as to prevent the coating of uniform, non-patchy films. Even with the higher concentration, there are still slight defects inherent to drop coating such as greater thickness in the center and by the edges of the film which could be eliminated by using spin coating once dopant ratios and process were dialed in.

The final procedure, detailed in Section 2.8.2 - Detailed Device Preparation, can be summarized as follows:

1. Add solid polymer and stir bar to vial “A” (in air).
2. Prepare dopant solution in vial “B” (in glovebox).
3. Transfer both vials to glovebox.
4. Dissolve polymer in vial “A” with chloroform.
5. Micropipette desired dopant solution into vial “A”.
6. Shake vial “A”, wrap with parafilm; heat and stir on 40 °C hotplate in glovebox overnight.
7. Drop cast 50 μ L of the blend doped solution onto a cleaned glass slide—cover immediately with jar to avoid airflow disturbing the film drying.
8. Transfer dried polymer films on glass into vials wrapped with parafilm before removing from glovebox.

All data shown in the sections to follow uses blend-doped samples, except for those in Section 2.6.3 involving DPP-TT doped with Magic Blue which use sequential i.e. 2-step doping.

2.5 Error Analysis

The variability of maximum thickness is in the range of 0.5 to 2.0 microns (Stddev% is $\sim 10\%$ over all samples). Since thickness and conductivity are directly proportional, maximum thickness does vary a fair amount even within one sample ($\sim 10\%$) and the way that may affect the analysis of any trends of RH% vs. conductivity or other analyte exposure vs. conductivity is that if there is a significant diffusion component, variable thickness films will lead to a less sharp response. In terms of total conductivity after long exposure to moisture however, the amount of error introduced by the variable thickness would correspond to a conductivity measurement of e.g. 2.7 S/cm vs. 3 S/cm. If a gas sensing response in terms of e.g. $\sim 40\times$ increase or decrease in conductivity is feasible, the error from thickness will not be an issue.

The thickness of the film is required to calculate conductivity. Three measurements of the film thickness were carried out and the average was taken. Error bars are constructed on the assumption that the non-uniform thickness of the drop coated films is the major contributor to measurement uncertainty. The variation in thickness of the film is primarily due to the method of film production: drop coating. As thickness of the film is directly proportional to the calculated conductivity and for 14 of the drop coated films, ranging in average thickness from ~ 8 microns to ~ 15 microns, an average

standard deviation of 10% in film thickness would translate to a 10% error in conductivity and thus led to us constructing 10% error bars.

2.6 Results

2.6.1 FeCl₃ doping

DPP-BT and DPP-TT have been reported as doped with FeCl₃. However, these reported conductivities were measured in a nitrogen glovebox e.g. by Liang et al. (2018).²³ The blend doping was carried out as done by Liang et al. in a nitrogen glovebox, however unlike that study, by necessity of the present goal to determine stability in air, the conductivity measurements were carried out in air. It was found that the doped DPP-BT and DPP-TT do show conductivity, though unexpectedly it was found that moisture was necessary for the doping effect to occur and in fact these doped polymers could be developed into humidity sensors. The values reported in Liang et al. (2018) for 10 mol% blend doped DPP-BT and DPP-TT are 3 S/cm and 1E-4 S/cm, respectively. DPPPpy-TT was shown to not be significantly doped by FeCl₃ with conductivity below 1E-4 S/cm. Even though FeCl₃'s LUMO is higher than all three of the polymer HOMOs, it has been shown to dope DPP-BT and DPP-TT e.g. by Liang et al. 2018.²³ Their result for DPP-BT here was replicated, as FeCl₃ was shown to dope DPP-BT synthesized in our lab. The longest-living sensors did not survive Day 10. This correlated with a color change in the film as well, see Figure 2-4.

Table 2-2: Conductivity and Air-Stability Results for FeCl₃-doped DPP copolymers

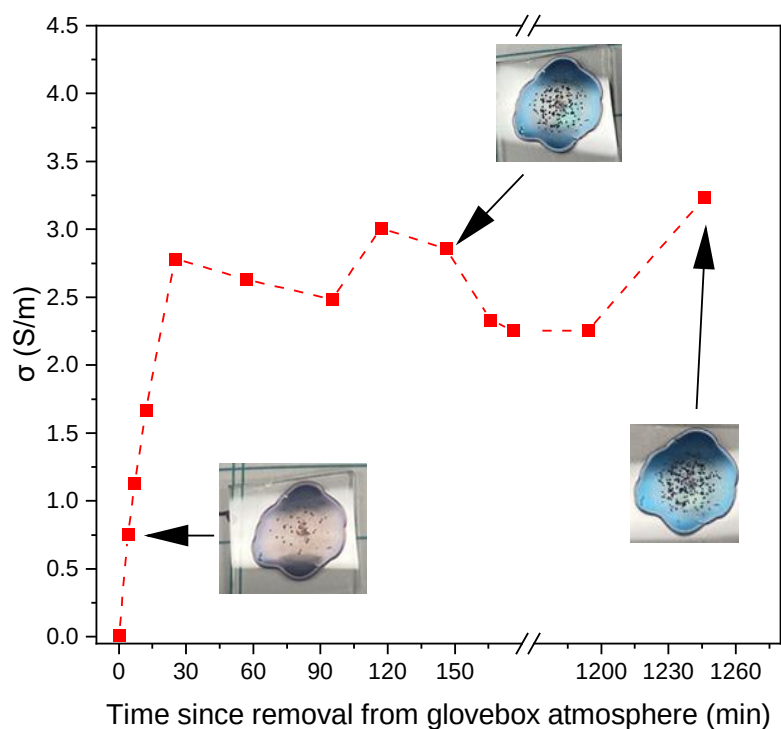
Polymer	Dopant	Dopant mol%	Method of doping	Max Conductivity [S/cm]	Average Conductivity [S/cm]	Days until conductivity below 10 ⁻³ S/cm
DPP-BT	FeCl ₃	10%	1 step	3.5	2.8	5-10
DPP-TT	FeCl ₃	10%	1 step	9.2	8.4	3-5
DPPPpy-TT	FeCl ₃	10%	1 step	None	None	N/A

It was observed that the conductivity increased over time in air, e.g. for a DPP-BT film blend doped with 10mol% FeCl_3 the conductivity was seen to increase over the course of ~30 minutes from 0.01 S/cm to 2.8 S/cm, see Figure 0-3. By using a desiccator (which should have all the components of lab air except water), the effect was narrowed down to water. It was even found that the DPP-BT doped with 10 mol% FeCl_3 could be used as a reversible moisture sensor (Figure 0-1). The moisture effect is a known issue for doped conjugated polymers and serves to further show the inadequacy of current polymer-dopant combinations. Below additional evidence in the form of UV-Vis data for the short-term stability of these dopant-polymer combinations is shown.

UV-Vis was used to track what was happening over this first 30 minutes of exposure to lab air where the conductivity was seen to increase by orders of magnitude which had been established was due to some effect of moisture. The study was replicated a month later and showed the same decaying (bi)polaron within a few hours of exposing the FeCl_3 blend doped DPP-TT to air.

Of note, the polaron peak disappears within ~ 2 hours. However, because light must pass through the film for the UV-Vis measurement, this film is about 100x thinner (~100 nm) than the films used for conductivity measurement (~10 μm).

The system is complex and fully elucidating the role of water would require further study. As a hypothesis, the shape of the conductivity vs. time in air graph may be explained by a fast rate of diffusion of water into the film due to water's small size, and the formation of some water- FeCl_3 or water-polymer complex, which then decays. FeCl_3 phase segregating out may be the final step in the film's degradation out of conductivity. Further data including experiments testing cycling humidity through use of a desiccator are shown in Appendix A.



a)

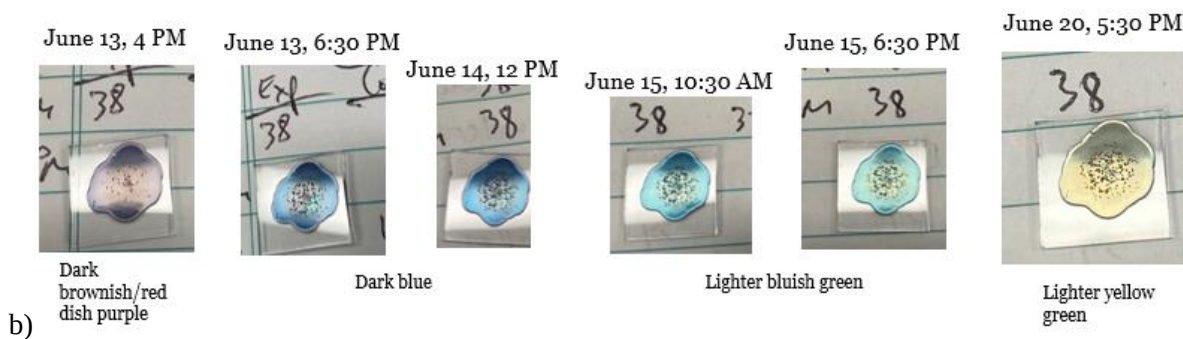


Figure 2-4: a) Conductivity and accompanying film colors of DPP-BT blend-doped with 10 mol% FeCl_3 in 0 %RH glovebox, measured immediately after introducing to lab air (40 %RH) and kept in lab air during the entirety of testing. b) Color change of ~10 micron drop casted film of DPP-BT blend-doped with 10 mol% FeCl_3 over the period of one week. All pictures taken with the same camera, under the same lighting conditions, with the same background. Below each image is a contemporaneous visual interpretation of the color.

The stability of DPP-BT 10mol% FeCl₃ was tested over roughly ~1 week in lab air and found it to be stable. The low values for “Day 0” measurements could later be explained by the fact that the samples were measured immediately after removal from the 0 %RH glovebox. The variability in the conductivity for the two batches may be in part due to changes in humidity in the lab (samples were measured at the beginning of June 2023 in Waterloo, ON where July is historically the month with the highest absolute humidity).

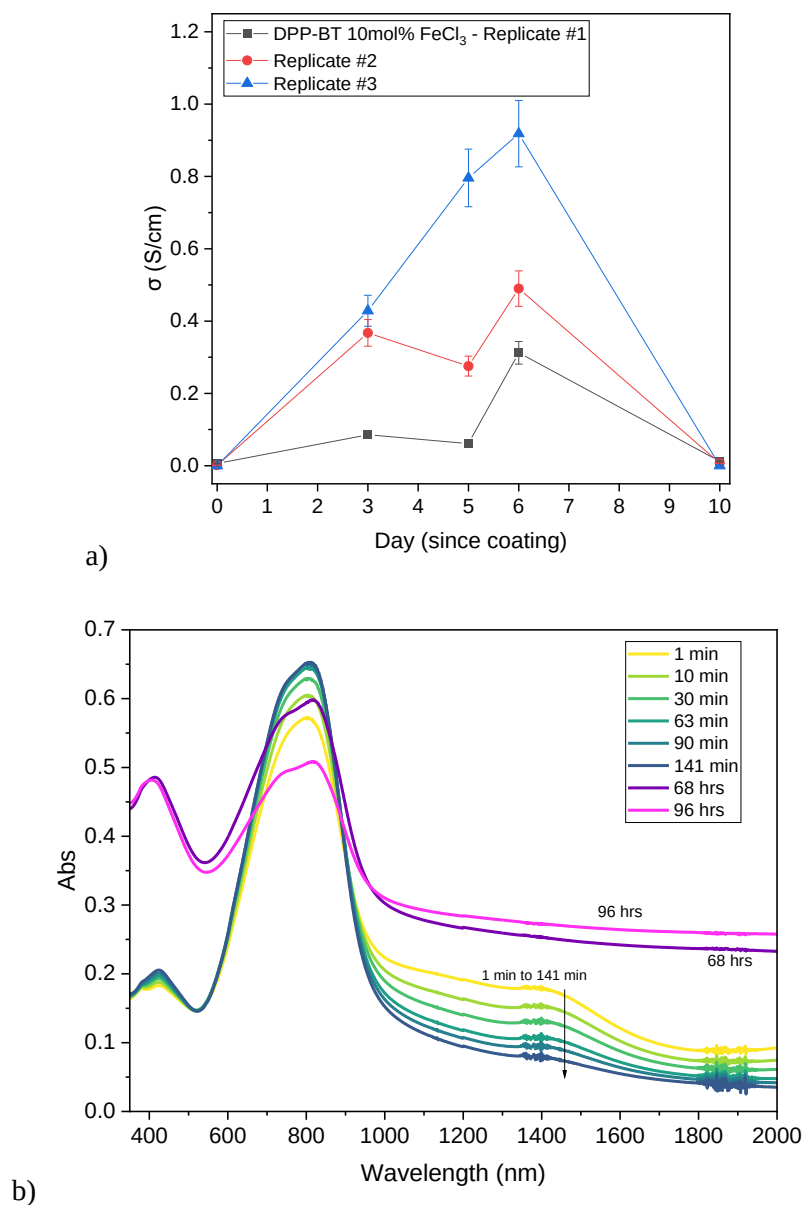


Figure 2-5: a) Conductivity of three replicate films of DPP-BT blend-doped with 10 mol% FeCl_3 cast from the same solution, over 10 days. b) For the thin films of DPP-TT blend doped with 10 mol% FeCl_3 , the (bi)polaron signal decreases monotonically after various times after exposure to lab air. After days of exposure to air, the FeCl_3 itself may diffuse out and increase the reflectivity of the surface, explaining the raising of the entire spectrum. Even though the polaron peak disappears, the main peak never recovers and instead sinks down to about $1/3^{\text{rd}}$ of its original height above the baseline.

2.6.1.1 Phase segregation of FeCl₃ from DPPPy-TT

In cases where there is not a strong and stable interaction between polymer and dopant, it is often the case that dopant molecules can over time be excluded from the polymeric matrix through phase segregation.³⁰ It is possible in the case indicated in **Error! Reference source not found.** that the FeCl₃ dopant, having found no interaction with the low HOMO polymer, instead migrated to the surface of the coated film at which point it may have reacted with moisture or oxygen in the lab air and a Lewis-acid (FeCl₃) and Lewis-base (pyridine) interaction occurred. It should also be noted that FeCl₃ and pyridine are used as reagents in an analytical chemistry test to form intense red, blue, purple, or green colored compounds to detect the presence of phenols or carbonyl compounds with high enol content.³¹ The bright blue color seen after 5 days may be an indication that in this polymer the ketones in the DPP unit have more “enol” than “keto” character.



Figure 2-6: Time-lapsed photos showing that the DPPPy-TT doped with 10mol% FeCl₃, which was not successfully doped, shows a dramatic color change around 5 days later which eventually fades away.

2.6.2 F4TCNQ doping

It was found that for the 10 mol% doping level of F4TCNQ in both DPP-BT and DPP-TT, both resulted in relatively low conductivity levels: the maximum value recorded for films of both was $\sim 1 \times 10^{-3}$ S/cm. While these polymer films reached measurable levels of conductivity, fully within the semiconductor range and near the low end for values reported for silicon, this low conductivity level is indicative of a low extent of doping. It is likely that the conductivity could be improved by an order of magnitude or so by optimizing the F4TCNQ loading level as only one value (10 mol%) was

attempted in this study. DPPPy-TT, just as with FeCl₃, was shown to not be significantly doped by F4TCNQ with a conductivity <10⁻⁴ S/cm.

Table 2-3: Conductivity and Air-Stability Results for F4TCNQ-doped DPP copolymers

Polymer	Dopant	Dopant mol%	Method of doping	Max Conductivity [S/cm]
DPP-BT	F4TCNQ	10%	1 step	1x10 ⁻³
DPP-TT	F4TCNQ	10%	1 step	1x10 ⁻³
DPPPy-TT	F4TCNQ	10%	1 step	None

These results are backed by literature, with several reports that F4TCNQ can only very lightly dope DPP-TT. In 2016, Karpov et al. using F4TCNQ to dope DPP-TT were able to achieve 0.4x10⁻³ S/cm at 10 mol% F4TCNQ and 1x10⁻² S/cm at 35 mol% F4TCNQ respectively, after trying a wide range of dopant concentrations.³² Their report was followed up the next year, where again they doped DPP-TT but this time employed F6TCNNQ, which has a lower LUMO level of -5.37 eV compared to F4TCNQ at -5.24 eV, and successfully improved conductivity up to 2 S/cm.³³ Two other reports using the same dopant and polymer, found a polaron peak at 30 mol% F4TCNQ loading (Mun et al., 2020) and a “measurable” conductivity at 33 mol% loading (Ditte et al., 2021).^{34,35} In conclusion, the method of doping used here is validated in that it reproduces the literature findings for this combination of polymer and dopant and at this concentration.

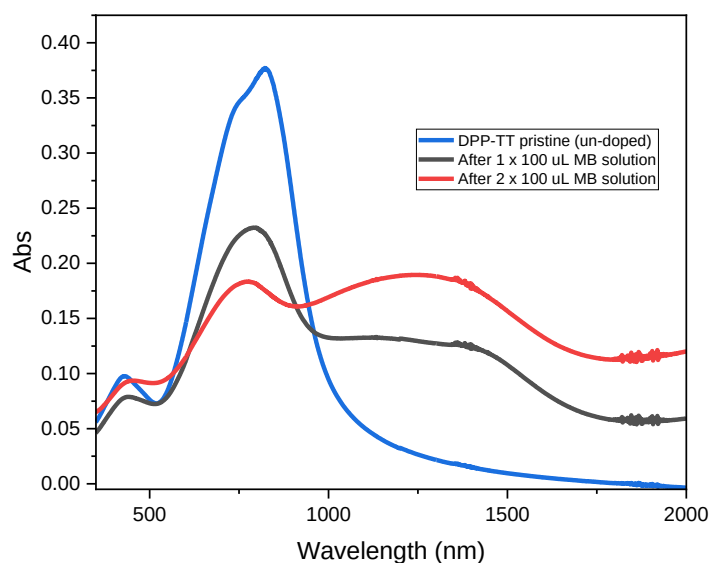
2.6.3 Magic Blue doping of DPP-TT

As FeCl₃ and F4TCNQ may not have sufficiently low LUMO levels to form stable polymer-dopant complexes with these three DPP copolymers, a lower LUMO level dopant, Magic Blue, was investigated to dope DPP-TT as reported in Hofmann et al. (2020).²⁸ Magic Blue’s LUMO of -5.8 eV compared to DPP-TT’s HOMO of -5.3 eV suggests a stable complex could be possible with a 0.5 eV difference.

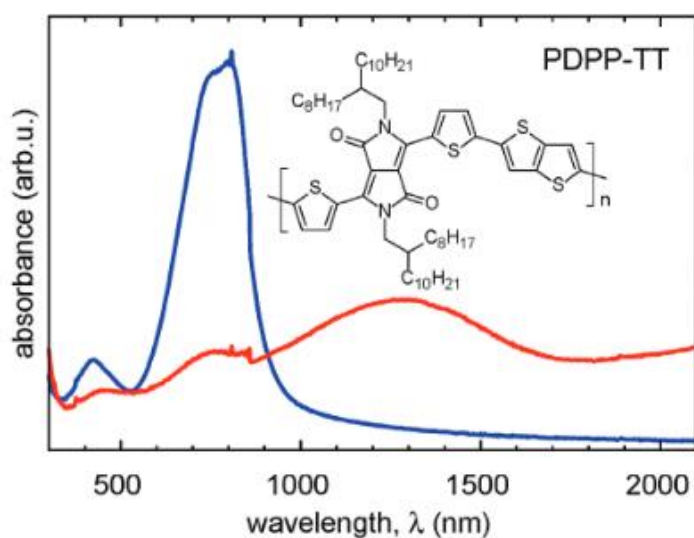
In Hofmann et al., they employ sequential doping, spin coating 100 microliters of dopant solution, made with a solvent blend, on top of a ~100 nm spin coated thin film of DPP-TT. At first, a

replication of their polymer solution preparation process (using 3 mg/ml chlorobenzene) was attempted, but this gave non-uniform film quality as the solution pooled up in the center of the glass slide and left coffee ring stains. Ultimately it was decided to return to our established effective method of creating uniform ~100 nm spin coated films by using 15 mg/ml in chloroform described in Section 2.8.4. After allowing the film to dry at room temperature, UV of the pristine film was measured, and then 100 μ L of Magic Blue solution was spin coated on top of the dried polymer film. The Magic blue solution was 0.62 mg/ml using as solvent 2:1 v/v acetonitrile:chloroform.

The goals were to attempt replication of the report of Magic Blue doping DPP-TT and if successful, determine the stability in air (in dark) as it was not reported by Hoffman et al.



a)



b)

Figure 2-7: UV-Vis spectra of a) this study's spin coated DPP-TT pristine film (blue line), along with the film after sequential doping (grey line) by spin coating 100 μ L of Magic Blue solution onto the surface. A second 100 μ L (red line) resulted in a very similar shape to Hoffman et al. (2020).²⁸ b) literature UV-Vis spectra from Hoffman et al. (2020). Modified caption: "Chemical structures of DPP-TT and corresponding UV-Vis absorption spectra of thin films in their undoped form (blue line) and upon sequential doping with Magic Blue (red line)."

The stability of the DPP-TT doped with Magic Blue was then assessed over two weeks. In summary, DPP-TT appears to show strong doping when sequentially doped with a solution of Magic Blue. However, the doping is somewhat unstable— still showing (bi)polaron peak after 1 day in air but gone by Day 4 (see Figure 2-8). Hofmann et al. reported relatively stable conductivity of DPP-BT, as it dropped by half of the original conductivity by Day 30 (it had dropped over an order of magnitude by Day 100) but they did not report the stability of DPP-TT doped with Magic Blue. As future work, the conductivity of films made with DPP-TT and Magic Blue could be tested to see if the reported value of 55 S/cm could be matched.

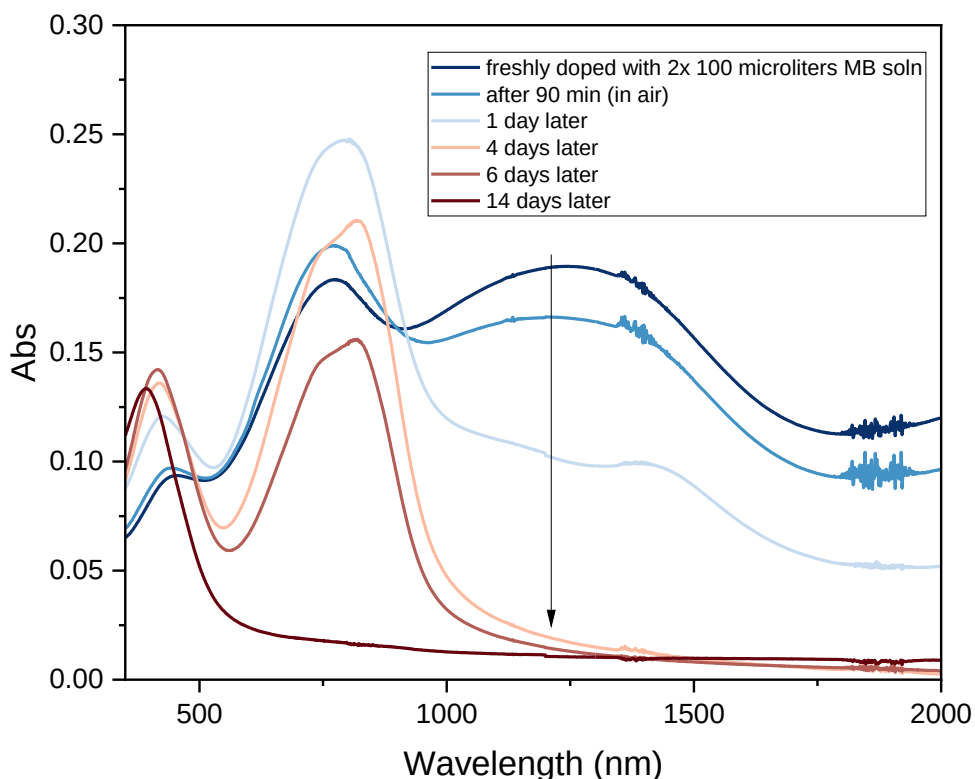


Figure 2-8: UV-Vis of the DPP-TT freshly doped with 200 μ L of MB solution (dark blue line) along with measurements of the spectrum at several time points: 90 minutes after the doping, 1 day, 4 days, 6 days, and 14 days later. A black arrow indicates the monotonic decrease of the (bi)polaron signal over time.

