Synthesis and Characterization of Donor-Acceptor Oligothiophenes

A Thesis

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By

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF DONOR-ACCEPTOR OLIGOTHIOPHENES

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The field of organic conductors is multidisciplinary in nature. This thesis introduces and characterizes new conducting materials based on heterosubstituted oligothiophenes. Substituted bithiophenes, terthiophenes, and quarterthiophenes are the primary materials investigated in this thesis.

Variation of the end-groups (often called α,ω- or α,α'-disubstitution) can dramatically influence the solid-state structure, giving highly conducting materials or materials with interesting electronic properties, such as a field effect current.
We have synthesized a series of such oligothiophenes with a variety of functional groups, R-T_n-R' (T = C_4H_2S) with R being either Br, I, NH_2, Hx or COOH, and R' being NO_2 or Hx (C_6H_{13}). These heterosubstituted oligothiophenes contain end-groups that are complimentary electronic donors and acceptors, which will generate push-pull compounds.

Acknowledgments

I would like to thank all the people who were involved in my research and the writing of my thesis and those who helped me by their love and support.

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Last but not least I would like to thank my parents, whom without their love and support none of this could have been possible. I would also like to thank my dad Dr. William Sears for running the conductivity tests on my samples. I also would like to thank Mirek who gave me the love and support I needed to stay sane throughout this long and hectic process.

To my parents

Dr. William Sears and Mrs. Susan Sears

For their love and support during my 7 years of university.

Table of Contents

List of Abbreviations

A	absorbance
AC	alternating current
Bu	n-butyl group
C	capacitance
C_o	air capacitance
°C	degrees Celsius
cm^{-1}	wavenumber
d	doublet (NMR descriptor)
DCM	4-(dicyanomethylene)-2-methyl-6-[*p*-(dimethylamino)styryl]-4H-pyran
DMF	N,N-dimethyformamide
d-DMSO	deuterated dimethylsulphoxide
dppp	1,3-bis(diphenylphosphino)propane
E	energy
e_1	electrode one
e_2	electrode two
ED	electron-donating
EDG	electron-donating group
E_g	energy gap/band gap
EL	electroluminescent
Et	ethyl group
EWG	electron-withdrawing group
EW	electron-withdrawing

FET	field-effect transistor
G	conductance
g	gram
HOAc	acetic acid
HOMO	highest occupied molecular orbital
Hp	heptyl group
hν	light
Hx	hexyl group
Hz	hertz
IR	infrared spectroscopy
J	NMR coupling constant
L	length of cylinder
	inductance
	litre
LDA	lithium diisopropylamide
LED	light-emitting diode
LUMO	lowest unoccupied molecular orbital
M	gram/mole
m/e	mass to charge ratio
mL	millilitre
mmol	millimole
mpt.	melting point
n	negative charge carrier (electron)

NBS	N-bromosuccinimide
NIS	N-iodosuccinimide
NLO	non-linear optics
nm	nanometre (wavelength)
NMR	nuclear magnetic resonance
p	positive charge carrier (hole)
Ph	phenyl group
ppm	parts per million
PPV	poly(*p*-phenylenevinylene)
PV	photovoltaic
R	alkyl group
	resistance
r	atomic radii
r_1	radius of electrode one
r_2	radius of electrode two
s	singlet (NMR descriptor)
	strong (IR peak descriptor)
SHG	second harmonic generation
T	thienyl
THF	tetrahydrofuran
w	weak (IR peak descriptor)
V	voltage
UV-Vis	ultraviolet-visible spectroscopy

χ	susceptibility
ΔB	susceptance
δ	NMR chemical shift
ω	angular frequency
σ	conductivity

Chapter 1

Introduction

The field of organic conductors covers a number of disciplines and the study of these materials is diverse, spanning many different subjects from synthetic chemistry to solid-state physics.

The choice of a material for such conductors is based on many factors such as the electronic properties of the molecules themselves and how they are arranged in the solid-state. Therefore, part of this chapter will look into the devices that require a semiconductor, i.e. field-effect transistors (FET), light-emitting diodes (LED), and non-linear optics (NLO), and how a molecular conductor might be used instead of a traditional inorganic one. The second part of this chapter will discuss different types of intermolecular interactions and how they can be manipulated to optimize solid-state structures.