2.7 Conclusion

In Chapter 2, doping of published DPP copolymers DPP-BT, DPP-TT, and DPPP_y-TT, with common p-type dopants FeCl₃, F4TCNQ, and Magic Blue was attempted. The extent of doping generally agreed with available literature values.

Crucially, none of the doped polymers were still conductive after ~10 days in air. This result encouraged further work to design and synthesize several novel high-HOMO DPP copolymers, seeking strong polymer-dopant interactions thereby promoting stability. This aim, ultimately towards enabling stable conjugated polymer gas sensors, is discussed in Chapter 3.

2.8 Experimental Section

2.8.1 Materials Source

The three DPP-copolymers DPP-BT, DPP-TT, and DPPP_y-TT used were prepared in-house in our lab by Dr. Venkateswarlu Samala using well-established methods. FeCl₃ (sold under “Iron (III) chloride, anhydrous”) was purchased from Alfa Aesar. F4TCNQ was purchased from Ossila, while Magic Blue was purchased from Sigma Aldrich. The anhydrous chloroform used was from EMD Millipore Corporation and all other solvents and compounds were purchased from Sigma Aldrich and used without additional purification.

2.8.2 Detailed Device Preparation

The step-by-step method used to produce blend doped films for testing stability of conductivity was as follows:

- 1) Add ~3 mg polymer to small vial (4 ml capacity) ensuring to use a cap that is good for heating chloroform up to 40 °C. (this step is done in air).
 - 1.1) Add small stir bar (this step done in air).
- 2) Prepare dopant solution in benchtop nitrogen glovebag, keeping the vial capped while weighing it outside of glovebag.
 - 2.1) Parafilm the dopant solution vial immediately after bringing out of benchtop glovebag.
- 3) Load both vials into glovebox. Set the hotplate to 40 °C so it can warm up.
- 4) Dissolve the polymers with chloroform.

5) Micropipette the appropriate amount of dopant solution into polymer solutions.

5.1) Shake for 30 seconds; then wrap vials with parafilm.

6) Put vials on the glovebox's hotplate (already at 40 °C) and allow them to stir overnight at 40 °C while they are covered by an Al-foil-covered jar.

7) The next day, in the glovebox, drop cast 50 microliters in one shot onto cleaned glass slides and immediately cover. Allow to dry 30 min at room temperature in the glovebox.

8) Put samples into 20 ml glass vials wrapped with parafilm and bring out of glovebox to measure conductivity.

"Dry" F4TCNQ Doping:

Solutions of F4TCNQ were prepared in acetonitrile, then the appropriate volume was pipetted into an empty vial which was allowed to fully dry in the hood at room temperature. Polymer was added directly to that vial with the solid F4TCNQ already dried.

Glass cleaning procedure:

- 1) 20 min sonication with DI water.
- 2) 20 min sonication with HPLC acetone.
- 3) 20 min sonication with HPLC isopropanol.
- 4) Blow off the isopropanol with N₂ and store in sealed glass vial until use.

2.8.3 Device Conductivity Characterization

50 microliters of blend-doped polymer solutions were drop casted in a glovebox on glass slides cleaned using the method described in Section 2.8.2 - Detailed Device Preparation. The samples were then sealed using parafilm into glass vials and transported out of the glovebox for immediate measurement (it is expected based on our lab's anecdotal evidence using air-sensitive inorganic materials, that parafilm glass vials would maintain the glovebox atmosphere for a few hours which is more than sufficient for the purposes here). Conductivity was measured using an Ossila Four-Point Probe System. The target current was set to either 50 μ A or 500 μ A depending on the measurement range maximum of 100 μ A or 1000 μ A, respectively. The maximum voltage to be used to achieve the target current was set to 1 Volt. Sample conductivities were measured by inputting 1 micron as

sample thickness. Later, once all the measurements were complete (weeks after the coating) the sample thicknesses were measured by an AlphaStep profilometer and these values were used to correct the conductivities to their thickness-adjusted values as presented in this thesis.

2.8.4 Device UV-Vis Characterization

A Cary 7000 UMS UV-Vis-NIR spectrophotometer was used to measure sample absorbance from 350 nm to 2000 nm. Polymer solutions were deposited on cleaned glass slides (cleaned using the method described in the Device Preparation section) and unless noted, 50 microliters of 15 mg/ml of polymer in chloroform was spin coated, by pipetting onto an already spinning clean glass slide. Spin speed was 1500 rpm, acceleration was 2000 rpm/s and the duration of the spin coating was 60 sec. Samples prepared by blend coating were spin coated in the glovebox; the samples for sequential doping were spin coated in air.

Chapter 3: Novel methoxythiophene-flanked DPP-based Donor-Acceptor copolymers for air-stable resistive sensors

3.1 Introduction

The motivation behind this thesis is to enable mechanically flexible, low cost, and stable sensors. The first two can be achieved by using conductive polymers which are soluble in printing solvents. The third requirement, stability of the sensor so it can be re-usable, is a big challenge in electronic devices made with conductive polymers. One main degradation mechanism comes from the fact that these polymers need exogenous dopant molecules in order to reach useful levels of conductivity.

The approach in this work to deal with the problem is two-fold: use DPP-based Donor-Acceptor copolymers which generally have good intrinsic stability (i.e. the polymer itself, before doping, is stable) and raise the HOMO level through use of methoxythiophene (MOTh) flanking groups to create a large gap between polymer HOMO and dopant LUMO so that the dopant will bind tightly.

3.2 Polymer Structure Targets

Before novel conjugated polymers are synthesized, it is only possible to roughly estimate how much alkylation will be required to separate the chains and allow the polymer to be soluble in common solvents at room temperature. Common practice is to add C8, C12, C16, C20, or C24 chains to the “R” group position indicated below in Figure 3-1 for the target structures. Branched structures tend to provide more solubilizing power than straight chains of equal carbon number.

For the choice of 3,4-Ethylenedioxythiophene (EDOT) and thienothiophene (TT) as comonomers, the EDOT group was chosen because it has electron-rich character and so it would be expected it to give the higher HOMO energy level of the two copolymers. The TT comonomer has been shown to very reliably produce DPP copolymers of satisfactory molecular weight and is less sterically hindered than the EDOT comonomer and so represented the higher chance of polymerization success of the two.

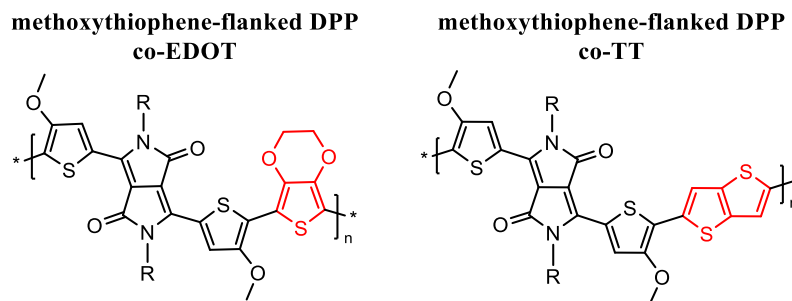


Figure 3-1: The target methoxythiophene-flanked DPP copolymers.

3.3 Simulated HOMO/LUMO levels and Dihedral Angles from Density Functional Theory (DFT)

For the proposed polymer structures, DFT was run on repeat unit dimers in order to determine simulated HOMO/LUMO levels and dihedral angles. A common practice in the conductive polymer research field is to replace the solubilizing alkyl side chains (C8 or C20) with methyl groups in the structure.³⁶ The reason is that these have relatively little influence on the electron arrangement and instead are mostly involved with providing separation between polymer chains—hence the improved solubility. As DFT simulations using isolated dimers do not consider interchain interactions, the size of the alkyl chain is largely irrelevant. With it being the case that the alkyl chains are replaced with methyl groups, both the PDPPMOThC8-co-EDOT and the C20 version can be represented by the same structure for input to the DFT simulation.

The DFT simulation for all the five structures was carried out using the method B3LYP and the basis set 6-31G(d). Before submitting the structures, the repeat unit dimers were first given a rough geometry optimization using the MMFF94s force field in Avogadro 1.2.0. The structures were then input into Gaussian 16 and all structures were submitted using following job:

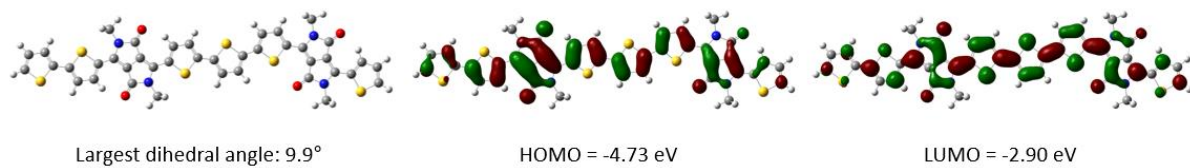
```
# opt freq b3lyp/6-31g(d) geom=connectivity
```

As can be seen from the results below in Figure 3-2, Figure 3-3, and summarized in Table 3-1, the use of MOTh as the flanking group raises the HOMO level substantially. In the Th-T case, which can be considered to have zero methoxy- groups, the HOMO is simulated to be -4.73 eV, compared to -4.36 eV in the MOTh-EDOT case which can be considered to have four methoxy- groups (one from each of the two flanking groups and two from the EDOT comonomer). This is a simulated increase in HOMO level by almost 0.4 eV, and an increase of this magnitude would be expected to increase the

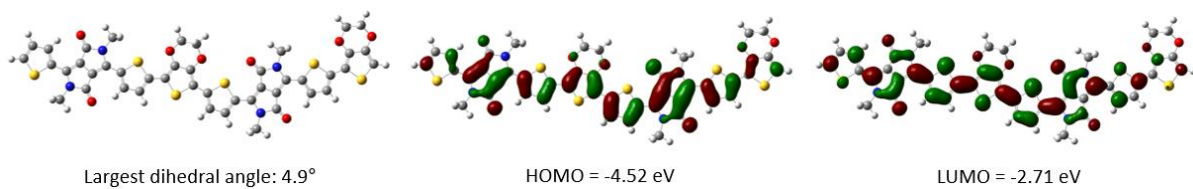
strength of the polymer binding with an appropriate dopant. Likewise, it was found in both cases where the co-monomer is held constant and only the flanking group is modified: Th-EDOT vs. MOTH-EDOT and Th-TT vs. MOTH-TT, that the HOMO level is increased by roughly 0.2 eV when MOTH is used as a DPP-flanking group in place of Th. These results give confidence that the proposed structural modifications will increase the HOMO level which should result in enhanced stability of the polymer-dopant interactions.

The dihedral angle results suggest that the repeat units of the proposed structures are relatively coplanar in that all except MOTH-EDOT is simulated to have their largest dihedral angle at $< 10^\circ$. Coplanarity is generally required to achieve high charge carrier mobility as much of the charge transport can happen intra-chain and coplanarity is required for p-orbital alignment, giving significantly large conjugation length along one chain. Therefore, it may be expected that the highest HOMO polymer, MOTH-EDOT (-4.36 eV by DFT) would have low mobility while MOTH-TT (-4.52 eV by DFT) may not have quite as high a HOMO level but may have higher mobility if its low dihedral angle allows the chains to pack and align themselves without twisting.

a)



b)



c)

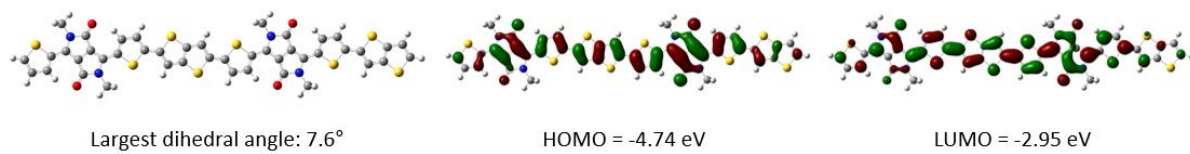
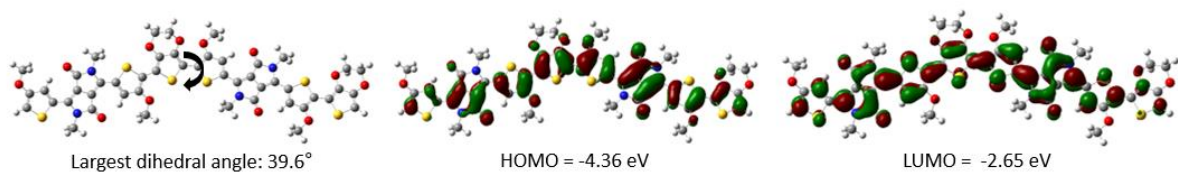


Figure 3-2: DFT-optimized geometry, HOMO, and LUMO of thiophene-flanked (as reference to methoxythiophene-flanked) DPP copolymer dimers: a) thiophene-flanked-DPP-co-thiophene, b) thiophene-flanked-DPP-co-EDOT, and c) thiophene-flanked-DPP-co-thienothiophene.

a)



b)

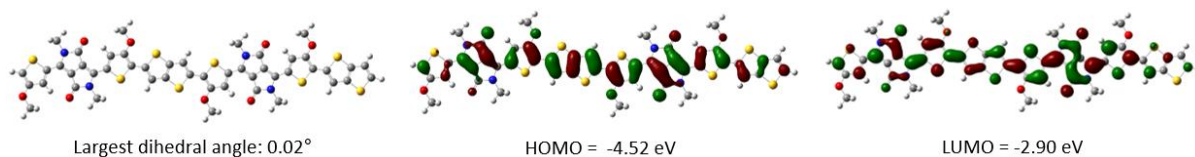


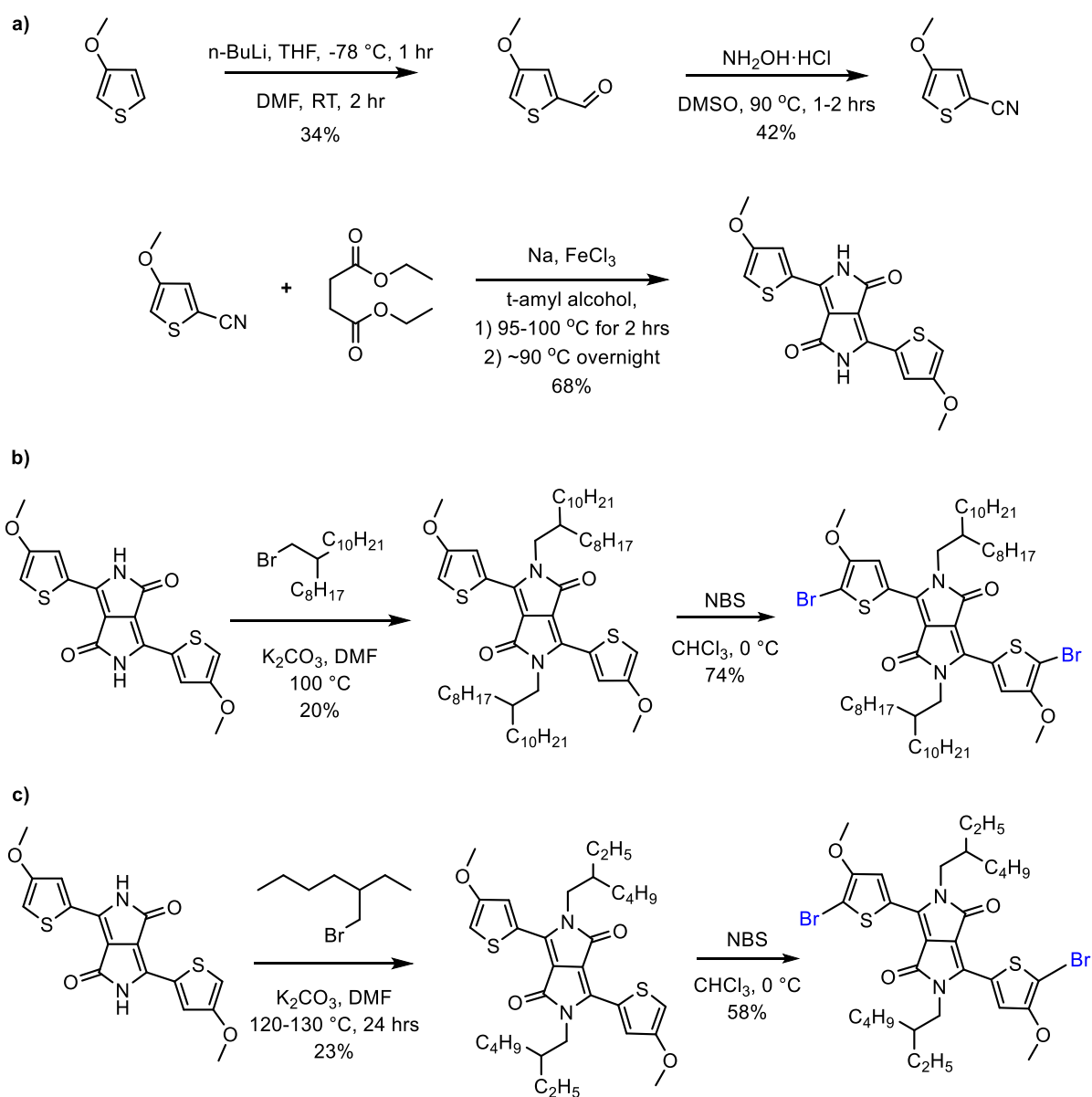
Figure 3-3: DFT-optimized geometry, HOMO, and LUMO of methoxythiophene-flanked DPP copolymer dimers: a) methoxythiophene-flanked-DPP-co-EDOT (largest dihedral angle indicated by black arrow), and b) methoxythiophene-flanked-DPP-co-TT.

Table 3-1: Summary of DFT simulation results for three thiophene-flanked-DPP dimers as reference, and the two target copolymer structures using methoxythiophene-flanked-DPP.

DPP-flanking group	Co-monomer	DFT E_{HOMO} [eV]	DFT E_{LUMO} [eV]	DFT E_g [eV]	DFT Largest dihedral angle [degrees]
Th	T	-4.73	-2.90	1.83	9.9
Th	EDOT	-4.52	-2.71	1.81	4.9
Th	TT	-4.74	-2.95	1.79	7.6
MOTh	EDOT	-4.36	-2.65	1.72	39.6
MOTh	TT	-4.52	-2.90	1.62	0.02

3.4 Synthesis Scheme

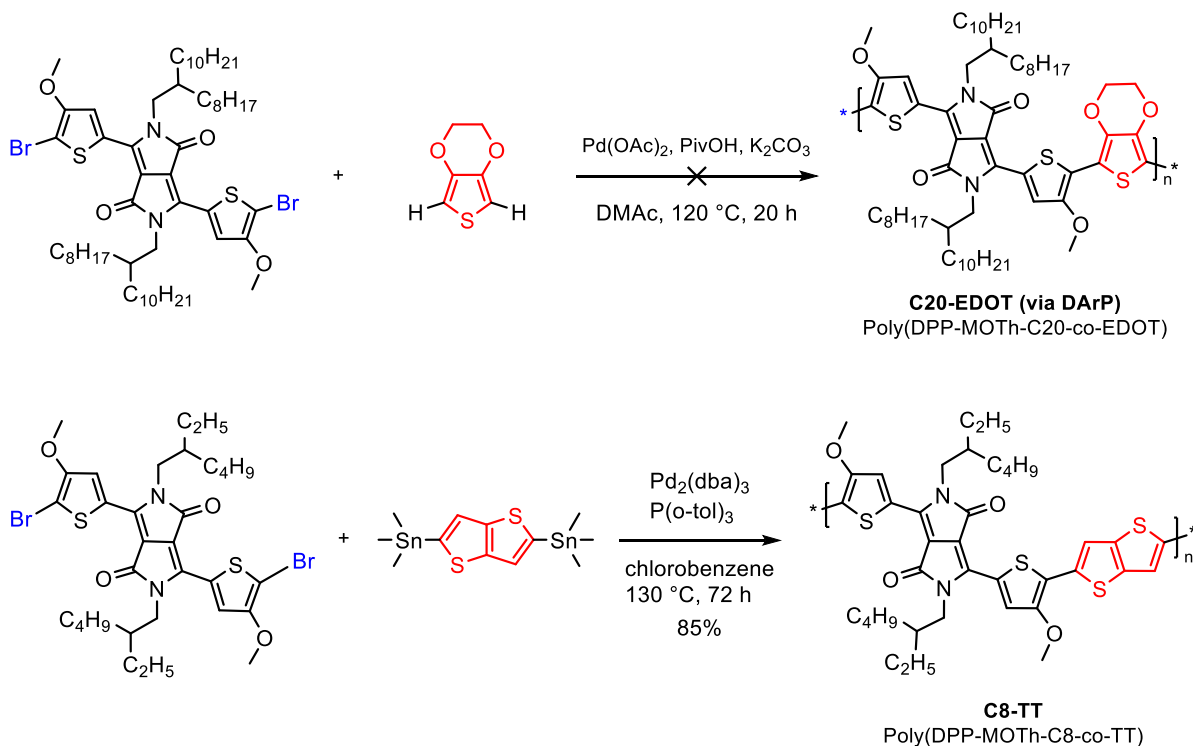
The synthesis procedure to make the DPPMOTh monomer was developed using the work of Domokos et al. as a starting point. The starting material for the methoxythiophene-flanked DPP is 3-methoxythiophene, to which after two synthesis steps a cyanide group has been attached. Then diethyl succinate is used to make the methoxythiophene-flanked DPP. The DPP monomer is then alkylated at the nitrogen position with either a branched C8 or C20 group, which should help ensure polymer solubility. Finally, the monomer is activated for polymerization through bromination. These steps are outlined below in Scheme 1. Either a methyl tin-functionalized compound (Stille coupling) or simply an aromatic compound with hydrogen atoms suitable for Direct Arylation Polymerization (DArP) can be reacted with the brominated monomer overnight to form the desired methoxythiophene-flanked DPP copolymer; see Scheme 2 and Scheme 3 in Section 3.5.



Scheme 1: Monomer synthesis. a) synthesis steps to produce methoxythiophene-flanked-DPP, b) C20 alkylation and bromination to produce the C20 monomer, c) C8 alkylation and bromination to produce the C8 monomer.

3.5 Results

The results of these attempts are summarized in Table 3-2 below. Three out of the five polymerizations succeeded in producing usable amount of soluble polymer, while two did not. Those two that did not, are addressed first: C20-EDOT (via DArP) and C8-TT, shown in Scheme 2.



Scheme 2: Polymerizations which did not produce usable amounts of soluble polymer. a) C20-EDOT via DArP did not produce usable amount of polymer. b) C8-TT was high yield (85%) but the polymer was completely insoluble.

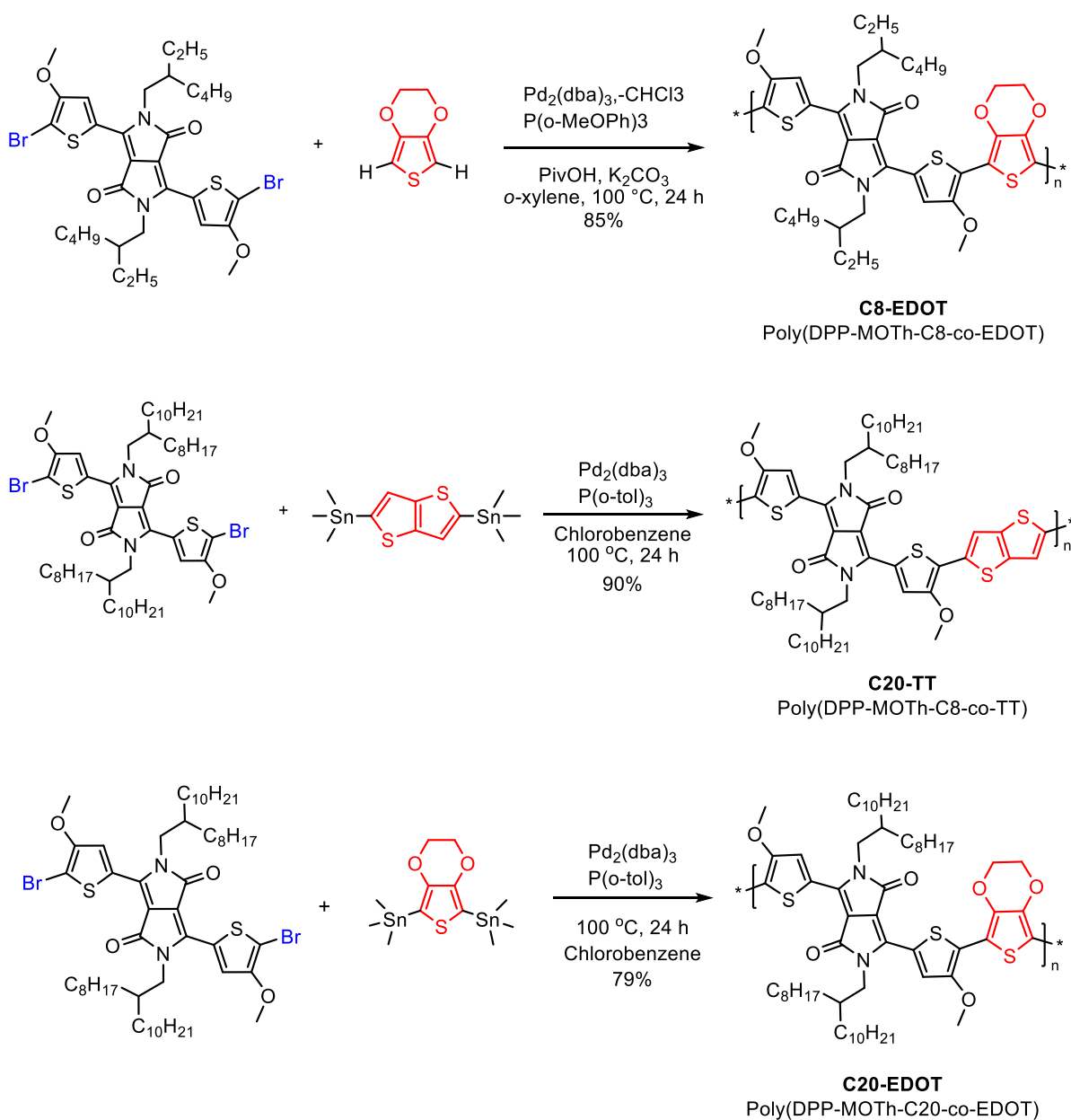
First to address is the attempt by Stille coupling to produce C8-TT. As expected for a successful polymerization, it was found that compared to the monomeric starting materials there was a color change (pink/red to blue), a decrease in solubility, and 85% yield of solid product. Potentially a high molecular weight polymer or very crosslinked material, it was found to be insoluble in any of the following refluxing solvents: acetone, hexane, DCM, and chloroform. Therefore, it was concluded that the branched C8 alkylation is insufficient to solubilize a methoxythiophene-flanked DPP copolymerized with thienothiophene. The thienothiophene comonomer is a common tool in DPP

copolymer synthesis and it typically assists conjugated polymer performance by promoting orderly packing. Indeed there are reports of record-setting high mobility materials involving DPP-co-TT polymers.²⁶ In addition, as expected by the computational results, the dihedral angle for this repeat unit was predicted to be very low (0.02°). Therefore, without significant alkylation providing steric interference between chain backbones, this material may pack very tightly. This prevents the entrance of solvent molecules to solvate and separate the chains thus explaining its insolubility. As the goal of this work is to enable sensor devices which are printable, the insoluble C8- served primarily as a guide for further refinement to target structure design.

In the case of the C20-EDOT attempted by DArP, a small amount of product was recovered in the hexane fraction of Soxhlet extraction, which is indicative of low/no molecular weight increase vs. the starting material. Based on later success in producing this structure using Stille coupling, it is believed that the issue is primarily due to the DArP reaction conditions employed here. A future work would be to use the same successful reaction conditions from DArP of C8-EDOT to produce C20-EDOT by DArP. Then an enlightening comparison could be made between the C20-EDOT produced by Stille coupling and C20-EDOT produced by DArP.

In addition to the main synthesis pathways developed in this work for making these polymers, alternate routes were attempted, seeking to improve yields or improve safety through altering the routes. Details of these syntheses can be found in Appendix B.

Three polymerization attempts, shown in Scheme 3, were successful in producing polymers not prematurely dissolved during the “low molecular weight removal” steps of Soxhlet extraction. The Soxhlet method employed starts with refluxing methanol before turning to acetone, then hexane, and finally extracting into chloroform. C8-EDOT and C20-TT were recovered in chloroform; C20-EDOT was recovered in the hexane fraction.



Scheme 3: Polymerizations which produced usable amounts of soluble polymer: a) C8-EDOT synthesized through DArP, produced a chloroform-soluble polymer with 85% yield, b) C20-TT synthesized through Stille coupling, produced a chloroform-soluble polymer with 90% yield, and c) C20-EDOT synthesized through Stille coupling, produced a hexane-soluble polymer with 79% yield.

Their structures are shown isolated below in Figure 3-4.

Table 3-2: Summary of polymerization attempts and outcomes.

Solubilizing alkyl chain	Comonomer	DArP Result	Stille Coupling Result
C20	EDOT	No high MW product	Success, soluble in hexane
C20	TT	NA (Not Attempted)	Success, soluble in chloroform
C8	EDOT	Success, soluble in chloroform	NA
C8	TT	NA	Insoluble

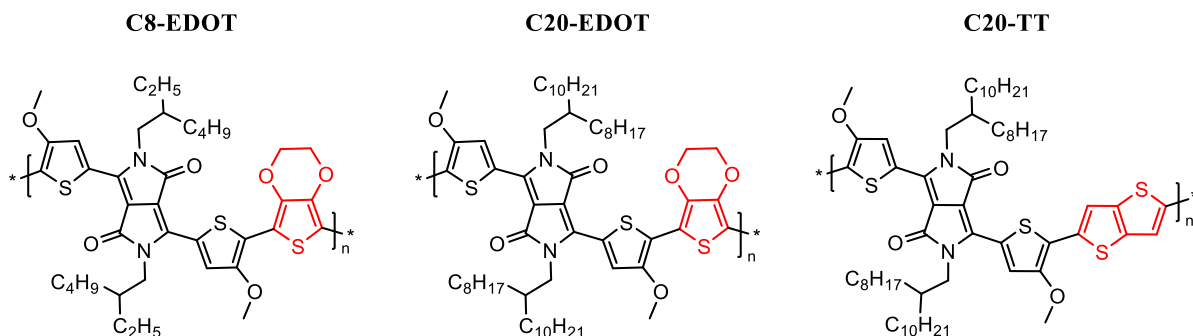


Figure 3-4: Structures of the soluble methoxythiophene-flanked DPP copolymers successfully synthesized in this work: C8-EDOT, C20-EDOT, and C20-TT.

In this work branched C20 and C8 as alkylation groups were used instead of C16 which was employed by Domokos et al. With C20, the alkylated DPPMOTh monomer has some solubility in methanol which makes the purification just as tedious as with the reported C16—requiring a dioxane refluxing step in order to remove the O,N- alkylated side product. The C8 alkylated DPPMOTh on the contrary was found to just require a washing step with water and methanol followed by a flash column. Thus, C8 alkylation allows for a simpler synthesis and is recommended for future workers.

3.6 Molecular Weight and PDI from Gel Permeation Chromatography (GPC)

Matching the literature report, GPC results for the three methoxythiophene-flanked-DPP copolymers were found to be unreliable, see below Table 3-3. The table contains GPC reference data from Domokos et al. (2019), showing that when methoxythiophene is used as a flanking group that GPC measures a very low molecular weight and PDI compared to the same polymer but thiophene-flanked. All other indications suggest polymeric material of substantial molecular weight: broadening of ^1H NMR peaks (see for example, Figure 3-19 for ^1H NMR of C20-EDOT), color change through reaction and a UV-Vis absorption peak of the product near ~ 900 nm, high yield indicating high extent of reaction, reduced solubility toward refluxing solvents compared to the monomer, and formation of films, however, GPC results suggest only $\sim$ trimers are formed. In the Domokos case, chloroform at 50°C was used as a mobile phase. This may be insufficient to fully dissolve the polymers to the molecular level. Likewise here, even though using trichlorobenzene at 150°C , an M_n of $\sim 1\text{-}5$ kDa is measured except for the case of DPP-TT. See Appendix C for data. In short, it appears these methoxythiophene-flanked DPP polymers are difficult to dissolve fully or interact with the stationary phase of the column. Also, they interact with chlorinated solvents, see Section 3.9. It may be that only trimers and dimers dissolve and these are the values recorded by the GPC. Even though these appear to make solutions, they may actually form nanoaggregates which are small enough to not settle, which does not impede the coating of high-quality films. Several commercial conjugated polymer “inks” (e.g. PANI, PEDOT:PSS) are actually sold as suspensions rather than solutions.

Table 3-3: GPC Results (including C16 results from Domokos et al.)

Solubilizing side chain and comonomer	Methoxythiophene-flanked DPP M_n [kDa]	Thiophene-flanked DPP M_n [kDa]
C16-co-T	3.3 (PDI = 1.76)	86.2 (PDI = 4.60)
C16-co-BT	3.5 (PDI = 2.16)	196.0 (PDI = 9.93)
C20-co-EDOT	Unable to establish baseline	
C8-co-EDOT	Unable to establish baseline	
C20-co-TT	9.2 (PDI = 6.71)	

The key for molecular weight is that due to the strong interaction between chains in conjugated polymers, effective conjugation lengths can rarely extend more than a few repeat units. Therefore, if a degree of polymerization of about ~10 repeat units is reached, the optoelectronic properties may not be affected by additional molecular weight growth.³⁷ However, as typical for polymers the mechanical properties such as tensile strength and elongation at break generally improve with increasing molecular weight due to an increased number of chain entanglements.

In the case of the current synthesized methoxythiophene-flanked DPP copolymers, it may be that chains of significant length are prone to forming aggregates. Then, the backbones are highly packed together and form a kind of micelle where only the alkyl chains are exposed to the GPC mobile phase. Polyolefins, which are structurally similar to alkyl chains, are known to have a lower refractive index than trichlorobenzene and thus show negative peaks. Near the end of that retention time, there may be some oligomers (~3 repeat units) with a weight around 3 kDa which are fully dissolved and not aggregated, and these show the more common positive RI peak. Without fully dissolved polymers, it is not possible to get an accurate molecular weight from this measurement. Additionally, the polymer may interact with the column packing. As future work, it is suggested to re-attempt GPC but instead of trichlorobenzene, using THF with 0.25 wt% tetrabutylammoniumbromide, as this was shown to be successful in preventing polymer-column interactions for other DPP-co-EDOT polymers when trichlorobenzene at 150 °C was unsuccessful.³⁸ Otherwise Dynamic Light Scattering may be attempted which could possibly determine the distribution of aggregate particle size, if any.

3.7 Thermal Stability from Thermogravimetric Analysis (TGA)

TGA can be used to check the thermal stability of the polymers, which is important to determine for the firefighting application in mind. The traces of decomposition are shown below in Figure 3-5. As firefighter gas sensors only need to be exposed when firefighters have taken off their SCBA gear, the sensors could be installed underneath their outer shell on either the moisture layer or innermost

thermal layer. The decomposition temperature values shown in Table 3-4 of 330 – 370 °C, though measured in nitrogen environments, are promising for the application.

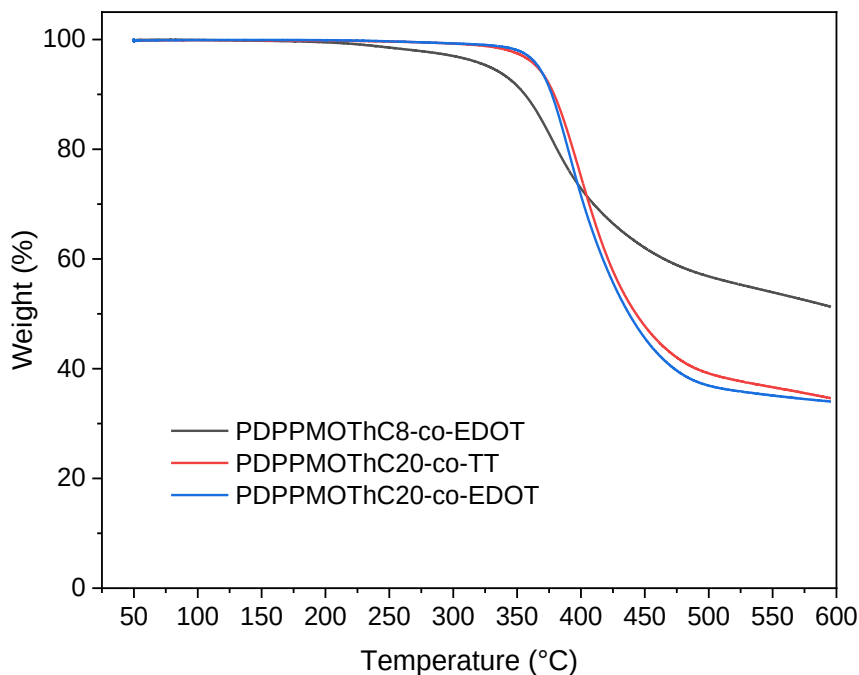


Figure 3-5: TGA traces of C8-EDOT, C20-EDOT, and C20-TT.

Table 3-4: TGA results for C8-EDOT, C20-EDOT, and C20-TT

	Temperature @ 95 wt% remaining (°C)	Peak Maximum of Derivative Weight Loss (°C)	Final wt% at 600 °C
C8-EDOT	328	378	51.3%
C20-TT	366	401	34.6%
C20-EDOT	367	389	34.0%

In conjugated polymers with sufficient thermal stability, typically there is one main decomposition process in nitrogen: side chains become detached from the aromatic backbone and evaporate from the

polymer matrix, leaving only the backbone behind. It is logical then that both C20-alkylated polymers have only 34-35 wt% remaining at 600 °C (the C20 represents 53 wt% of the repeat unit) while the C8 polymer has a more substantial 51.3 wt% remaining (C8 represents 31 wt% of the repeat unit).

3.8 HOMO/LUMO levels from UV-Vis Spectroscopy and Cyclic Voltammetry

The measured HOMO/LUMO levels may differ from computational results for many reasons, not least of which in conjugated polymers is the importance of interchain interactions. The π - π stacking common in these materials may either increase or decrease the effective conjugation length which is critical in determining the band gap and frontier orbital energies.

As is common in the field, the onset of UV-Vis absorption is used to determine the optical band gap (E_g) while CV is used to determine the HOMO level. LUMO level can then be determined by combining both through the equation:

$$\text{LUMO}_{\text{opt/CV}} = E_{g, \text{opt}} + \text{HOMO}_{\text{CV}}$$

Below are displayed the UV-Vis spectra in film, Figure 3-6, and in solution for all three polymers and well as in Figure 3-7 are displayed the CV for all three polymers.

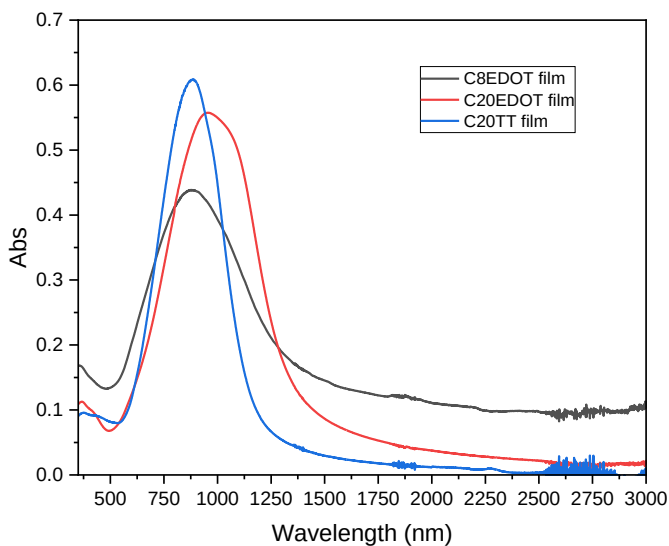


Figure 3-6: UV-Vis spectra of C8-EDOT, C20-EDOT, and C20-TT spin coated onto glass from anhydrous chloroform solutions.

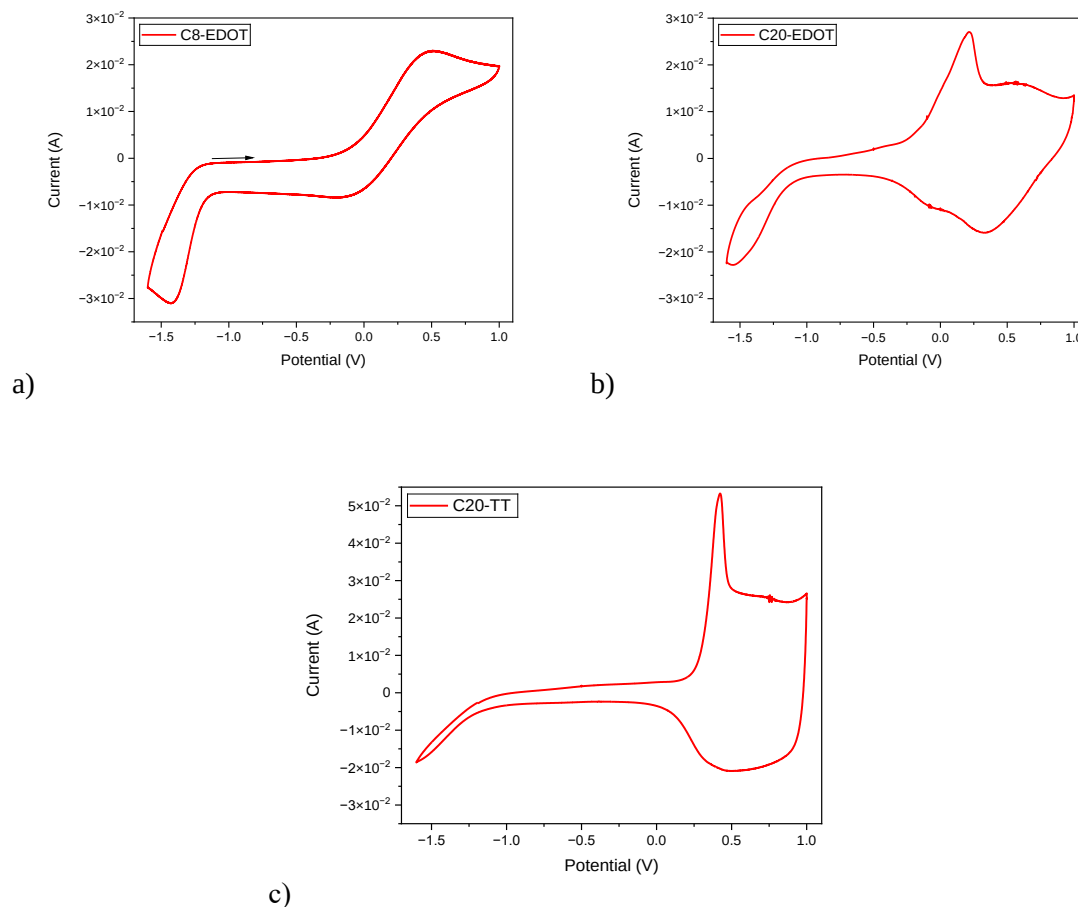


Figure 3-7: Cyclic Voltammograms for a) C8-EDOT, b) C20-EDOT, and c) C20-TT polymers, from -1.6 V to +1.0 V. Direction of scan is indicated by a black arrow on C8-EDOT.

Below see Table 3-5 with the bandgap (E_g), HOMO, and LUMO levels for all three polymers. The HOMO energy level is determined from the onset of the oxidation peak from CV, using the following equation for determining absolute energy level using the onset of oxidation of the electrochemical reference, Ferrocene, and the literature value of Ferrocene's HOMO of -4.8 eV.

$$E_{HOMO} = e(V_{onset}) - 4.8 \text{ eV}$$

The bandgap was determined from the onset of optical absorption by the polymer film in the UV-Vis spectrum, with onset in this case referring to the lowest energy or highest wavelength light which is absorbed by the polymer. It should be acknowledged that for the C8-EDOT film, determination of the

baseline and thus onset is complicated by the fact the C8-EDOT film is doped by the trace HCl present in chloroform, shown and discussed further in 3.9 - Doping and Stability by UV-Vis. The C20-EDOT film, as it does not show the polaron signal in the film state after being coated from chloroform, would allow for a more trustworthy determination of the λ_{onset} , and thus a more reliable estimate of the E_g of both EDOT copolymers. However, even if the λ_{onset} is different for C8-EDOT vs. C20-EDOT, the resulting values calculated for E_g (0.93 and 0.92 eV) are an indication that the polaron signal is minor enough to not interfere.

Table 3-5: Optical E_g , HOMO_{CV}, and LUMO_{opt/CV} levels for the three polymers C8-EDOT, C20-EDOT, and C20-TT, from coated films cast from anhydrous chloroform solutions and solution UV-Vis results using anhydrous chloroform solutions.

Polymer	λ_{max} , soln [nm]	λ_{onset} , soln [nm]	λ_{max} , film [nm]	λ_{onset} , film [nm]	$E_{g, \text{opt}}$ [eV]	HOMO _{CV} [eV]	LUMO _{opt/CV} [eV]
C8-EDOT	906	1454*	880	1334*	0.93*	-4.71	-3.78
C20-EDOT	1030	1311*	956	1355	0.92	-4.66	-3.74
C20-TT	902	1106	887	1150	1.08	-5.09	-4.01

*Note: determining onset is complicated by polaron signal. Solutions are in chloroform which likely contains small amounts of HCl, shown in this work to dope both C8-EDOT, C20-EDOT.