1.1 Molecular Conductors

All materials can be divided into one of three conductivity categories: metallic, semiconducting, and insulating. In the band picture of conduction, charge carriers are generated when an electron jumps from the valence band to the conduction band. The valence band is the highest fully filled electronic band, whereas the conduction band is the lowest empty or partially filled electronic band. Metallic conductors are generally composed of atomic metals (e.g. copper); their conduction band is partially filled. Insulators have an empty conduction band well above the energy of the valence band (e.g. diamond). Semiconductors (e.g. silicon) have the electrical conductivity somewhere in between metals and insulators, so that thermal activation of charge carriers is possible.

The difference between an insulator and a semiconductor is the size of the band gap; if it is too large, the material is an insulator, if it is smaller the material is a semiconductor. Figure 1 gives an illustration of these band orientations.

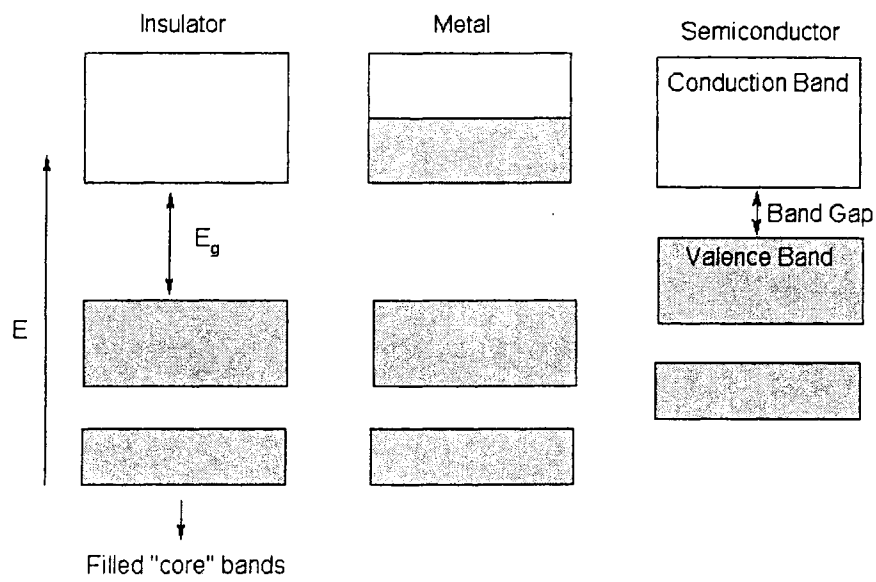
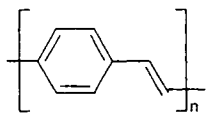


Figure 1: Schematic band diagram of an insulator, a metal, and a semiconductor.[1]

Traditional semiconducting devices are made with elemental silicon. Silicon is a good choice because it is plentiful, environmentally stable, and can be used in virtually any semiconducting device. By comparison, molecular semiconductors are lighter in weight and have higher mechanical flexibility, higher efficiency, and lower processing temperatures.[2] Theoretical limitations on the performance of organic semiconductors, such as lower environmental stability (reaction with atmospheric oxygen), lower operating temperature ranges, prevent these materials from being suitable in applications where silicon excels.[3] However, the properties of organic semiconductors make them

ideal substitutes in many devices where amorphous silicon is currently used, e.g. large area, disposable, or flexible devices. Amorphous and polycrystalline silicon need high temperature production, which prevents their use with lightweight and flexible polymeric substrates. Another potential use for molecular conductors is in the fabrication of single molecule devices, the so-called 'molecular electronics,' which would result in a further reduction of the size of microelectronics. Thus far, polythiophenes and PPV (**1**) have shown the most promise as organic semiconductors due to the high stability of their semiconducting state.[2] Unfortunately, they are often limited by structural and chemical disorder. This makes it difficult to correlate structural characteristics to the electronic properties, or to alter properties systematically.



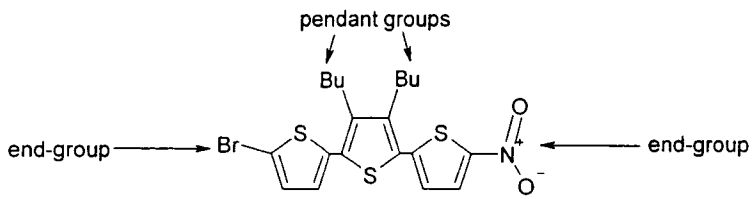
PPV

1

Polythiophene crystal structures are difficult to determine because they are polydisperse. Oligothiophenes are often used as models for polythiophenes, since they have the same basic electronic and optical properties. By modeling polythiophenes it should be possible to elucidate their crystal structure.