As predicted by the DFT simulations, the methoxythiophene-flanked DPP polymers have significantly higher HOMO levels and using EDOT as a comonomer increases the HOMO even further (Table 3-6). Comparing the polymers using TT as the comonomer, the HOMO level rises from -5.25 eV (thiophene-flanked) to -5.09 eV (methoxythiophene-flanked) which corresponds to a 0.16 eV increase, agreeing well with the DFT prediction. In the case of the EDOT comonomer polymers, the HOMO level rises e.g. from -5.40 eV (thiophene-flanked) to -4.66 eV (methoxythiophene-flanked) which represents a substantial 0.74 eV increase.

Table 3-6: HOMO_{CV} values measured (and predicted by DFT) in this study for methoxythiophene-flanked DPP copolymers, along with reference thiophene-flanked DPP copolymer HOMO_{CV} values.

DPP-flanking group	Co-monomer	HOMO _{CV} [eV]	DFT E _{HOMO} [eV]
Th	Th	-5.75 ³⁹	-4.73
Th	EDOT	-5.73 ³⁸	-4.52
Th	EDOT	-5.40 ⁴⁰	-4.52
Th	TT	-5.25 ²⁶	-4.74
MOTh	EDOT	-4.71	-4.36
MOTh	EDOT	-4.66	-4.36
MOTh	TT	-5.09	-4.52

As for the band gap results, undoped conjugated homopolymers such as polyacetylene, polyaniline, and P3HT generally have band gaps ~1.5 - 3 eV. On the other hand, Donor-Acceptor conjugated polymers can have significantly lower band gaps, such as DPP-TT's value of 1.23 eV.²⁶ The E_g values of 0.92 eV and 0.93 eV reported for the -EDOT copolymers, are among the lowest ever reported for DPP copolymers (there are two lower reports of 0.82 eV⁴¹ and 0.84 eV⁴²). As they have E_g values less than 1.0 eV, these would be commonly referred to as “ultralow” or “ultrasmall” bandgaps. There are several strategies that could be used to decrease the band gap even further, e.g. Shahid et al. (2012) discussed literature that successfully decreased the band gap in conjugated polymers by replacing thiophenes with selenophene (lower lying LUMO than thiophene) and provided experimental results showing that it had this effect in a DPP-based polymer.⁴³ The onset of light absorption around 1350 nm is near the long wavelength end of the Near-IR IIa window (1000-1400 nm) and thus the material could potentially find use in NIR photodetectors.⁴⁴ One of the most exciting new applications of polymers with band gaps in this range is in laser ablation therapy to eliminate cancer cells, which has been successful *in vitro* for example by Anderson et al. (2023).⁴⁵ Like the ultralow bandgap polymers in Anderson, the methoxythiophene-flanked DPP copolymers

reported in this study could potentially be introduced proximal to cancer cells, and then through absorption of targeted IR laser light, convert that light into heat in thereby inducing cell apoptosis.

3.9 Doping and Stability by UV-Vis

As alluded to in the previous section, C8-EDOT unexpectedly seemed to have a (bi)polaron absorption indicating a doped state, even when no dopant molecule had been intentionally introduced. In this Section a number of experiments using UV-Vis spectra are described to show that the cause of this unexpected doping is trace hydrochloric acid found in chloroform.

Much work was carried out to determine if it was due to a spurious cause: glass substrate was re-cleaned, concentration was varied, solution was carefully filtered, and both the solvent and solution were dried separately using sodium sulfate drying agent. The high wavelength absorbance remained in all these cases, and it remained constant in intensity relative to the main absorption peak at around ~900 nm. Assuming it was genuinely doped (p-doped) by some means and that excess hole charge carriers forming (bi)polarons was the reason for the high wavelength absorbance, investigation turned to the possibility that the polymer was doped by the aforementioned trace HCl which can be found in chloroform as a result of air and UV exposure by: $2 \text{CHCl}_3 + \text{O}_2 \rightarrow 2 \text{COCl}_2 + 2 \text{HCl}$. For the 99.98% HPLC Grade Chloroform stabilized with amylene which was used as solvent, the specification for freshly manufactured solvent is “Free Acid (HCl) < 0.001%” which is equivalent to 10 ppm HCl, though it may of course increase over time with exposure to air and UV.

The evidence that trace HCl in chloroform doped C8-EDOT began with the fact that the (bi)polaron absorption was not seen in solutions of C8-EDOT dissolved in toluene in contrast to the result in chloroform, Figure 3-8a. The doped state was also seen in films cast from another chlorinated solvent, chlorobenzene, Figure 3-8b. By adding triethylamine base to the C8-EDOT chloroform solutions, dedoping was observed by disappearance of the (bi)polaron absorption, Figure 3-8c. Finally, by adding HCl acid to toluene solutions in Figure 3-8d, appearance of (bi)polaron absorption was observed, and

likewise adding pure HCl to chloroform solutions increased the (bi)polaron absorption even further, Figure 3-9.

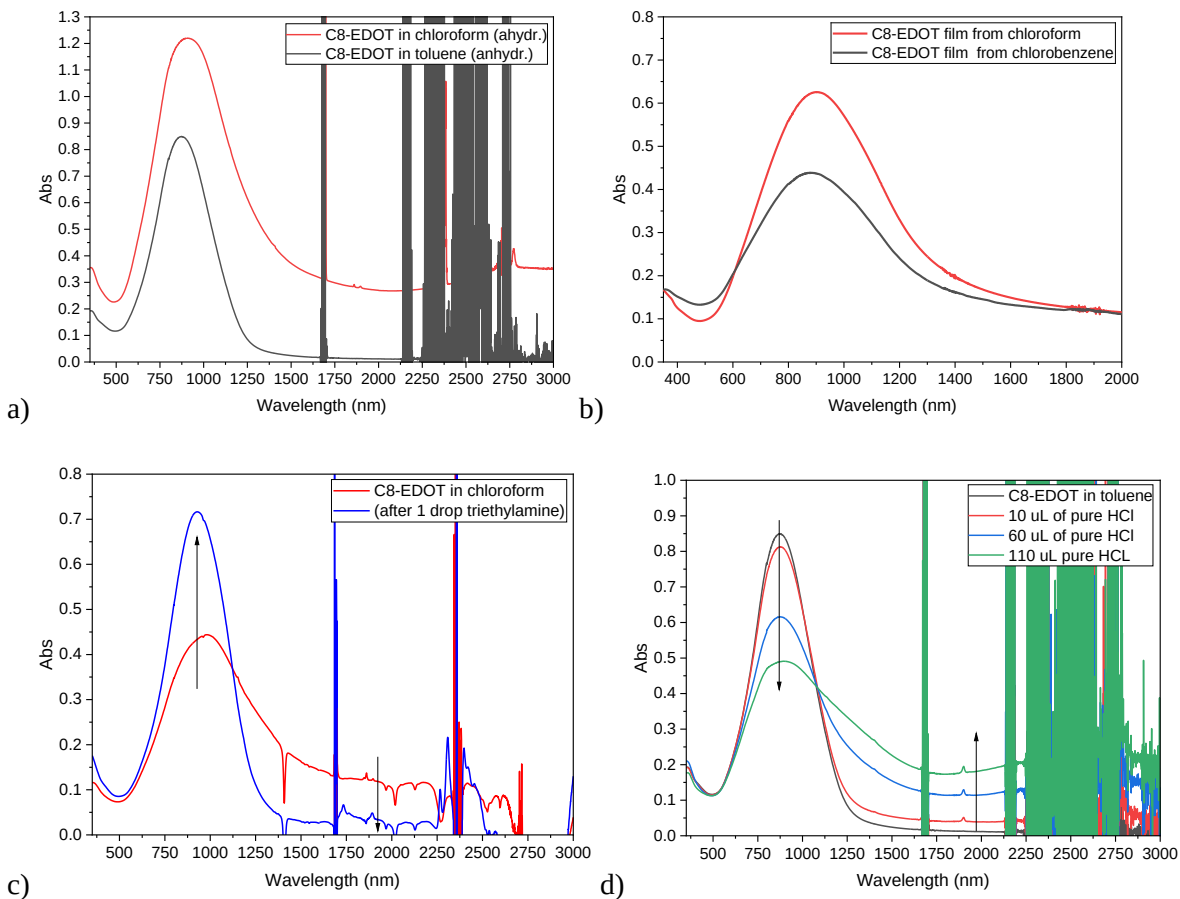


Figure 3-8: a) UV-Vis spectra recorded for solutions of C8-EDOT dissolved in anhydrous chloroform (grey line) and anhydrous toluene (red line). The high absorbance of ~ 0.3 at 2000 nm, expected to be the (bi)polaron signal, is not seen in the toluene solution. b) UV-Vis spectra of C8-EDOT films coated from two chlorinated solvents: chloroform (grey) and chlorobenzene (red), both showing absorption at 2000 nm. Note that the chloroform sample was re-run later to extend the range to 3000 nm (see Appendix D) and it shows the same result although higher overall absorption, most likely due to increased reflectivity of the film over time. c) C8-EDOT solution in chloroform de-doped by a drop of triethylamine. Black arrows included to guide the eye. d) UV-Vis spectra of a C8-EDOT toluene solution before adding HCl (black line) and after adding up to 110 μL of pure HCl.

As can be seen in Figure 3-8c above, upon adding a drop of triethylamine to the pristine polymer in chloroform, the absorbance at high wavelength drops to near zero e.g. at 2100 nm (wavelength picked to avoid strong chloroform and triethylamine peaks) dropping from 0.11 to 0.03. Meanwhile the main absorption peak around 900 nm nearly doubles in intensity and narrows, typical for de-doping. It can be seen from the solution spectra that it is not only the film samples that have this absorbance.

Triethylamine does not have UV absorbance in the relevant range (peaks are 1188, 1392, 1737, and >2200 nm) and so it does not interfere with the UV measurement directly.

This (bi)polaron signal seemed to be persistent, as we compared the spectrum of a freshly coated C8-EDOT film with the same film after being stored in air for 70 days and it was seen that the signal was very stable with no significant peak shift and no decay of absorption, Figure 3-12. The increase “Abs” over time may actually be attributed to an increase in reflected light rather than absorbed light based on the qualitative observation that the sample became shinier over time.

The measured solution UV of all three polymers in chloroform can be seen below, before and after adding hydrochloric acid (pure; 37 wt%):

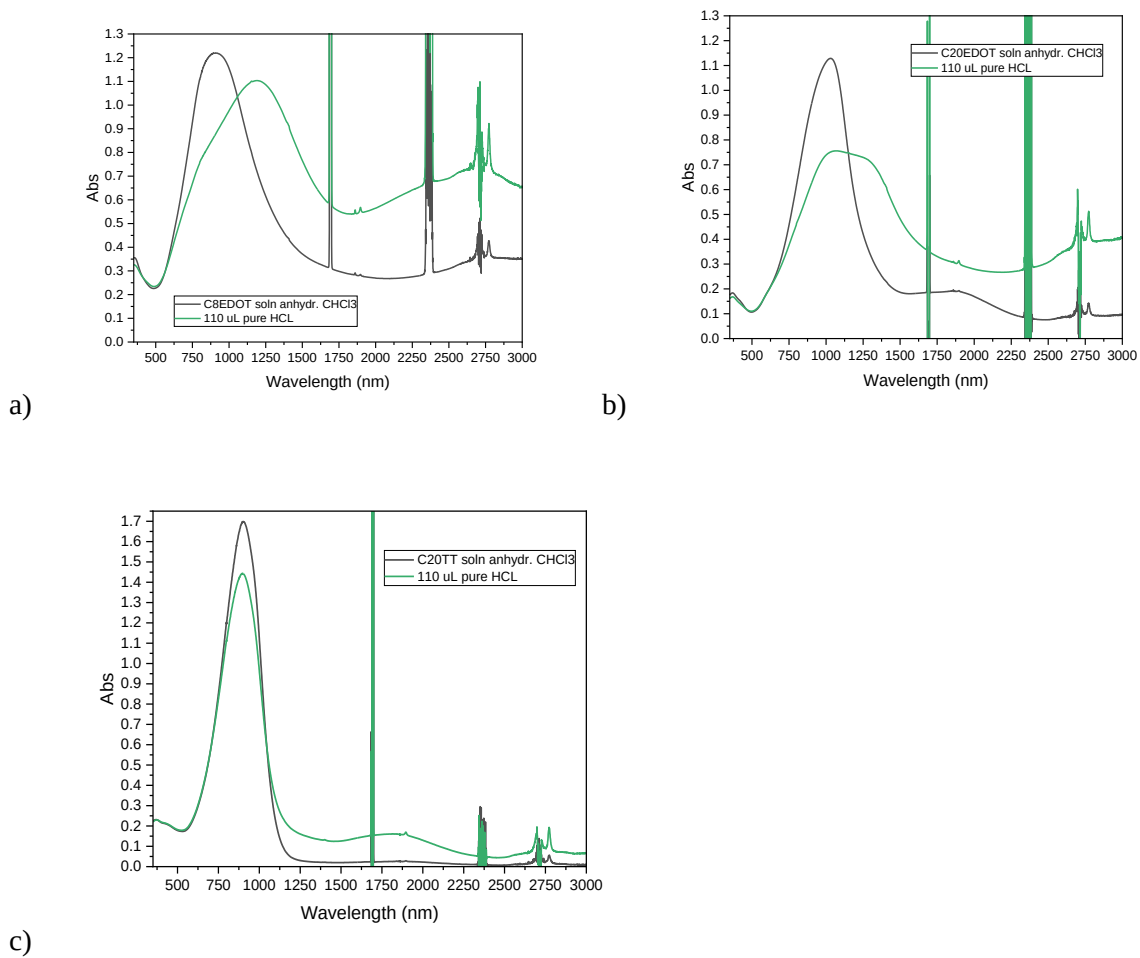


Figure 3-9: UV-Vis spectra of a) C8-EDOT, b) C20-EDOT, and c) C20-TT in chloroform solution, before (black) and after (green) adding 110 μL of pure HCl.

Likewise, when a solution of Magic Blue (oxidant – electron acceptor) is spin coated on to the pristine sample, the polaron peak signal increases:

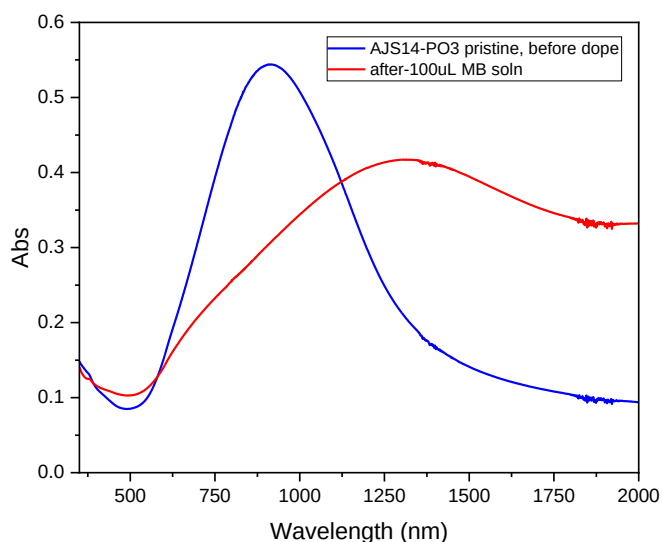


Figure 3-10: C8-EDOT doped by sequential doping using a Magic Blue solution.

3.9.1 I-V Curves and Conductivity Calculation

One way to prove that a “pristine” polymer is in fact doped is to show that it has measurable conductivity and a linear I-V curve without any gate voltage applied. Most conjugated polymers without exogenous doping may be measured to have conductivity of between 10^{-6} - 10^{-10} S/cm.⁴⁶ As this is the range of insulators, in many cases attempts to run I-V curves on undoped polymers are met with noise instead of linear curves. A transistor substrate coated with C8-EDOT and measured by sweeping from -10V to 10 V without the gate electrode attached is shown below in Figure 3-11.

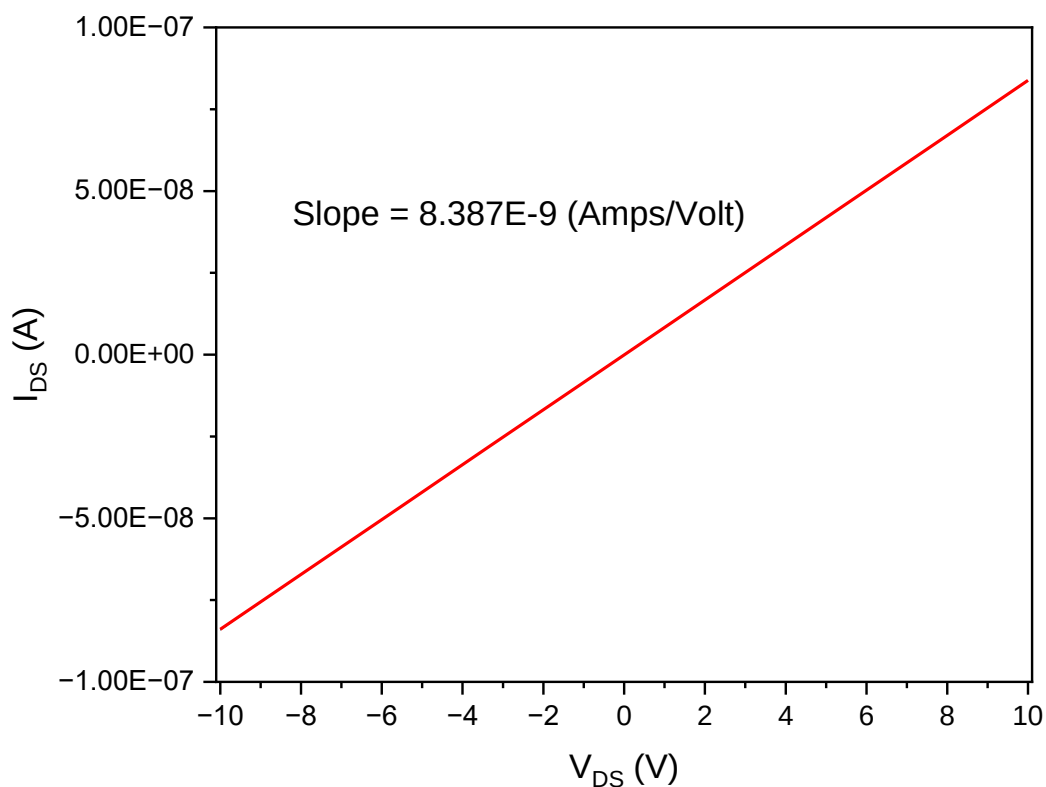


Figure 3-11: C8-EDOT polymer spin coated on transistor wafer but measured in air without gate voltage, showing a linear response to voltage sweep from -10 V to +10V.

A linear regression was fit to the resistor-like voltage sweep in air and this resulted in a slope of 8.39×10^{-9} Amps/Volt. The regression gave an $r^2 = 1$, meaning the deviation from resistor-like behavior is negligible. The geometry of the transistor is as follows: 1 mm wide and 30 micron gap which gives a W:L ratio of 33.33. Assuming the spin coated film is roughly ~25-40 nm thick, this yields a conductivity of between 1.01×10^{-4} - 6.31×10^{-5} S/cm. This conductivity for a pristine (i.e. has not been doped exogenously) conjugated polymer is on the high end. Though polymer backbone conjugation provides a pathway for electric charge, without the large number of charge carriers provided by dopant molecules the pristine conductivities are rarely higher than 10^{-8} S/cm.⁴⁷ Before the establishment of HCl as the cause of the doping, it was possible that the doping seen for C8-EDOT was due a) to impurities left over from polymerization or b) doping due to environmental factors

namely the oxygen and/or moisture in the lab air. It was determined that oxygen was not the cause for the pristine conductivity, once both resistor and transistor devices made with C8-EDOT were measured in lab air and then moved into a nitrogen glovebox (< 10 ppm O_2 ; < 1 ppm H_2O) to be re-measured before returning to lab air where it was found the conductivity was not recovered—likely due to HCl being removed during the vacuum antechamber purge cycles. It is worth noting that a similar conductivity of 2.97×10^{-4} S/cm has been reported for a high-HOMO (-4.68 eV) DPP polymer coated from chloroform.⁴⁸

Turning to stability, a UV-Vis spectra of single C8-EDOT film coated from chloroform was measured on the day of coating and also two months later, Figure 3-12. The film initially shows the high absorption in the long wavelength regions (>2000 nm) due to absorption by a (bi)polaron. Remarkably, after 2 months of sitting in air on a lab benchtop, both the (bi)polaron peak and main absorption peak are stable.

When C8-EDOT was coated from chloroform on a transistor substrate without any exogenous dopant nor, it still showed conductivity after 2 months, having decreased in output current by 45% which would only correspond to a decrease of $\sim 0.75\%$ /day which could potentially be accounted for through calibration. The stability results align with a study by Ngai et al. (2021) where a high HOMO (-4.68 eV) DPP copolymer was doped by HCl and over the same time period of 2 months of ambient air exposure, showed a decrease of $\sim 65\%$ original current.⁴⁸ The C8-EDOT was coated on a resistor substrate, stored in air and monitored over thirty days as shown in Figure 3-13. This shows relatively stable conductivity over a month. Although preliminary on a single sample, it should be mentioned that a conductivity of ~ 3 -5 S/cm was reached by a film cast from a chloroform solution of C8-EDOT where exogenous HCl was added, and this conductivity was maintained at least over the same thirty days as the data shown in Figure 3-13.

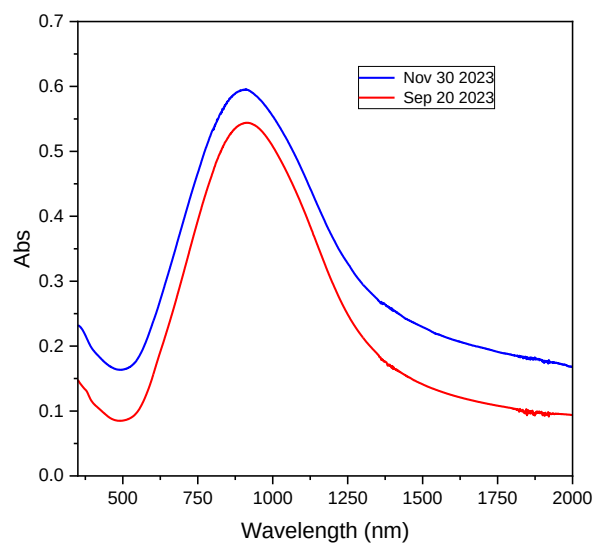


Figure 3-12: UV-Vis spectra of a single C8-EDOT film which was coated on September 20th, 2023, and re-measured 70 days later on November 30th. Film shows no decay of absorption nor substantial peak shift over 2 months in air.

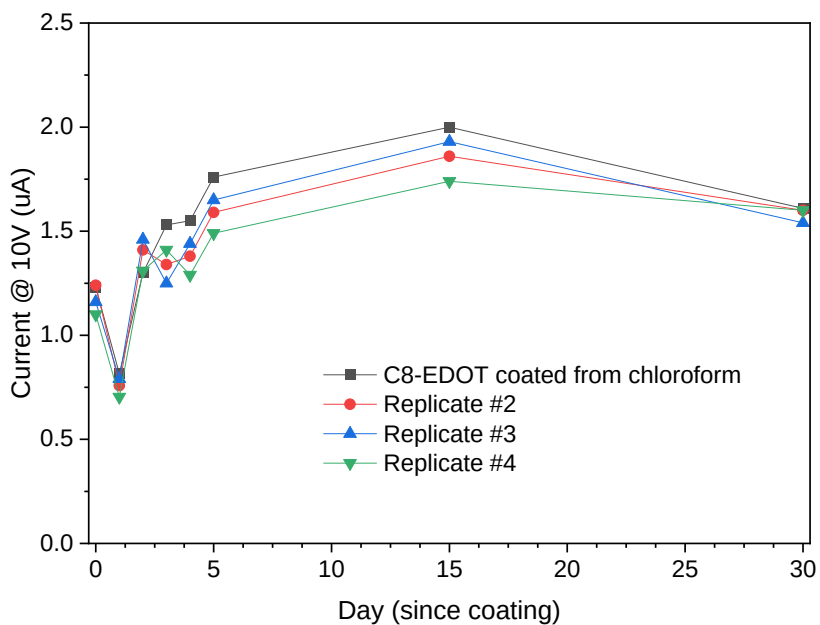


Figure 3-13: Preliminary data measuring the stability of current at 10 Volts from four devices of C8-EDOT coated from chloroform (without additional HCl added).

3.10 Conclusion

It is expected that the newly developed methoxythiophene-flanked DPP copolymers will enable stable doped conductive polymers with e.g. F4TCNQ. A rule of thumb in the field is that for the successful p-doping of polymers by oxidizing dopants, the difference between the polymer HOMO and dopant LUMO should be greater than ~ 0.5 eV.²² In the case of the newly synthesized methoxythiophene-flanked DPP copolymerized with EDOT, a HOMO of -4.7 eV is found. This value, compared with F4TCNQ's LUMO of -5.24 eV, results in a difference of greater than 0.5 eV, which suggests there may be effective and stable doping between these two.

In addition, the polymer was found to be stably doped over more than 1 month by trace amounts of HCl found in chloroform and preliminary evidence suggests that by adding additional (exogenous) HCl, a conductivity of ~ 3 - 5 S/cm is achievable with additional development and optimization.

3.11 Experimental Section

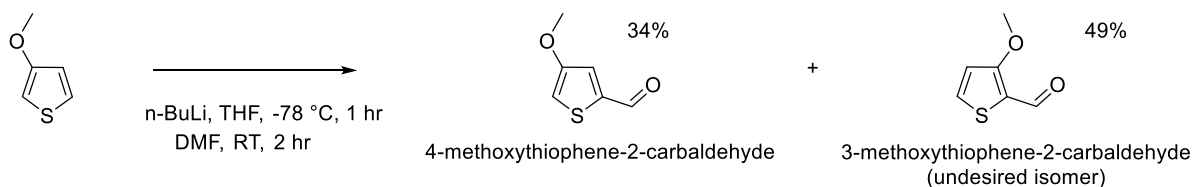
3.11.1 Materials Source & Characterization

3-methoxythiophene and EDOT were purchased from Oakwood Chemical. The bromo alkanes (2-octyl-1-dodecylbromide and 2-ethylhexyl bromide) were purchased from TCI. All other reagents and anhydrous solvents were purchased from Sigma Aldrich, in addition to common solvents from VWR or Fisher Chemical. The hydrochloric acid used in all cases was pure (i.e. 37 wt%). Detailed synthetic methods are described below in Sections 3.11.2 and 3.11.3.

^1H NMR spectra were obtained using a Bruker DPX 300-MHz instrument and CDCl_3 as the solvent. TGA scans were recorded in a nitrogen atmosphere by first holding 10 minutes at 50 °C to remove moisture followed by ramping the sample at 10 °C/min from 50 °C to 600 °C. UV-Vis Spectra were measured on a Cary 7000 UMS UV-Vis-NIR spectrophotometer, capturing the spectral absorbance from 350 nm to 3000 nm, and following the procedure detailed in Section 2.8.4. CV data was acquired using a rate of 20 mV/s, scanning 3 cycles from -1.6 V to 1.0 V and starting at -0.5 V. The working and counter electrodes were platinum, while the reference electrode was Ag^+/AgCl . The electrolyte was a 0.1M NBu_4PF_6 solution in acetonitrile. The current of the device was measured by spin coating films on to resistive sensing interdigitated electrodes, attaching only the source and drain electrodes of a Keysight B2902A Precision Source / Measure Unit and recording current while applying a voltage, scanning a linear sweep from -10V to +10V while collecting 300 data points over ~ 5s. To coat the resistive sensing interdigitated electrodes, a 50 μL of a 5 mg/ml solution of the polymer in anhydrous chloroform was spin coated using the following settings: 3000 rpm, 1500 rpm/s, 80 sec. The resistive sensing interdigitated electrodes were prepatterned bottom-contact gold (Au) on SiO_2 (300 nm)/Si wafer substrates. The electrodes had channel length (L) of 30 μm and total channel width (W) of 15.8 mm for a W/L ratio of 527.

3.11.2 Synthetic Routes (Monomers)

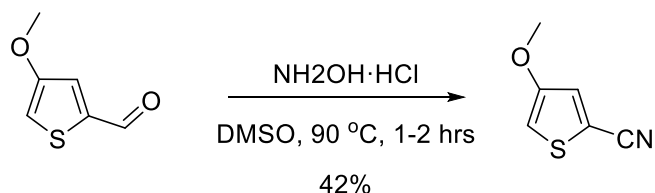
4-methoxythiophene-2-carbaldehyde



Scheme 4: 4-methoxythiophene-2-carbaldehyde.

A stir bar was added to a 500 ml two-necked round bottom flask which was then attached to a Schlenk line, and the free neck stoppered by rubber septum. The flask was placed under nitrogen and vacuum pumped and purged with nitrogen three times. 3-methoxythiophene (5.8 ml, 58 mmol, 1 eq) was added through the septum, followed by 60 ml anhydrous THF. The flask was set to stir and to cool to $-78\text{ }^{\circ}\text{C}$ using a dry ice and acetone bath. Once cooled, a 2.5M solution of $n\text{-BuLi}$ in hexanes (25.5 ml, 64 mmol, 1.1 eq) was added dropwise. The reaction was allowed to stir for 1 hour, while maintaining $-78\text{ }^{\circ}\text{C}$. After the hour of stirring, DMF was added (5.5 ml, 70 mmol, 1.2 eq) and the reaction was allowed to warm to room temperature and stir for 2 hours. TLC was checked using 20:80 ethyl acetate:hexane mobile phase, revealing two UV-active spots of R_f values ~ 0.35 (product) and ~ 0.2 (side product, isomer 3-methoxythiophene-2-carbaldehyde, confirmed by NMR). The reaction was then poured into DI water (125 ml) and extracted three times with DCM (3 x 75 ml). The organic phase was then washed with DI water (50 ml) and dried with Na_2SO_4 before rotary evaporation. To purify and isolate the desired 4-methoxythiophene-2-carbaldehyde isomer, flash chromatography on silica was employed, using 20:80 ethyl acetate:hexane as the mobile phase. After rotary evaporation, a yellow liquid was obtained which after a few hours in a freezer formed a solid made up of small yellow crystals. (Yield: 2.77 g, 34%) ^1H NMR (300 MHz, CDCl_3 , δ [ppm]): 9.79 (d, 1H), 7.37 (t, 1H), 6.72 (d, 1H), 3.82 (s, 3H).^{49,50}

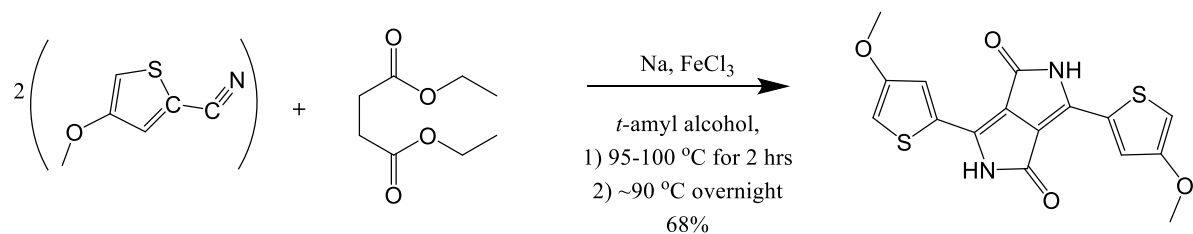
4-methoxythiophene-2-carbonitrile



Scheme 5: 4-methoxythiophene-2-carbonitrile.

A stir bar was added to a 100 ml two-necked round bottom flask. 4-methoxythiophene-2-carbaldehyde (4.29 g, 30 mmol), $\text{NH}_2\text{OH}\cdot\text{HCl}$ (2.33 g, 33 mmol, 1.1 eq), and 24 ml DMSO were added to the flask. The flask was attached to a condenser and heated to $90\text{ }^\circ\text{C}$ while stirring. The reaction was left to stir at $90\text{ }^\circ\text{C}$ for 3 hours. Once reaction was confirmed to be completed by TLC using a 40:60 DCM:hexane mobile phase, revealing a UV-active spot of R_f value ~ 0.25 , the flask was cooled to room temperature. The reaction was poured into a separatory funnel with ~ 75 ml DI water followed by 3x extraction with diethylether. The organic fraction was then washed 5x(20 ml DI water) and dried with Na_2SO_4 . After rotary evaporation, the product was isolated and purified using flash chromatography on silica, with a 1-2'' plug and starting with 10:90 ethyl acetate:hexane increasing to 20:80 ethyl acetate:hexane as the mobile phase. The collected product was dried under vacuum and found to be a yellow crystalline solid. (Yield: 1.78g, 42%) ^1H NMR (300 MHz, CDCl_3 , δ [ppm]): 7.25 (d, 1H), 6.55 (d, 1H), 3.86 (d, 3H).¹⁵

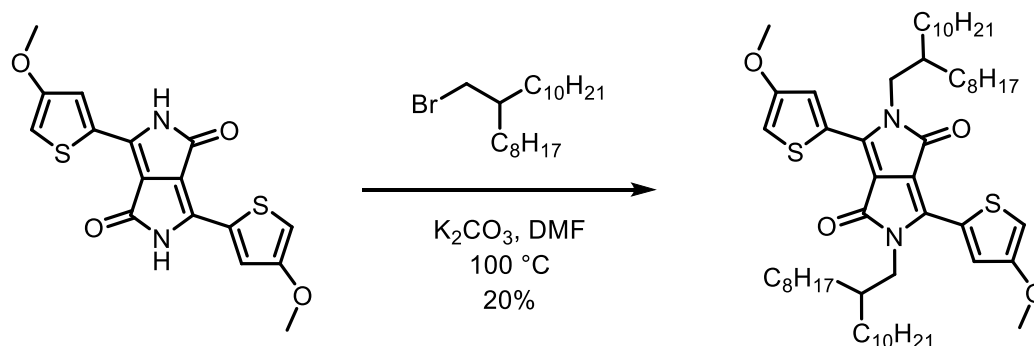
3,6-bis(4-methoxythiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione



Scheme 6: 3,6-bis(4-methoxythiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione.

A stir bar was added to a 100 ml three-necked round bottom flask. The flask was attached to a condenser on a Schlenk line. On the remaining necks of the flask a 25 ml addition column and a rubber septum were attached. The flask was placed under nitrogen and vacuum pumped and purged with nitrogen three times while using a heat gun to drive off moisture. *T*-amyl alcohol (10 ml) was added through the septum followed by sodium metal (0.41 g, 18 mmol, 3.5 eq) and Iron (III) chloride (catalytic amount, 11 mg). The flask was stirred for 1.5 hours at 95 – 100 °C to dissolve sodium metal before being cooled to 90 °C. 4-methoxythiophene-2-carbonitrile (1.78 g, 13 mmol, 2.5 eq) was added. The addition column was filled with diethyl succinate (0.85 g, 3.3 mmol, 1 eq) dissolved in another 10 ml of *t*-amyl alcohol, and this solution was added to the reaction dropwise over 1 hour. A color change from dark brown to dark red was noted. Once the addition was complete, the reaction was allowed to continue overnight (15 hours) at 95 °C. The reaction was then cooled to 50 °C and slowly neutralized with ~4 ml glacial acetic acid. The reaction was then diluted with 20 ml of methanol and refluxed for 30 minutes. To isolate the product, the reaction was filtered and the solids transferred to a volumetric flask. The solid residue was rinsed twice with hot methanol and then once with DI water. The solid was filtered again and dried overnight in a vacuum oven at 60 °C. The product was found to be a dark purple solid. (Yield: 1.25g, 68%).^{51,52}

3,6-bis(4-methoxythiophen-2-yl)-2,5-bis(2-octyldodecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione



Scheme 7: 3,6-bis(4-methoxythiophen-2-yl)-2,5-bis(2-octyldodecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione.

A stir bar was added to a dry three-necked 100 ml round bottom flask. 3,6-bis(4-methoxythiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (0.62 g, 1.72 mmol) and anhydrous K₂CO₃ (0.71g, 5.16 mmol, 3 eq) were dissolved in 27 ml anhydrous N,N-dimethylformamide (DMF). The reaction was heated to 100 °C under nitrogen for 1 hour. 2-octyl-1-dodecylbromide (2 ml, 5.4 mmol, 3 eq) was then added drop-wise, and the reaction was further stirred and heated overnight at 100 °C. As this octyldodecyl-alkylated product (C₂₀) did not precipitate into methanol as reported for a hexyldodecyl- (C₁₆) alkylated product in Domokos et al. 2019,¹⁵ the product was dissolved in chloroform, washed with water 3x and the water extracted with chloroform. The organic fractions were combined, washed with brine, dried with sodium sulfate, filtered through filter paper and dried under rotary evaporator. In order to remove O-alkylated products, this crude product was then dissolved in 20 ml dioxane, and while stirring, 67 µL of pure hydrochloric acid (37%) was added. This solution was heated and stirred under refluxing conditions overnight. The solution was cooled to room temperature and K₂CO₃ (3.3g) was added and stirred for 3 hrs. The solution was then further purified through use of a plug column of silica using DCM as the mobile phase. The filtrate was collected and dried in vacuo and purified by column chromatography using 25:75 DCM:hexane moving up to 80:20 DCM:hexane. The product was dried in vacuo to yield a dark purple sticky/muddy solid (Yield: 0.31 g, 20%). ¹H NMR (300 MHz, CDCl₃, δ [ppm]): 8.50 (d, 2H), 6.59 (d, 2H), 3.93 (d, 4H), 3.87 (s, 6H), 1.94-1.83 (m, 2H), 1.33-1.12 (m, 64H), 0.89-0.81 (m, 12H).

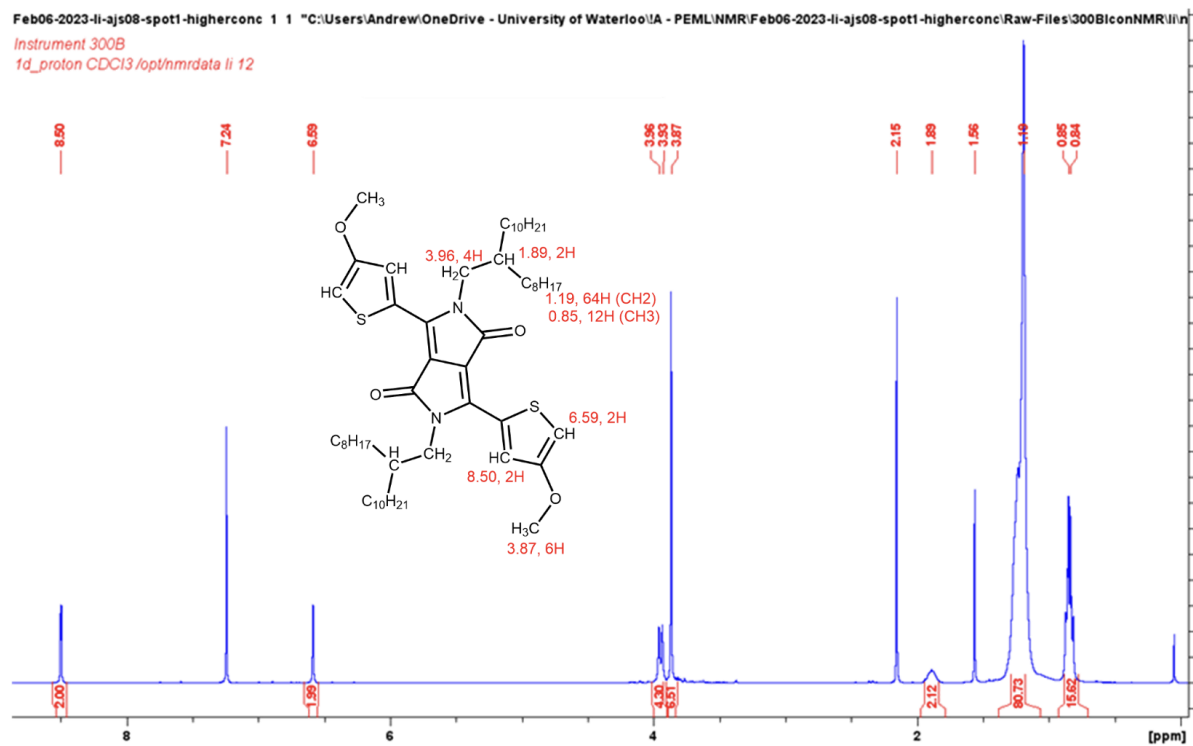
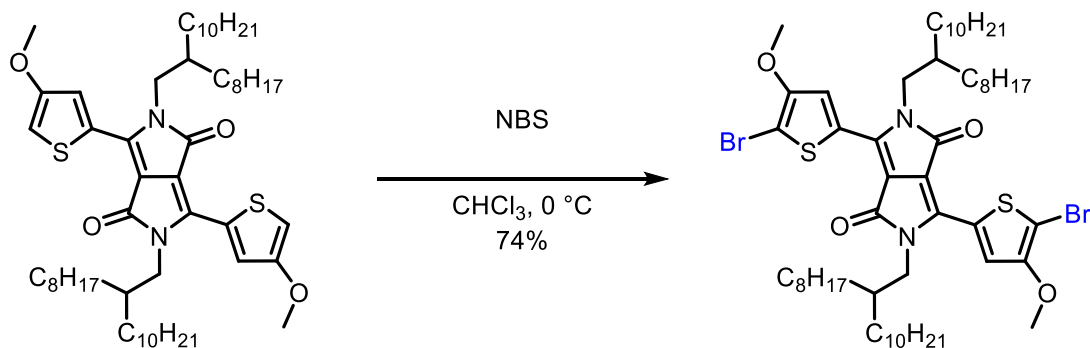


Figure 3-14: ^1H NMR of 3,6-bis(4-methoxythiophen-2-yl)-2,5-bis(2-octyldodecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione, including the structure of the molecule with peak shifts and integrations assigned.

3,6-bis(5-bromo-4-methoxythiophen-2-yl)-2,5-bis(2-octyldodecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione



Scheme 8: 3,6-bis(5-bromo-4-methoxythiophen-2-yl)-2,5-bis(2-octyldodecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione.

A stir bar was added to a 50 ml round bottom flask. The flask was vacuum pumped and purged with nitrogen three times. To the flask was added 3,6-bis(4-methoxythiophen-2-yl)-2,5-bis(2-octyldodecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (0.31 g, 0.34 mmol) and 9 ml chloroform which were stirred in order to achieve full dissolution. The flask was then cooled to 0 °C in an ice bath. While continuing to stir, N-bromosuccinimide (0.13 g, 0.74 mmol, 2.2 eq) was added to the reaction in small portions over a 5 minute period. The flask was then removed from the ice bath and allowed to reach room temperature, during which a color change from red/pink to purple was observed which indicated the completion of the reaction. The solution was transferred to a flask and 100 ml methanol was used to precipitate the product. The solid product was filtered and the solid retained. The solid was dried over rotary evaporator to ensure methanol was completely removed before being further purified in a plug column. The mobile phase of the column started at 50:50 DCM:hexane and increased to 80:20 DCM:hexane. The product was then subject to rotary evaporation and further room temperature vacuum drying. Product was found to be a flaky, very dark purple solid. (Yield: 0.27g, 74%) ¹H NMR (300 MHz, CDCl₃, δ [ppm]): 8.84 (s, 2H), 4.03 (s, 6H), 3.90 (d, 4H), 1.95-1.87 (m, 2H), 1.32-1.18 (m, 32H), 0.88-0.81 (m, 12H).

Reaction conditions informed by analogous reaction done in Domokos et al. 2019 using a branched hexyldodecyl (C16) instead of here branched octyldodecyl (C20).¹⁵

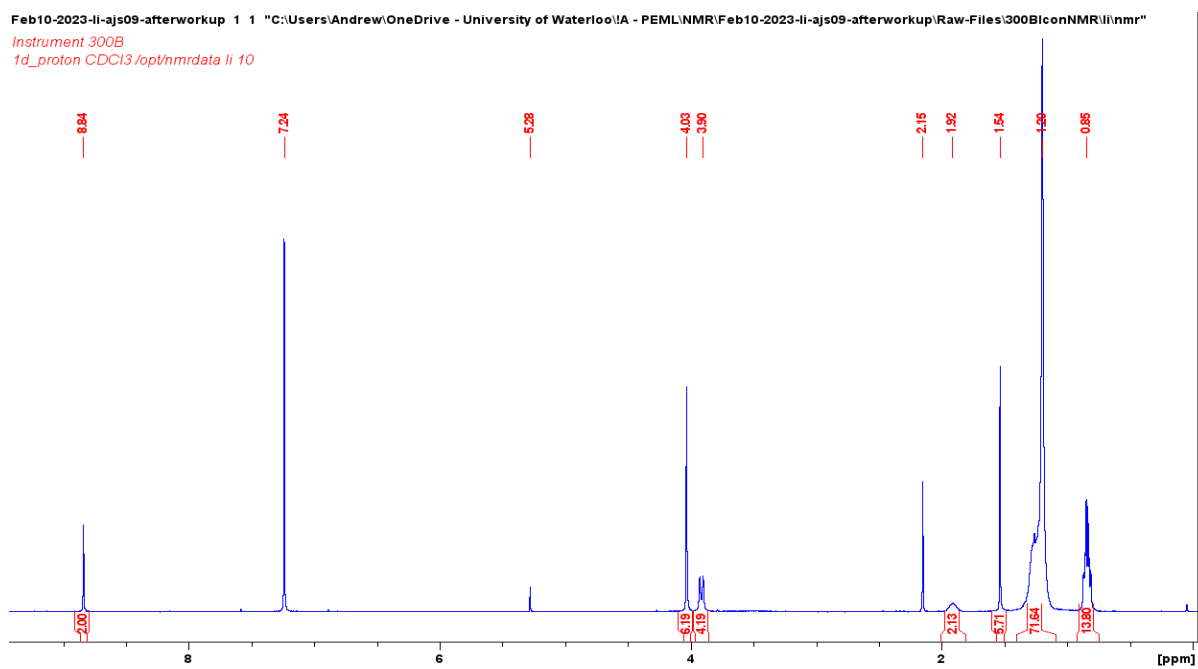
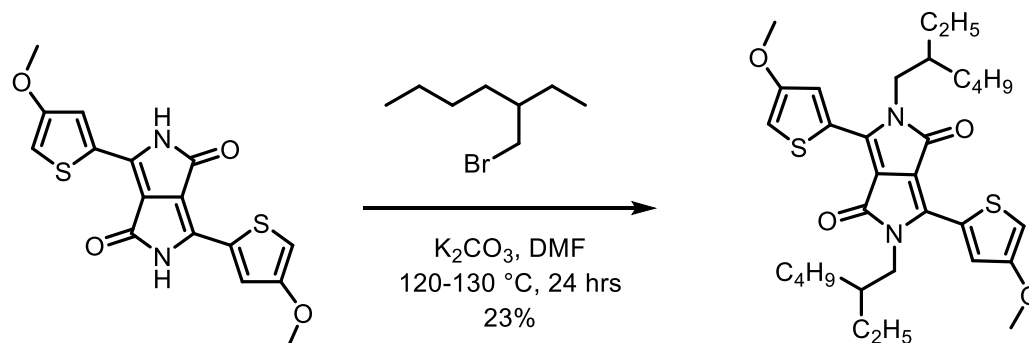


Figure 3-15: ^1H NMR of 3,6-bis(5-bromo-4-methoxythiophen-2-yl)-2,5-bis(2-octyldodecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione.