It is expected that the oligothiophene equivalents will have a crystal structure similar to the corresponding polymers. Also, it has been shown that oligothiophenes themselves are excellent candidates for electronic materials[4] due to their small band gap and high stability.[2] In fact, certain oligothiophenes, e.g. **2**, show double the field-effect mobility of polythiophenes.[2] It is also possible to fine-tune the electronic properties of

oligothiophene by chemical modifications. End-group substitution can greatly increase the field-effect mobility, whereas substitution of pendant groups often reduces mobility while increasing ease of processability. Unfortunately, oligothiophene devices have short lifetimes due to low melting points (thermal degradation) and have long-term purity issues (self-doping by reaction with ambient oxygen).



2

1.2 Semiconducting Devices

In this electronic age, "smaller and more efficient" are the key emphases for developing new semiconducting materials. For the reasons given in section 1.1 organic semiconductors are ideal for this purpose. Organic semiconductors can be used in a variety of devices, some examples of which are outlined here.

1.2.1 Organic Light-emitting Diodes

An organic light-emitting diode (OLED) is a thin-layer device containing an organic substance that emits light when a current is applied through it. The larger the band gap, the more blue-shifted the light. Therefore the colour of an OLED is strictly related to the band gap,[5] which is usually close in energy to the HOMO-LUMO gap. The goal is to create a compound with electrons that are mobile and energetic enough to span the band-gap. Figure 2 shows a schematic of a simple OLED.

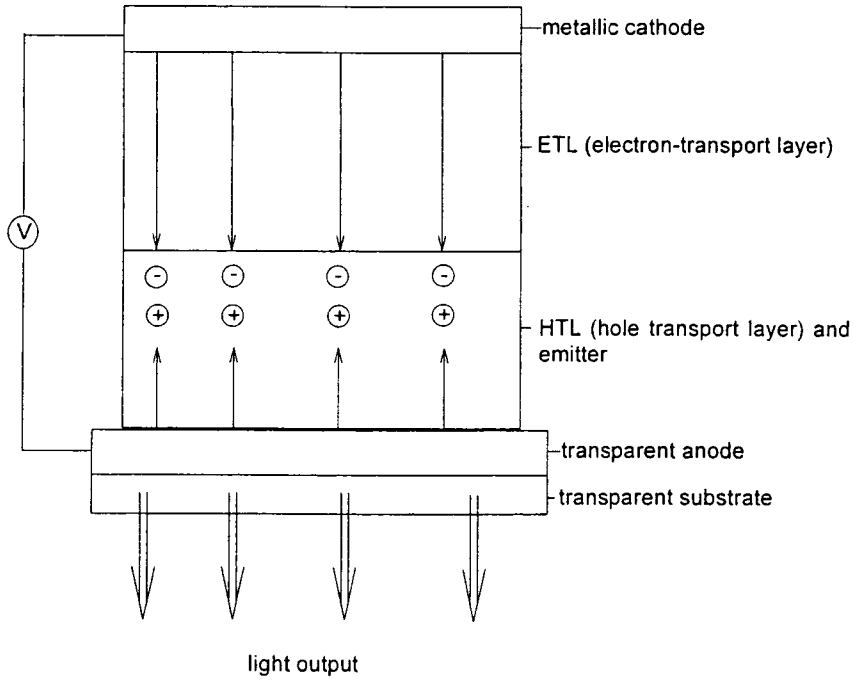
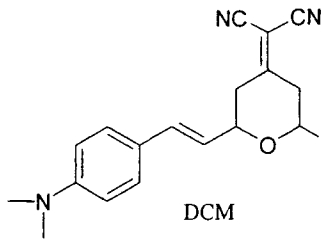


Figure 2: Schematic of an organic light-emitting diode.[6]

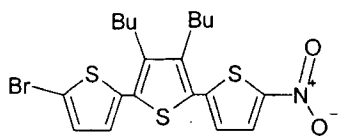
A challenge with building an efficient OLED lies in achieving charge balance within the emissive layer. An imbalance will occur if the anode-HOMO energy gap is different from the cathode-LUMO energy gap.[7] A solution to this problem is to have the electrons and the holes in the same compound, e.g. a "push-pull" compound. Push-pull compounds generally have a conjugated π-system with an EWG on one end and an EDG on the other. One end is then capable of generating holes and the other end is capable of generating electrons. The improved EL performance of push-pull compounds is due to a better balance in the number of injected holes and electrons compared to other compounds (e.g. "pull-pull", "push-push"), as the emitting compound now contains both hole- and electron-transporting groups. Push-pull compounds, e.g. DCM (**3**), have been used as effective emitters in OLED structures for quite some time.[8] A wide range of

functionalized π-conjugated compounds have been synthesized to tune for desirable electronic properties.[9]