2,5-bis(2-ethylhexyl)-3,6-bis(4-methoxythiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione



Scheme 9: 2,5-bis(2-ethylhexyl)-3,6-bis(4-methoxythiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione.

A stir bar was added to a dry 100 ml three-necked round bottom flask. The flask was placed under nitrogen and vacuum pumped and purged with nitrogen three times while using a heat gun to drive off moisture. DPP-MOTh (0.493 g, 1.4 mmol), anhydrous K₂CO₃ (0.68 g, 4.9 mmol, 3.5 eq), and 14 ml anhydrous dimethylformamide were added. Stirring was used to dissolve the solids. A catalytic amount of 18-crown-6 (9 mg) was added. The flask was heated to 120 °C under nitrogen for 1 hour. Dropwise, 2-ethylhexyl bromide (1.09 g, 1.0 ml, 5.6 mmol, 4 eq) was added over 5 minutes. The reaction was stirred for 24 hours at 120-130 °C. Reaction completion was confirmed by TLC using pure DCM as a mobile phase to reveal a pink spot of R_f value ~0.4. The flask was cooled to room temperature. To isolate the product, the reaction was precipitated by pouring it into DI water (4 eq w.r.t. DMF), stirring for 1 hour, filtering and then washing the solid several times with DI water and methanol, followed by air drying. To further purify the product, a flash column of 12" silica and mobile phase starting with 50:50 hexane:DCM and moving up to pure DCM was used. The product was dried under vacuum and found to be a dark purple solid. (Yield: 183 mg, 23%) ¹H NMR (300 MHz, CDCl₃, δ [ppm]): 8.50 (d, 2H), 6.59 (d, 2H), 3.94 (dd, 4H), 3.87 (s, 6H), 1.81-1.89 (m, 2H), 1.20-1.34 (m, 16H), 0.81-0.88 (m, 12H).

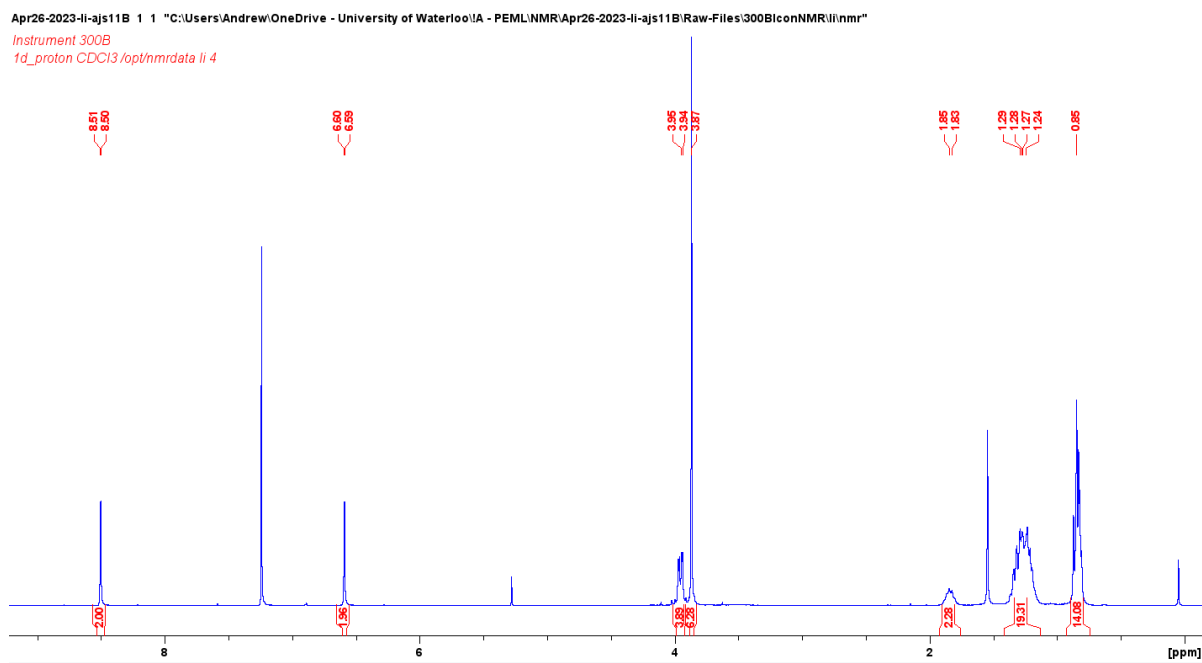
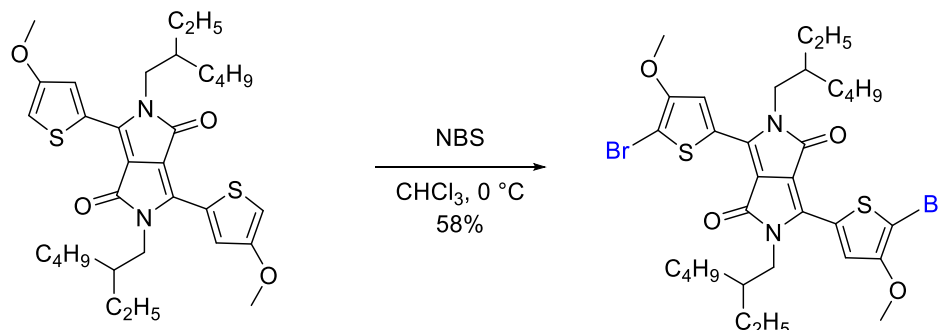


Figure 3-16: ^1H NMR of 2,5-bis(2-ethylhexyl)-3,6-bis(4-methoxythiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione.

3,6-bis(5-bromo-4-methoxythiophen-2-yl)-2,5-bis(2-ethylhexyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione



Scheme 10: 3,6-bis(5-bromo-4-methoxythiophen-2-yl)-2,5-bis(2-ethylhexyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione.

A stir bar was added to a dry 50 ml round bottom flask. The flask was placed under nitrogen and vacuum pumped and purged with nitrogen three times while using a heat gun to drive off moisture. The 2,5-bis(2-ethylhexyl)-3,6-bis(4-methoxythiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (0.180 g, 0.31 mmol) was added. Chloroform (3 ml) was added and stirring used to dissolve the solid. The reaction was cooled to 0 °C in an ice bath. Over 5 minutes in small portions while stirring, NBS (0.125 g, 0.70 mmol, 2.3 eq) was added. The ice bath was removed and the reaction wrapped in aluminum foil and allowed to warm to room temperature. A drastic color change from red to purple was observed, indicating reaction completion. The reaction was quenched into a separatory funnel filled with DI water and the organic fraction was subsequently dried with sodium sulfate. For further purification, the dried organic fraction was wet loaded into a short (6") silica column and DCM was used as a mobile phase. (Yield: 132 mg, 58%) ¹H NMR (300 MHz, CDCl₃, δ [ppm]): 8.83 (s, 2H), 4.04 (s, 6H), 3.91 (d, 4H), 1.82-1.92 (m, 2H), 1.38-1.20 (m, 16H), 0.87 (q, 12H).

Reaction conditions informed by analogous reaction done in Domokos et al. 2019 using a branched hexyldecyl (C16) instead of here branched ethylhexyl (C8).¹⁵

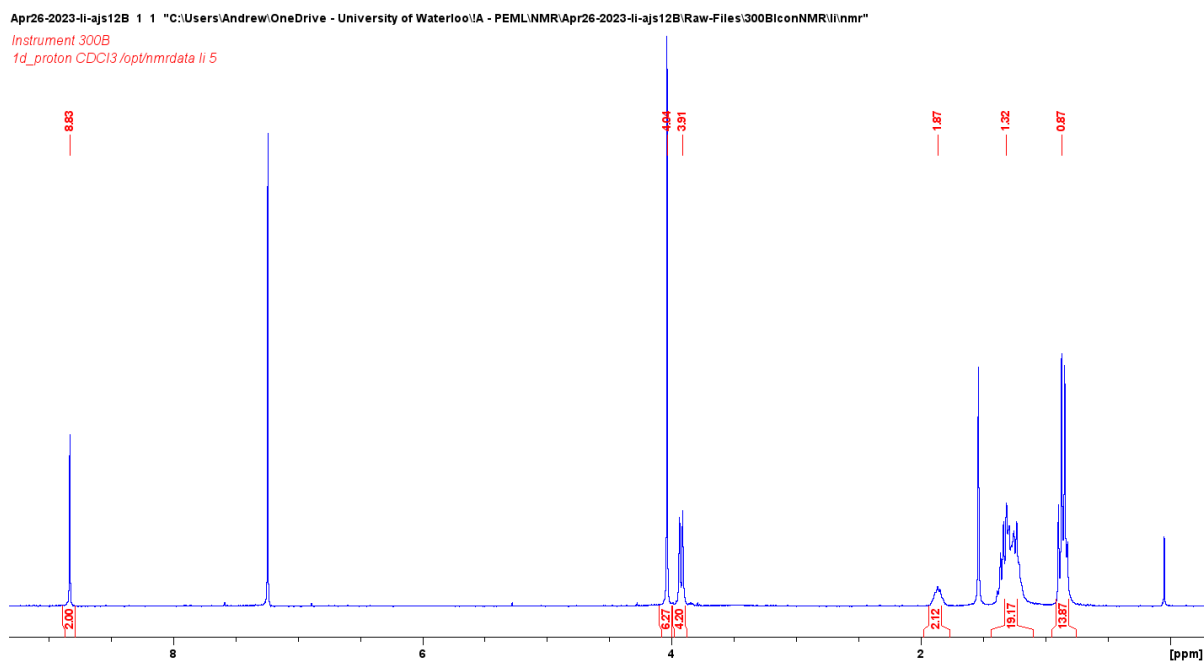
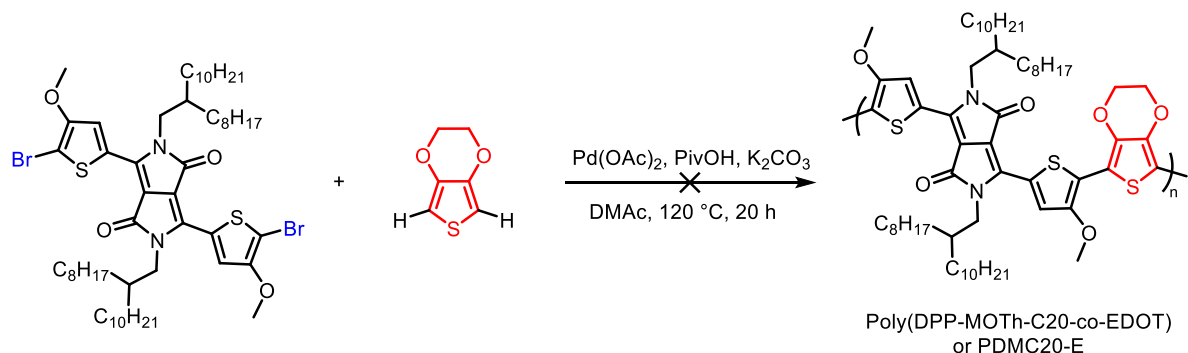


Figure 3-17: ^1H NMR of 3,6-bis(5-bromo-4-methoxythiophen-2-yl)-2,5-bis(2-ethylhexyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione.

3.11.3 Synthetic routes (Polymers)

Poly(DPP-MOTh-C20-co-EDOT) via Direct Arylation Polymerization

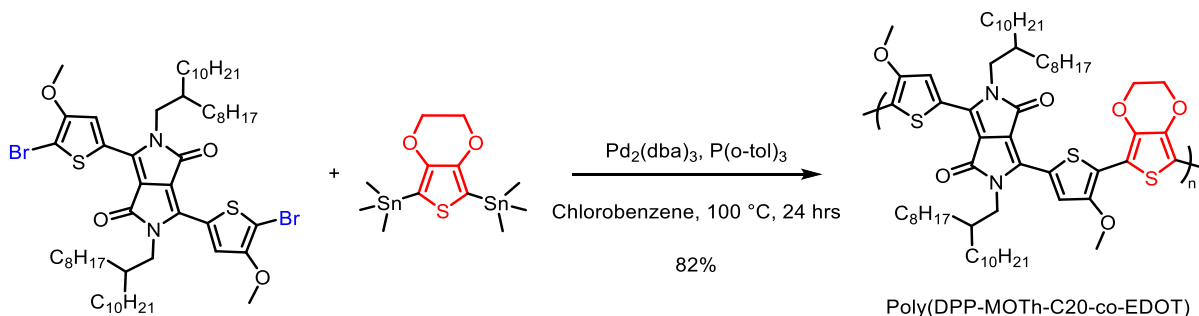
“C20-EDOT (via DArP)”



Scheme 11: Unsuccessful poly(DPP-MOTh-C20-co-EDOT) via Direct Arylation Polymerization.

A stir bar was added to a 25 ml round bottom flask. EDOT(0.0211g, 0.1484 mmol) and the dibromo monomer (0.1590g, .1484 mmol) were added. Pd(OAc)₂ (0.7 mg, eq), pivalic acid (4.7 mg, 0.3 eq), and K₂CO₃(0.0523g, 2.5 eq) were added. The vessel was put under vacuum for 10 minutes. Then, after the flask was refilled with argon, 1.5 ml DMAc was added before being sealed under argon and placed in an oil bath at 120 °C and stirred for 20 hours. While heating, the color changed from violet to very dark purple. The reaction was cooled to room temperature and precipitated into 50 ml methanol. It was allowed to stir for 2 hours. The solid was purified by Soxhlet extraction first with acetone and then with hexane, with most of the material dissolving in the first acetone extraction, leaving about ~10 mg (would represent a ~6% yield) of material in the hexane extract. This material was blue-colored and it is expected to be oligomeric rather than polymeric due to 1) the high solubility in methanol/acetone/hexane, 2) the fact that the reaction solution stayed purple rather than achieving blue or green color, and 3) the low yield of the reaction.

Poly(DPP-MOTh-C20-co-EDOT) via Stille Coupling, “C20-EDOT”



Scheme 12: Poly(DPP-MOTh-C20-co-EDOT) via Stille Coupling.

To a dry 25 ml round bottom flask containing a stir bar, the following were added: DPPC20-Br (0.1 g, 0.091 mmol), 5,7-bis(trimethylstannyl)-2,3-dihydrothieno[3,4-b][1,4]dioxine (0.0433 g, 0.091 mmol), P(o-tol)₃ (0.0049 g, 0.016 mmol), Pd₂(dba)₃ (7.3 mg, 0.008 mmol), and anhydrous chlorobenzene (4 mL). The reaction was stirred as it was heated to 100 °C. Stirring was continued for 24 hours, at which point 0.25 ml bromobenzene was added (to end cap any unreacted trimethylstannyl groups). The reaction was further stirred at 100 °C for 1 hour before it was allowed to cool to room temperature. The reaction was quenched by pouring it into 100 mL of stirring methanol. The solid was filtered off, washed with methanol, and then dried. The solid was subject to Soxhlet extraction using: acetone and hexane. The hexane fraction contained the polymer product. Hexane was removed from the product through rotary evaporation and it was further fully dried under vacuum. The product was found to be a shiny dark blue film. (Yield: 79 mg, 82%).

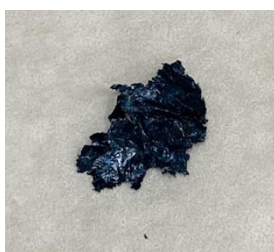


Figure 3-18: Visual appearance of Poly(DPP-MOTh-C20-co-EDOT) via Stille Coupling.

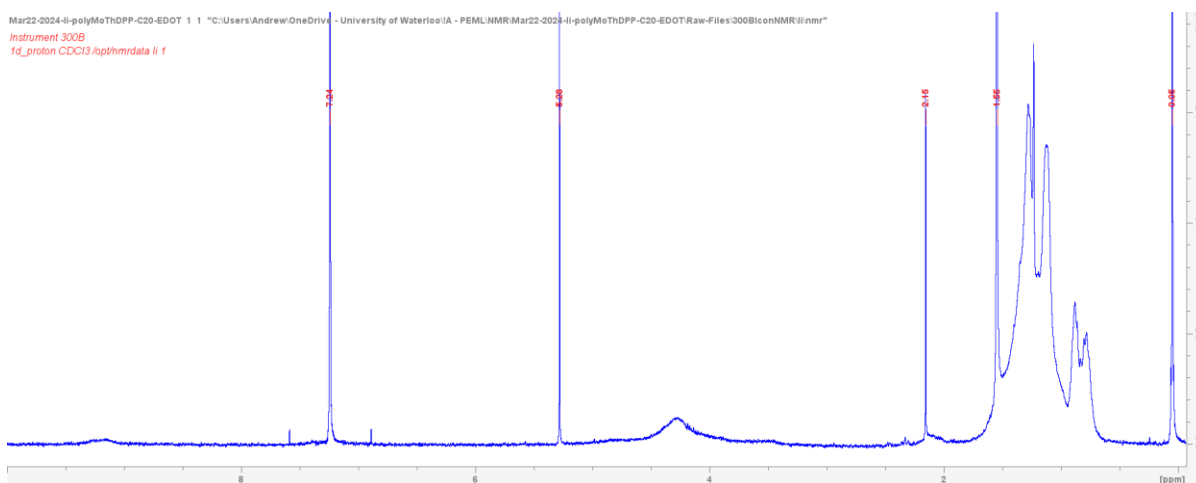
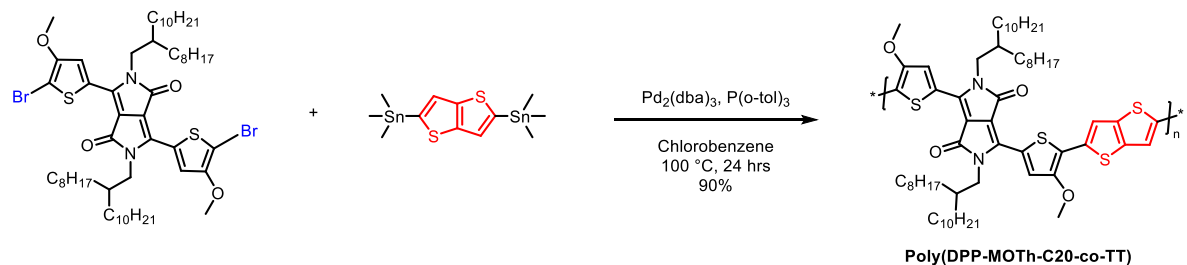


Figure 3-19: ^1H NMR of Poly(DPP-MOTh-C20-co-EDOT). Polymer shows broad peaks 0.5-2 ppm as typical for DPP copolymers.⁵³ The sharp peaks can be attributed to trace contaminants, e.g. chloroform = 7.24 ppm, dichloromethane = 5.28 ppm, acetone = 2.15 ppm, water = 1.56 ppm.

Poly(DPP-MOTh-C20-co-TT) via Stille Coupling, “C20-TT”



Scheme 13: Poly(DPP-MOTh-C20-co-TT) via Stille Coupling.

To a dry 25 ml round bottom flask containing a stir bar, the following were added: DPPC20-Br (0.1 g, 0.091 mmol), 2,5-bis(trimethylstannyl)thieno[3,2-b]thiophene (0.0425 g, 0.091 mmol), P(o-tol)₃ (5 mg, 0.016 mmol), Pd₂(dba)₃ (7.3 mg, 0.008 mmol), and anhydrous chlorobenzene (4 mL). The reaction was stirred as it was heated to 100 °C. Stirring was continued for 24 hours, at which point 0.25 ml bromobenzene was added (to end cap any unreacted trimethylstannyl groups). The reaction was further stirred at 100 °C for 1 hour before it was allowed to cool to room temperature. The reaction was quenched by pouring it into 100 mL of stirring methanol. The solid was filtered off, washed with methanol, and then dried. The solid was subject to Soxhlet extraction using: acetone, hexane, and finally chloroform. The chloroform fraction contained the polymer product. Chloroform was removed from the product through rotary evaporation and it was further fully dried under vacuum. The product was found to be a shiny reddish-brown film. (Yield: 87mg, 90%).



Figure 3-20: Visual appearance of Poly(DPP-MOTh-C20-co-TT) via Stille Coupling.

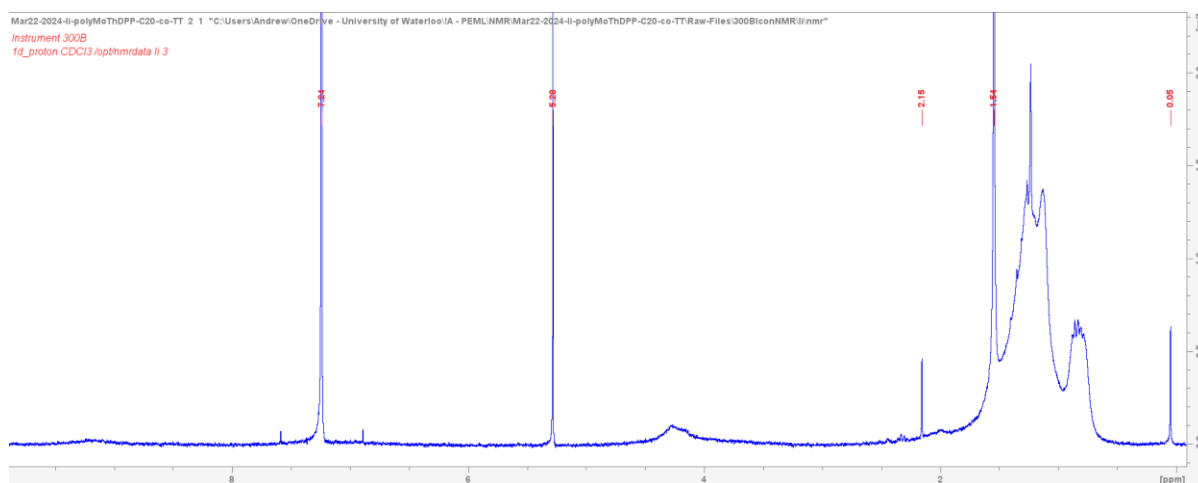
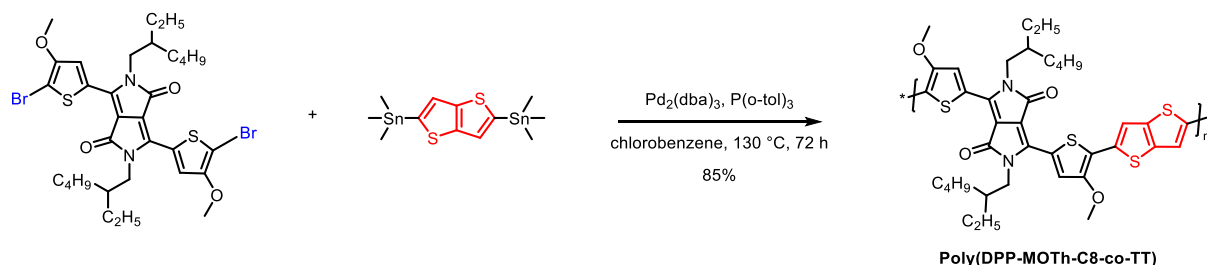


Figure 3-21: ^1H NMR of Poly(DPP-MOTh-C20-co-TT). Polymer shows broad peaks 0.5-2 ppm as typical for DPP copolymers.⁵³ The sharp peaks can be attributed to trace contaminants, e.g. chloroform = 7.24 ppm, dichloromethane = 5.28 ppm, acetone = 2.15 ppm, water = 1.54 ppm.