3

By choosing the correct end-groups it should be possible to create a compound with either an efficient light-emitting property or a large photovoltaic effect (*vide infra*). Such groups as CN lead to LED properties[9] whereas NO_2-substituted compounds have shown photovoltaic properties.[10] Specifically, nitro-functionalized terthiophenes have shown to be very promising as electroactive molecular materials since: (i) they behave as push-pull systems, (ii) they present a very intense photoinduced charge transfer in the visible region, and (iii) they can act as both *n*- and *p*- channel conductors in organic electronic transistors. Casado[10] *et al.* found that compound **4** acts as a push-pull system with intense photo-induced intramolecular charge transfer from the electron-donor bromine group to the electron-acceptor nitro group.



4

The efficiency of an OLED can be improved by introducing a fluorescent dye, such as a fluorescent oligothiophene.[8] Organic dyes can be used to dope OLED's in order to improve the intensity or purity of the colour. This is done by adding a low

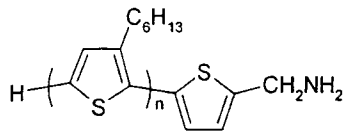
concentration of dye, which will produce colour by an energy transfer from the electroluminescent host to the guest dye. When this occurs, only emission from the dye is seen. The impetus for using dyes is to solve the difficulty in producing colours, such as blue, that have a large band-gap. The dye can help the electron to span the gap. In this way, dyes improve the equality of colour.

One of the major concerns with producing a full-colour display OLED is with the equal performance of the three colours, red, green, and blue.[11] The two ways to produce full-colour display are: (i) to use three chromophores, each producing one primary colour; or (ii) to use one chromophore, which emits light over the entire visible spectrum (with filters to change the colour transmitted).[6] Unfortunately, no known white light emitter covers the whole spectrum equally, so a combination of at least two emitters is required. Monochromatic OLED's are available commercially, but full-colour displays depend on finding a cheap, safe, and available series of EL material that emit the three primary colours.

1.2.2 Photovoltaic Cells (Solar Cells)

Solar cells convert solar energy (photons) into electricity. They require semiconductors that are photovoltaic. When sunlight is absorbed by these materials, the solar energy excites electrons allowing them to flow through the material to produce electricity. This process of converting light (photons) to electricity (voltage) is the photovoltaic (PV) effect. Thin film solar cells use layers of semiconductor materials only a few micrometers thick. Thin film technology has made solar cells flexible and thin enough to be used as roof shingles. In solar cells using molecular conductors, the active layer is a solution-processed mixture of an electron-donor phase (π-conjugated polymer)

and an electron-acceptor phase. Liu[12] *et al.* have shown that the use of an amine as an end group on oligothiophenes (**5**) could produce more efficient and more flexible photocells.



5

1.2.3 Field-effect Transistors

Field-effect transistors (FET's) are so named because a weak electrical signal from one electrode (the gate) creates an electrical field perpendicular to it through the rest of the transistor. This induced field flips from positive to negative with a corresponding flip in the gate voltage. A current perpendicular to the gate voltage, flowing from a source to a drain electrode, will be modulated by the gate voltage.

The simplest and most common organic FET device is a thin-film transistor, in which a thin film of an organic semiconductor is deposited on top of a dielectric with an underlying gate electrode. The contacts for the charge-injecting source-drain electrodes are either on top of the organic film (top-configuration) or on the substrate surface of the FET prior to deposition of the semiconductor film (bottom configuration). Figure 3 shows a schematic of these FET configurations.[13] Historically, FET's were made from metal oxides; the first organic transistor was based on sexithiophene (T_6).[14] The compounds of Pappenfus[15] *et al.*, e.g. **6**, have also been shown to be good as the active layer in FET's due to their redox behavior and solid-state structure.

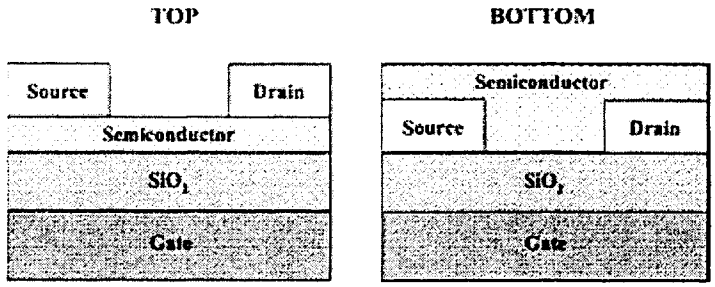
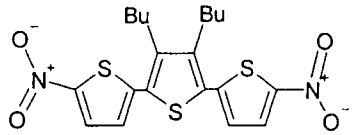


Figure 3. Schematic representation of top- and bottom-configuration thin-film transistor.[13]

Compound **6** is arranged in co-facial π-stacks instead of the herringbone stacks of most other oligothiophenes. This is beneficial because this allows for an increase in field-effect mobility. Since electrons must hop from π-system to π-system, coplanar π-stacks minimize the energy barrier by minimizing the intermolecular distance.