Poly(DPP-MOTh-C8-co-TT) via Stille Coupling, “C8-TT”



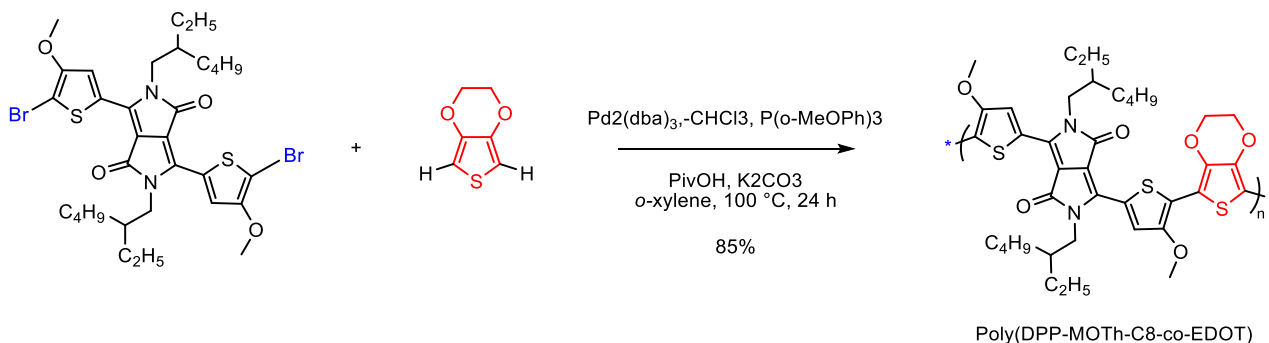
Scheme 14: Poly(DPP-MOTh-C8-co-TT) via Stille Coupling.

A stir bar was added to a dry 25 ml round-bottom flask. The flask was placed under argon and vacuum pumped and purged with argon. Inside a nitrogen glovebox, DPP-MOTh-C8-Br (0.742g, 0.1 mmol, 1eq), bis(trimethylstannyl)-thienothiophene (0.0469g, 0.1 mmol, 1 eq), and tris(dibenzylideneacetone)dipalladium(0) (3.9 mg, 4 μmol , 0.04 eq), and tri(o-tolyl)phosphine (2.4 mg, 8 μmol , 0.08 eq) were added to the flask. The flask was then pump-purged twice with Argon gas. Anhydrous chlorobenzene (10 ml) was added stirring used to dissolve the solids. The reaction was placed into a preheated oil bath and left stirring for 3 days at $130\text{ }^\circ\text{C}$. A color change of pink/red to blue within 15 minutes was observed and the color remained a dark blue over the course of the reaction. To purify the product, the reaction was cooled to room temperature and then precipitated into a mixture of (8 ml concentrated HCl + 100 ml MeOH) and left to stir overnight. The precipitated product was collected via filtration before subjecting it to Soxhlet extraction. Soxhlet extraction was carried out using refluxing acetone, hexane, DCM, and then chloroform. None of the extraction solvents showed any color other than very light purple (acetone) or very light blue (DCM, chloroform). Crude product was insoluble in room temperature methanol, DCM, and 1,2-chlorobenzene. Product was found to be a dark reddish-brown chunky solid. (Yield: 61 mg, 85%).



Figure 3-22: Visual appearance of Poly(DPP-MOTh-C8-co-TT) via Stille Coupling.

Poly(DPP-MOTh-C8-co-EDOT) via Direct Arylation Polymerization, “C8-EDOT”



Scheme 15: Poly(DPP-MOTh-C8-co-EDOT) via Direct Arylation Polymerization.

A stir bar was added to a 5 ml single-necked round bottom flask. To the flask were added EDOT (0.016 g, 0.113 mmol, 1.0 eq), DPP-MOTh-C8-Br (0.083 g, 0.112 mmol, 1.0 eq), $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (6 mg, 6 μmol , 0.05 eq), $\text{P}(\text{o-MeOPh})_3$ (4.4 mg, 12 μmol , 0.1 eq), K_2CO_3 (48 mg, 0.35 mmol, 3 eq), and PivOH (5.7 mg, 0.06 mmol, 0.5 eq). The flask was purge-pumped two times with Argon gas. Anhydrous *o*-xylene (0.6 ml) was added and the flask was stirred 5 min to dissolve. The flask was placed into a preheated oil bath and stirred 24 hrs at 100°C . The reaction was observed to change color from pink/violet initially to a blue/green suspended solid which was formed overnight. The reaction was then cooled to room temperature, precipitated into cold methanol, and precipitate was collected via filtration. Soxhlet extraction was then carried out using methanol, then hexane, then chloroform. The chloroform fraction was rotovapped until dry and transferred using methanol into a vial, which was then allowed to air dry. The product was found to be very dark powder/particles, and shiny with slight purple color when viewed under bright light. (Yield: 69 mg, 85%)



Figure 3-23: Visual appearance of Poly(DPP-MOTh-C8-co-EDOT) via Direct Arylation Polymerization.

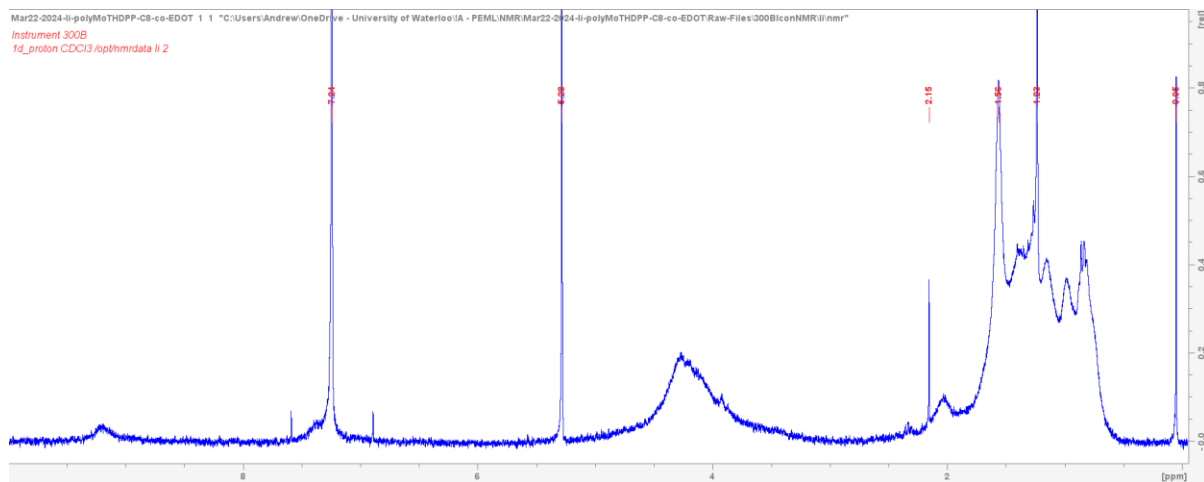


Figure 3-24: ^1H NMR of MOTHdPP-C8-co-EDOT. Polymer shows broad peaks 0.5-2 ppm as typical for DPP copolymers.⁵³ The sharp peaks can be attributed to trace contaminants, e.g. chloroform = 7.24 ppm, dichloromethane = 5.28 ppm, acetone = 2.15 ppm, water = 1.56 ppm.

Chapter 4: Conclusions

The overall motivation of this thesis was to enable flexible, robust gas sensors for firefighters.

Conjugated polymer gas sensors could be woven directly into firefighter clothing and have many advantages such as being lightweight, drawing little power, and being tunable to different analyte gas targets. Conjugated polymers were thus investigated as they have a huge potential. However, stability holds them back and this was the issue addressed by the thesis.

In Chapter 2, a baseline was established and it was found that for three previously reported DPP copolymers, the sensors could only achieve ~10 days of in-air stability at most. Issues with coating quality and moisture sensitivity were discussed as well. This prompted the development of entirely new DPP copolymers to have higher HOMO levels in the following chapter.

In Chapter 3, methoxythiophene-flanked-DPP copolymer structures were computationally designed to have higher HOMO levels which was anticipated to help with the dopant-polymer stability issue established in Chapter 2. The syntheses of five copolymer targets were then attempted. One was insoluble, another may not have had the proper reaction conditions, and ultimately three novel copolymers which were soluble in chloroform were successfully synthesized: C8-EDOT, C20-EDOT, and C20-TT. Proving the hypothesis of the design and in agreement with computational results, these three indeed had higher HOMO levels. This is expected to lead to more stable doping using the common p-type dopants employed in Chapter 2, and indeed it was discovered that even the trace HCl in chloroform was enough to partially dope C8-EDOT. This unintended doping was measured to be relatively stable over at least 1 month.

Promising future paths of work include optimizing the addition of HCl to increase the conductivity of C8-EDOT. By using methanol as a co-solvent/diluent, a target ratio of dopant:polymer could be achieved. With their high HOMO levels, the methoxythiophene-flanked DPP copolymers are highly likely to be sensitive to oxidizing gases. After HCl, doping the three novel copolymers with standard dopants such as FeCl₃, F4TCNQ, and others, would also help establish the promise of these materials for stable doping. Furthermore, the -EDOT copolymers have the third lowest bandgap of any DPP copolymers reported. This may have applications in OPV as well as in detecting NIR light. Finally, methoxythiophene-flanked DPP monomer yield could be improved by e.g. reducing the formation of the unwanted 3-methoxythiophene-2-carbaldehyde isomer in the first step from 3-methoxythiophene and/or improving alkylation yield.

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Appendices

Appendix A: Detail on Moisture-sensitive behavior of FeCl₃-doped DPP copolymers

Even though the response and recovery times when exposed to high and low RH are quite long, roughly ~30 minutes, these films were coated quite thickly (specifically, 13.9 microns for the device shown in Figure 0-1) and made through drop casting in order to provide screening data and sufficient current for the 4-point probe measurement of conductivity. The signal could be magnified through larger sensor area, the use of interdigitated electrodes, larger voltage, etc. while the thickness of the film decreased in order to facilitate faster diffusion of water molecules in and out.

Hypothesis: water molecules from moisture in the air diffuse in very quickly due to their small size, within ~30 min it has fully saturated into 10 micron film and could interact with FeCl₃ to increase the doping effect. The water-FeCl₃ complex (or products) dopes the polymer but also may slowly evaporate or degrade, explaining why a stable plateau of conductivity is not reached. FeCl₃ even more slowly leaves through irreversible phase segregation from the polymer (days-weeks). Note that this process may not necessarily involve HCl but likely some product of a water-FeCl₃ interaction.

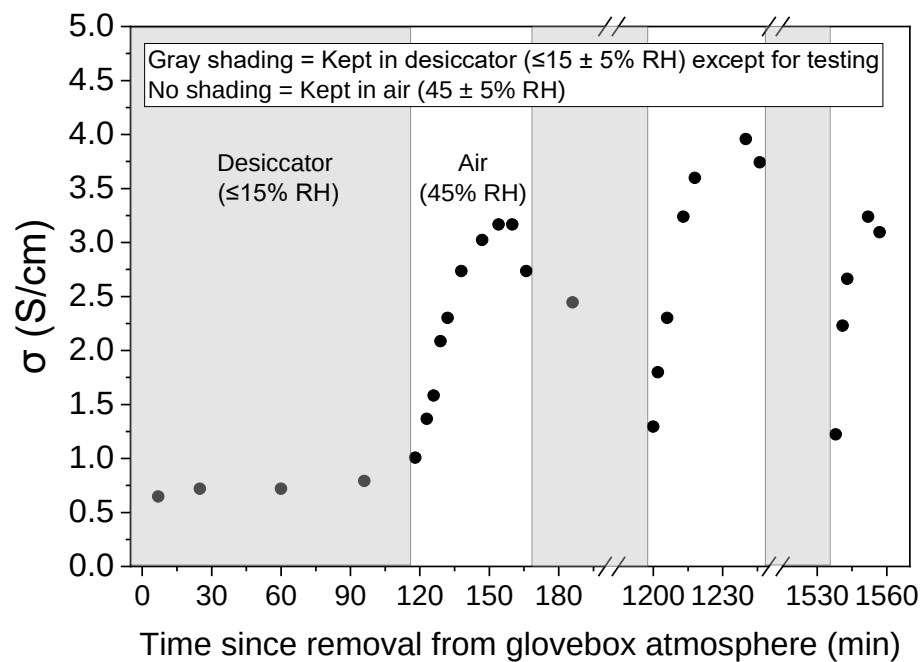


Figure 0-1: Moisture sensing behavior for DPP-BT 10 mol% FeCl_3 is reversible across three cycles of removal from desiccator and 24 hours. Doped polymer film was measured to be $13.9 \mu\text{m}$ thick.

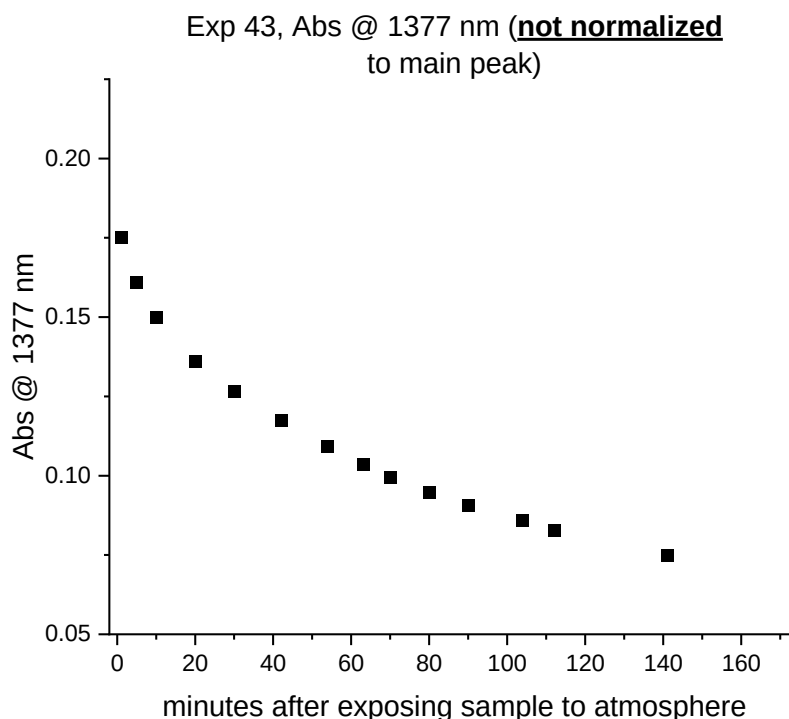


Figure 0-2: For the film of DPP-TT blend doped with 10 mol% FeCl_3 with UV-Vis spectra shown in Figure 2-5b, here is plotted the absorbance value at a peak wavelength (1377 nm) within the (bi)polaron signal region. The plot shows an exponential decay which could suggest a diffusion process e.g. HCl diffusing away.

In very thin films, e.g. the ~100 nm UV-Vis films (vs. ~10,000 nm films for conductivity, the water makes all the HCl essentially instantly, which fully dopes the polymer, and so it shows maximum (bi)polaron signal in the first measurement and as the HCl evaporates the (bi)polaron signal decreases.

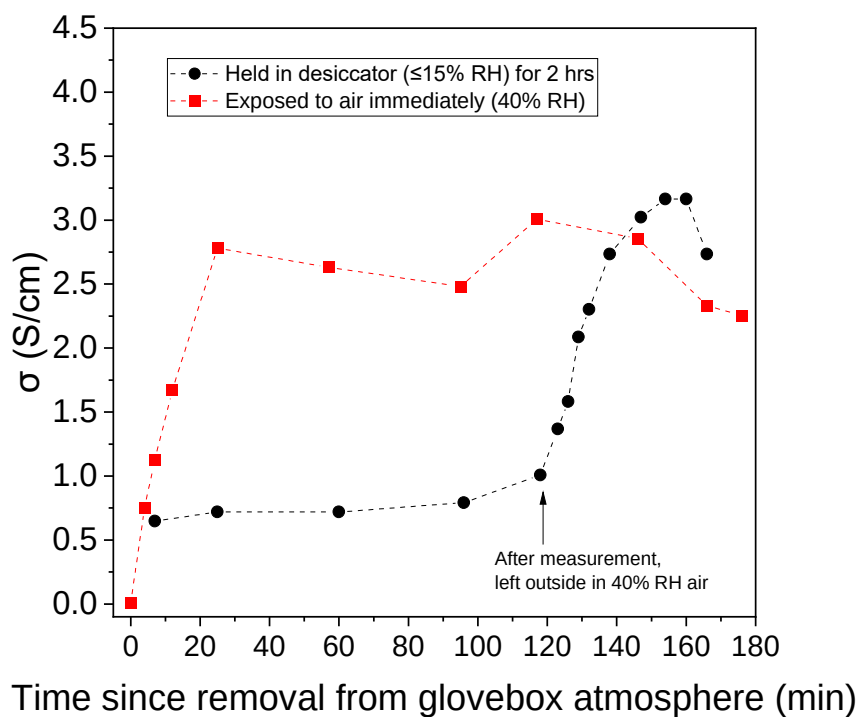


Figure 0-3: Two replicate films of DPP-BT doped with 10 mol% FeCl_3 but exposed to different %RH treatment. The red square sample was doped in a 0% RH nitrogen glovebox and transferred to lab air (40% RH) for conductivity measurement where it was kept while testing over 3 hours. The black circle sample was likewise doped in the same 0% RH glovebox and then transferred directly to a desiccator ($\leq 15\%$ RH) where it was stored except for ~ 30 s lab air exposures during measurement. After 2 hours, the sample designated by black circles was left outside of the desiccator, in air for the remainder of the measurements.

Appendix B: Additional Syntheses

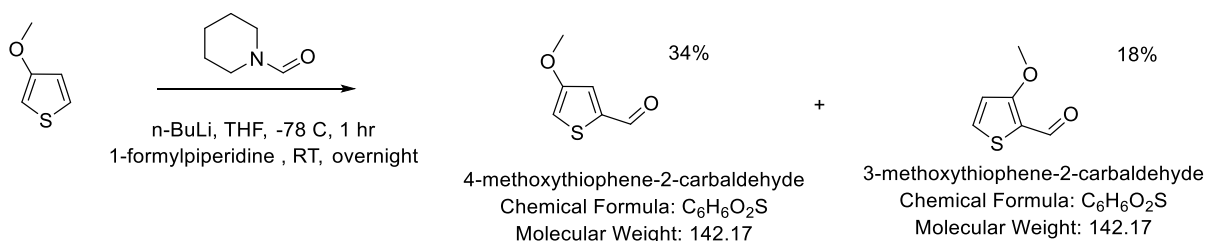
This Appendix is concerned with the syntheses which were carried out in order to either improve yield, attempt the use of new reagents or different routes to previously reported targets.

Scheme 16: This reaction was proposed because of dissatisfactory results with the selectivity of the first step of the synthetic route toward methoxythiophene-flanked DPP, the production of 4-methoxythiophene-2-carbaldehyde. The total yield of methoxythiophene-carbaldehyde is 83%, however that yield is made up of 34% desired 4-methoxythiophene-2-carbaldehyde isomer and 49% undesired 3-methoxythiophene-2-carbaldehyde isomer. For a reported synthesis starting with 3-methylthiophene (rather than 3-methoxythiophene) there is a high yield, high selectivity (97%) synthetic procedure which uses a more sterically hindered base t-butyllithium rather than our n-butyllithium.⁵⁴ As t-BuLi has a reputation for danger due to extreme flammability, it was attempted to keep the n-BuLi and use instead a sterically hindered aldehyde in place of DMF, inspired by a lower yield but still selective (52%) reported synthesis which again used the 3-methylthiophene as a starting material.⁵⁵ The hypothesis was that using the sterically hindered aldehyde 1-formylpiperidine would result in the desired 2,4 isomer being the majority product. This was found to be the case, although unfortunately it was accomplished solely through reducing the amount of the 3,4 isomer from ~50% to ~20%. The desired product, 4-methoxythiophene-2-carbaldehyde, is present in the NMR. However, there is another aldehyde peak at 9.45 ppm which integrates to 0.27 H so a substantial impurity. In the synthesis method using DMF, the product is easily purified and also the similar overall yield of the 2,4 isomer in this synthesis method vs. the DMF method led us to abandon this step in our route.

Scheme 17, Scheme 18, Scheme 19: Initially a route to methoxythiophene-flanked-DPP polymers was attempted according to the route published by Domokos et al. The first two steps: attaching two bromine atoms and then removing one were carried out according to the Domokos procedure. In the third step, cyanation, the procedure was followed with the exception of attempting the use of Copper (I) cyanide as a reagent instead of Zinc cyanide. Copper (I) cyanide has been shown to have lower toxicity⁵⁶ and is also lower cost as of this writing. Our goal was to see if it would function similarly and thus improve the safety and cost of the reaction. The reaction did result in pure product, unfortunately the yield was below 5% and so this route was abandoned.

Scheme 20, Scheme 21: As it was seen that Domokos had higher yield (29%) in the alkylation step using iodo-alkanes than our results using bromo-alkanes (~20%), 2-ethylhexyl bromide was converted to 2-ethylhexyl iodide using a facile and high yield (expected: 88%; actual: 70%) reaction involving sodium iodide.⁵⁷ The iodo- product was then used to alkylate methoxythiophene-flanked DPP in analogous fashion to Domokos et. al.¹⁵ As expected, a yield of 27% was seen, which provided 4% additional yield over using the bromo-alkane (23%). Using the iodo-alkane over the bromo-alkane was not so much better yield as to be a necessary step. As another explanation for the low yield, possibly the alkane is just degrading in the presence of the base so it would need to be added over longer periods of time. For example, dropwise add 2 eq of the bromo-alkane at the beginning of the reaction, let it run overnight, then add another 2 eq at the beginning of the second day. Then 1 eq at end of second day and run it overnight (for 5 eq of bromo-alkane total).

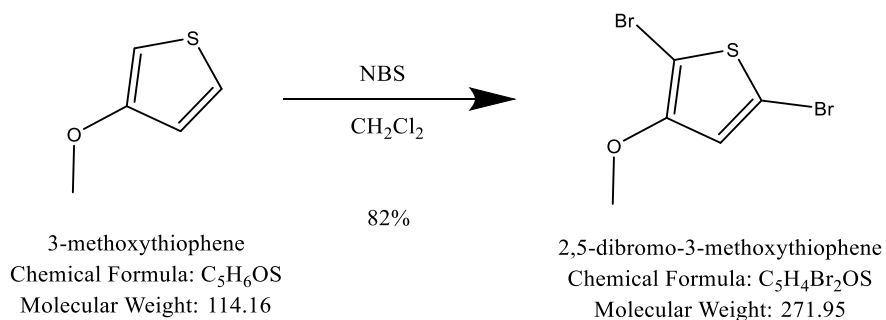
4-methoxythiophene-2-carbaldehyde (alternate route)



Scheme 16: 4-methoxythiophene-2-carbaldehyde (alternate route)

Except for the use of 1-formylpiperidine in place of DMF, the procedure was carried out following Scheme 4: 4-methoxythiophene-2-carbaldehyde. The scale was 6.86 g (6 ml, 60 mmol) of the starting material 3-methoxythiophene. The product was found to be a yellow-green-brown olive oil colored liquid which eventually solidified at -20 °C. It was found to be impure by NMR, showing another aldehyde peak at 9.45 ppm which integrated to 0.27H. (Yield 2.9g, 34%). ¹H NMR: 9.80 (d, 1H); 7.38 (d, 1H); 6.73 (t, 1H); 3.83 (s, 3H).

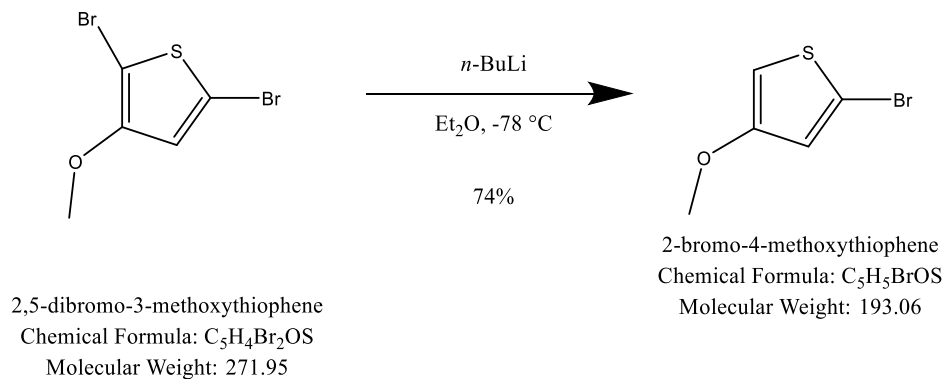
2,5-dibromo-3-methoxythiophene



Scheme 17: 2,5-dibromo-3-methoxythiophene

Domokos et al. (2019) procedure was followed.¹⁵ Scale: 2.0 g starting material. Yield: 3.88 g, 82%. ¹H NMR matched reference.

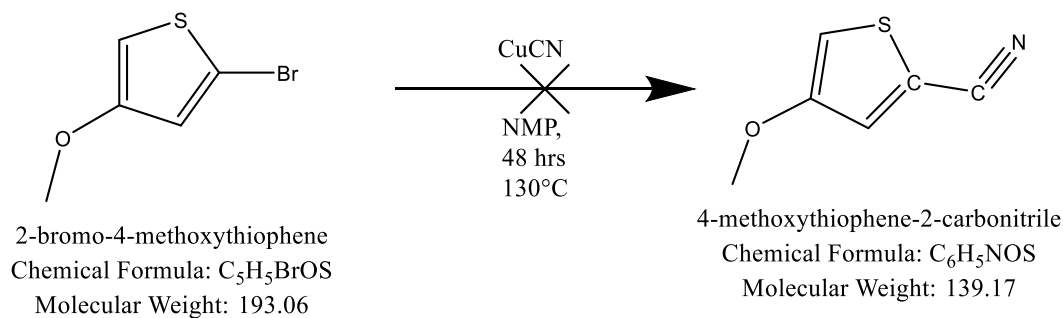
2-bromo-4-methoxythiophene



Scheme 18: 2-bromo-4-methoxythiophene

Domokos et al. (2019) procedure was followed.¹⁵ Scale: 3.86 g starting material. Yield: 2.03g, 74%.

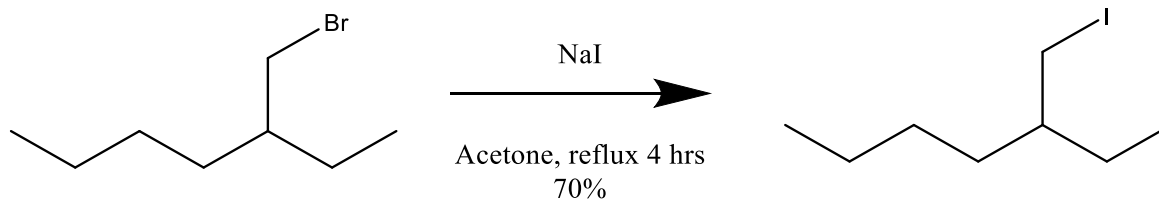
4-methoxythiophene-2-carbonitrile (failed step in Domokos route)



Scheme 19: 4-methoxythiophene-2-carbonitrile (failed step in Domokos route)

Domokos procedure¹⁵ was followed with the exception of $Zn(CN)_2$ being replaced by $CuCN$. Domokos had reported $Cu(II)$ cyanide resulted in no yield but they had not reported attempting the $Cu(I)$ cyanide. The reaction did not yield product.

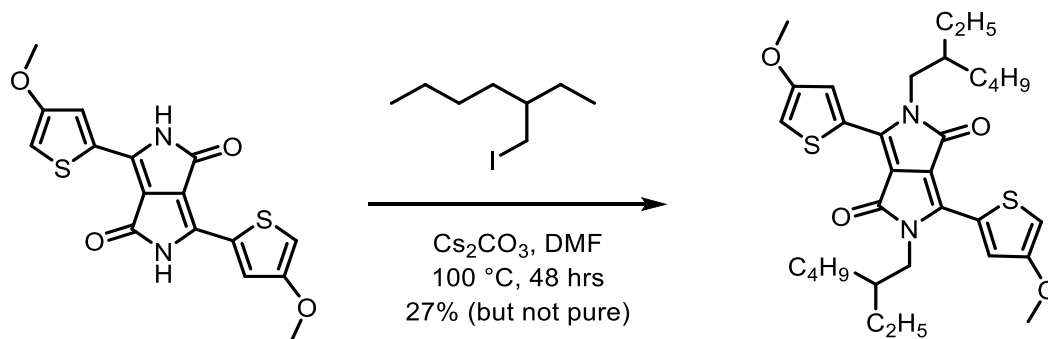
2-ethylhexyl iodide



Scheme 20: 2-ethylhexyl iodide

Followed reference He et al. (2013).⁵⁷ Scale: 3 g starting material. Yield: 2.6g, 70%. Product found to be a pinkish clear oil and matched reference NMR. ^1H NMR: 3.25 (m, 2H), 1.28 (m, 9H), 1.05 (m 1H), 0.85 (m, 6H).

2,5-bis(2-ethylhexyl)-3,6-bis(4-methoxythiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione



Scheme 21: 2,5-bis(2-ethylhexyl)-3,6-bis(4-methoxythiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione

Domokos et al. (2019) procedure followed.¹⁵ Scale: 0.80g starting material. Yield: 0.35g, 27% but impure.

Appendix C: GPC Data for methoxythiophene-flanked DPP copolymers

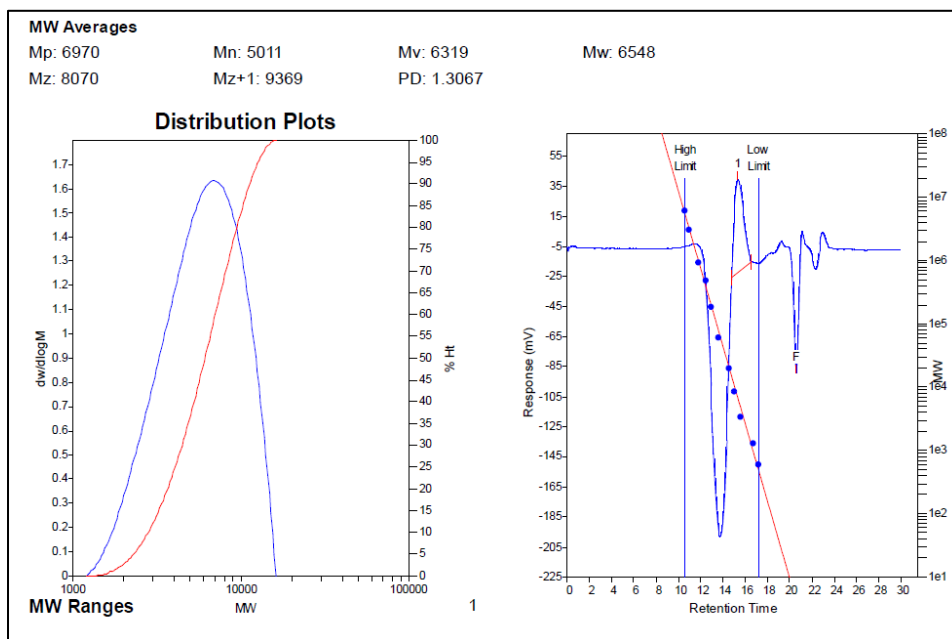


Figure 0-4: GPC of methoxythiophene-flanked DPP copolymer C20-co-TT.

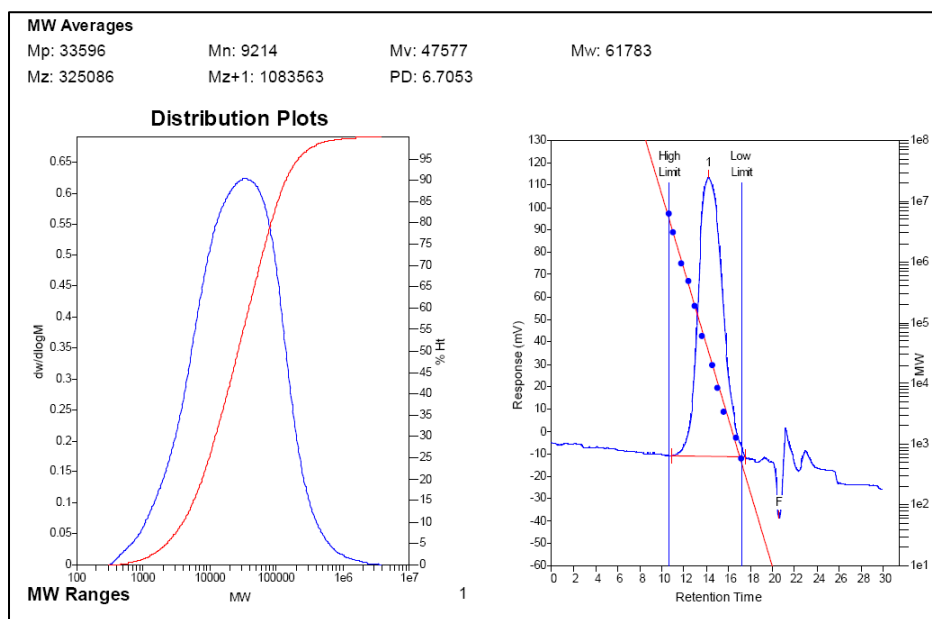


Figure 0-5: Second GPC run of methoxythiophene-flanked DPP copolymer C20-co-TT.

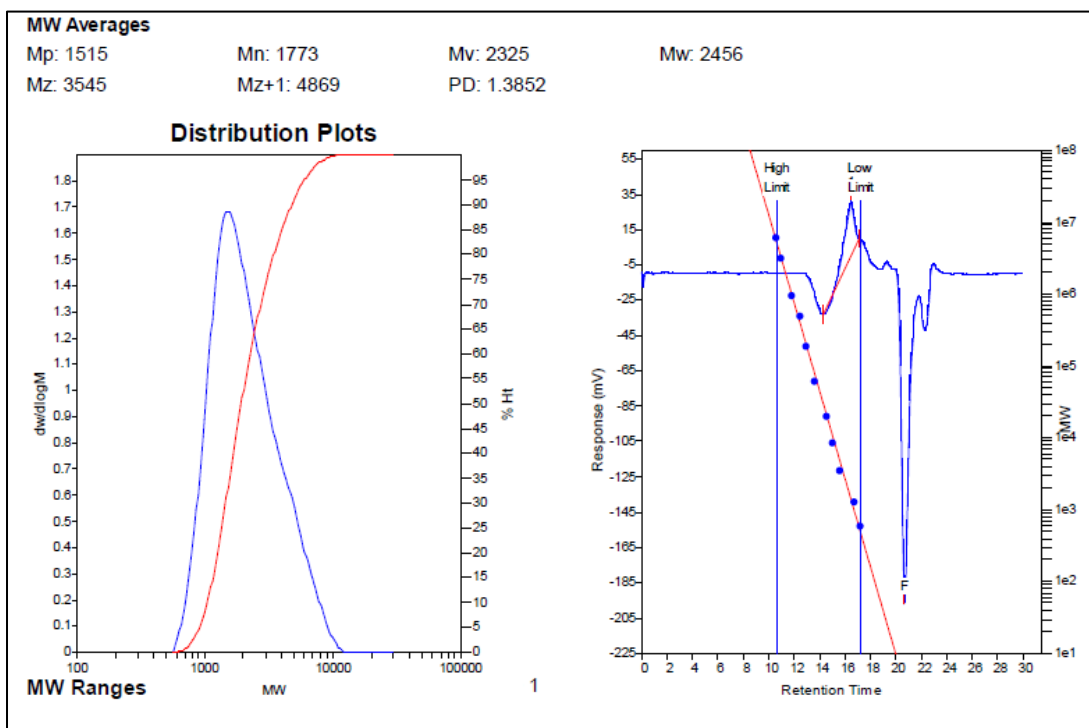


Figure 0-6: GPC of methoxythiophene-flanked DPP copolymer C8-co-EDOT.

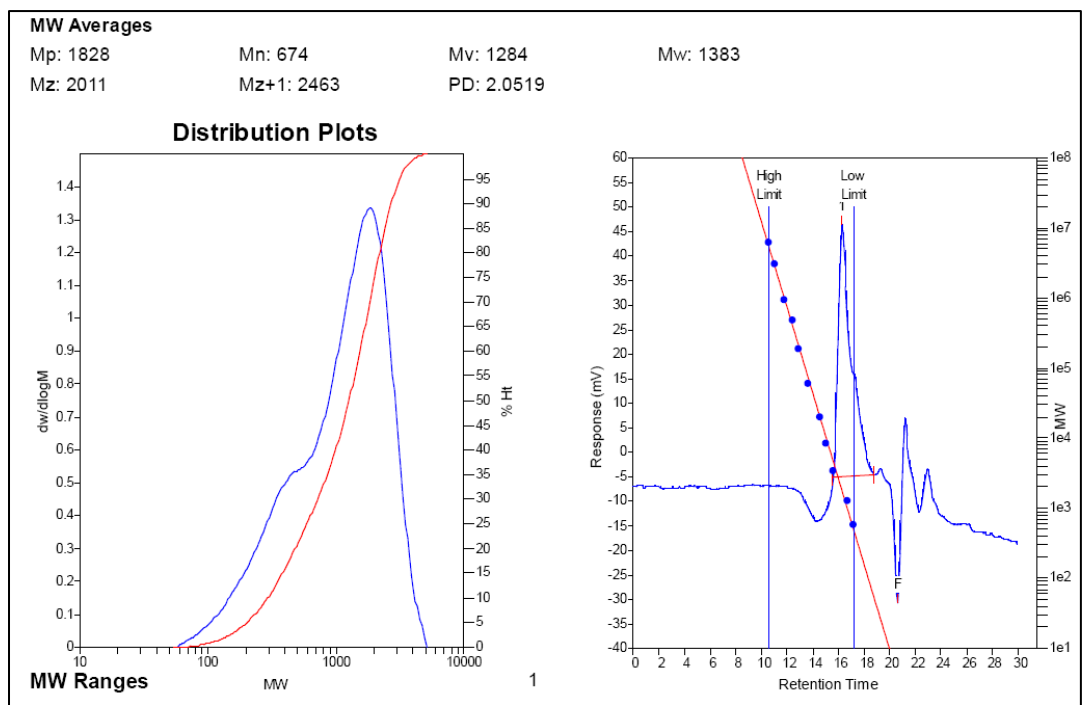


Figure 0-7: Second GPC run of methoxythiophene-flanked DPP copolymer C8-co-EDOT.

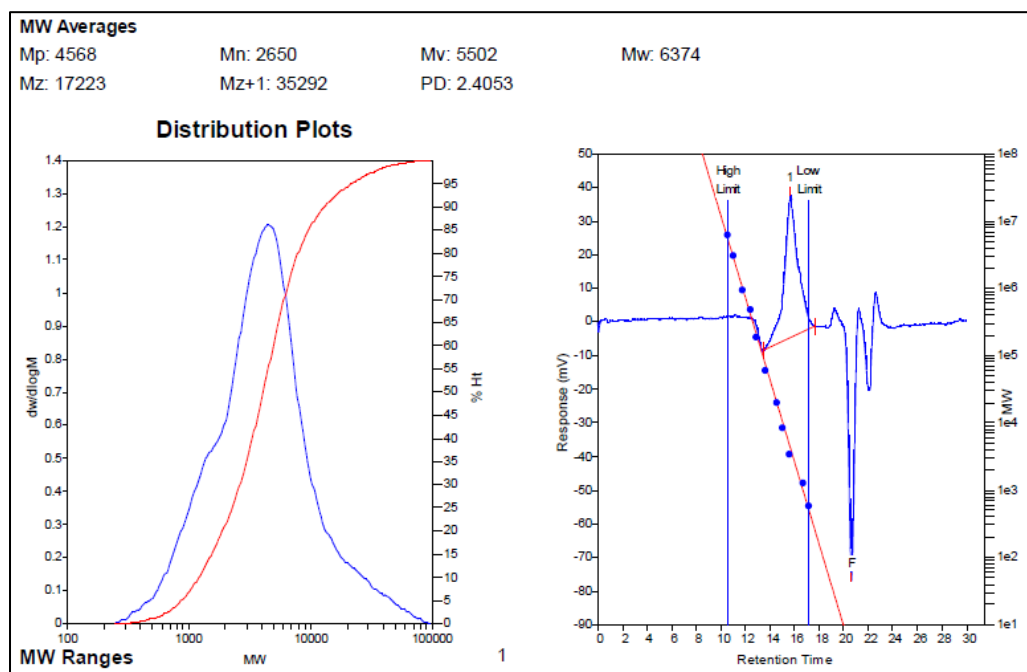


Figure 0-8: GPC of methoxythiophene-flanked DPP copolymer C20-co-EDOT.

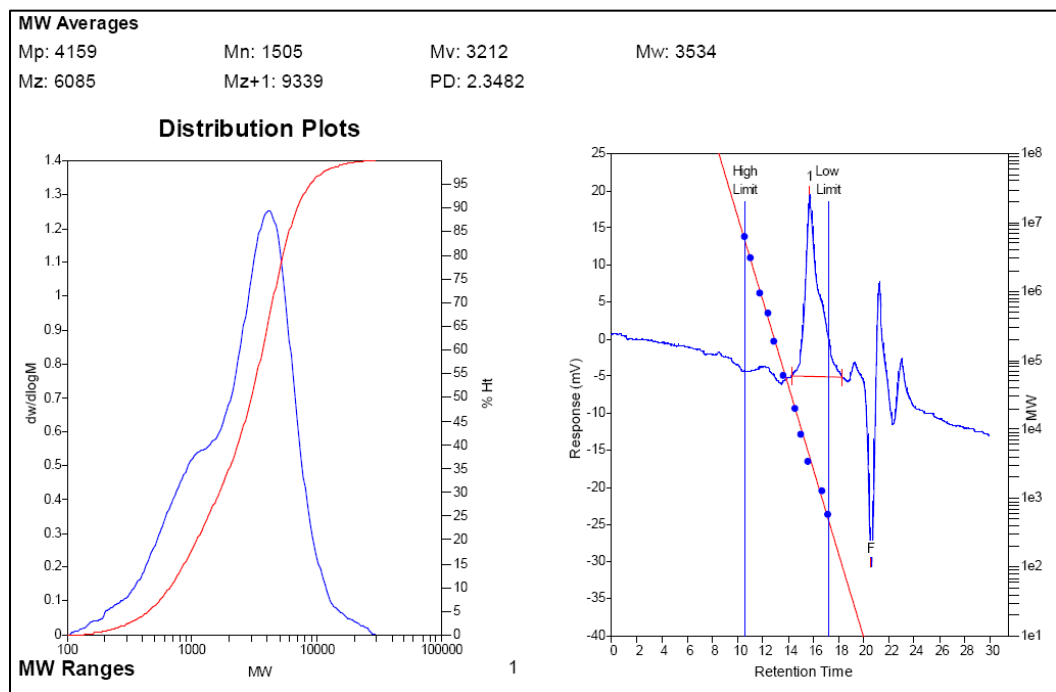


Figure 0-9: Second GPC run of methoxythiophene-flanked DPP copolymer C20-co-EDOT.

Appendix D: Additional UV-Vis for C8-EDOT

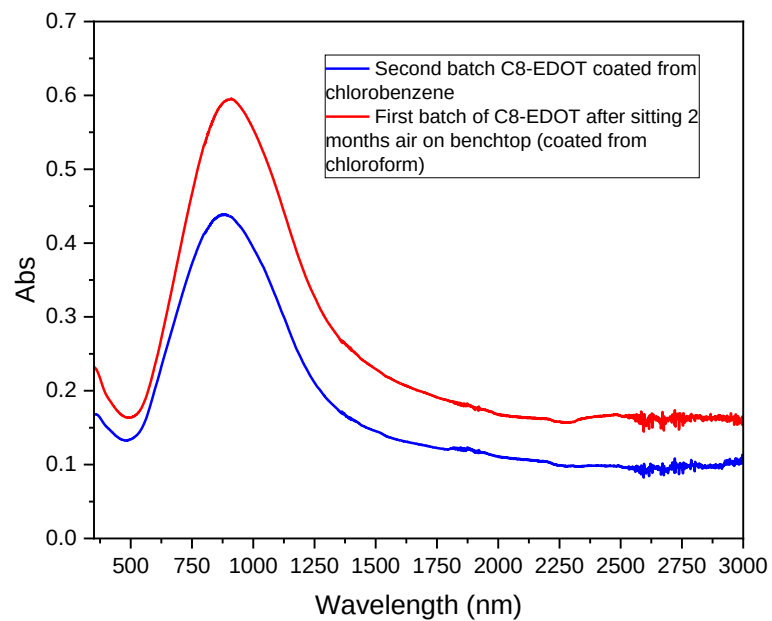


Figure 0-10: Two batches of C8-EDOT compared.