6

Compounds with only α,ω-substitution have the advantage of inducing only very small conformational distortions of the outermost rings, thus maintaining the conjugation and the electronic properties of the materials. Structural data[16] have shown that oligothiophenes are essentially planar with a fully conjugated carbon skeleton which allows for π-stacking between the molecules.

1.2.4 Non-linear Optics

Active photonic devices use a material with the property of optical nonlinearity. A nonlinear response is one that does not vary in direct proportion to the stimulus. All physical systems exhibit a nonlinear behavior if the driving force is large enough, and

generally this type of behavior is undesirable. However, in some instances it can be used constructively to generate a desired outcome. A diode is an example of a nonlinear electronic component: its output current remains negligibly low until the driving voltage reaches a threshold value, whereupon the output current increases sharply. This makes the diode a switch that is off when driven by voltages lower than the threshold and on for above-threshold voltages. A transistor can act as a more advanced version of a diode: a switch that also amplifies the signal through it.

A nonlinear optical (NLO) response is one where the intensity of light transmitted through a substance is not proportional to the intensity of incident light;[1] i.e. doubling the intensity of the latter will not necessarily double the intensity of the former. Instead, the incident light changes the way that the material responds to light—for example, by altering the materials transparency or refractive index. Basically, nonlinear optical behavior is a consequence of the ease with which charges in the material can be polarized by an electric field. For example, with second-harmonic generation (SHG), incident photons are converted to half the number of photons with double the frequency. Some π-conjugated oligothiophenes have exhibited nonlinear optical properties, such as push-pull and chiral compounds.[2]

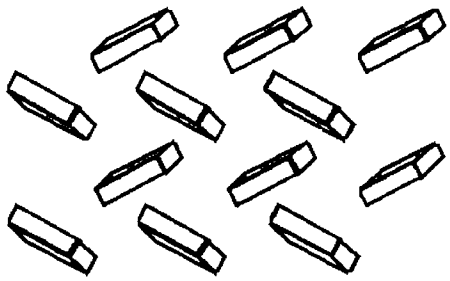
1.3 Optimizing solid-state structure from molecular compounds

In the field of crystal engineering it is very important to understand how molecules orient themselves in space through their non-covalent inter- and intramolecular interactions. While covalent interactions are well understood, non-covalent intermolecular interactions are less so. How a particular molecule will interact with other molecules is not always clear cut, as intermolecular interactions are relatively weak and

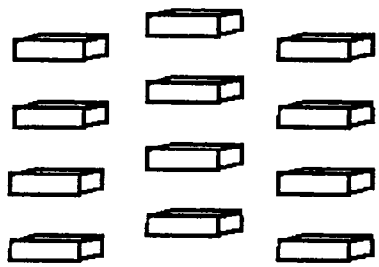
may be non-directional. In the devices we are interested in, a planar structure is desirable to maximize the conjugation, which allows electronic communication between the two end groups. This section will describe some of the many different ways that molecules can orient with each other and the impact this has on the solid-state structure.

1.3.1 Phenyl-phenyl interactions

Benzene adopts a herringbone motif in the solid state (**7A**).[17] In fact, all known fused aromatics (i.e. naphthalene,[18] anthracene,[19] and others[20]) as well as the oligomeric biphenyl,[21] terphenyl,[22] and quaterphenyl[23] species adopt this packing pattern. Unsubstituted oligomers of thiophene[4] show this packing structure as well. This herringbone structure **7A** may not appear intuitively to be the most efficient packing structure compared to planar π-stack **7B**, but is in fact the lowest energy structure.

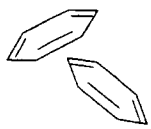


7A



7B

The local arrangement of the molecules in the packing structures **7A** and **7B** can be represented by the three diagrams **8A**, **8B**, and **8C**. A solid dominated by the T-shaped structure of **8A**, which forms due to the interaction between δ^+ hydrogens and the negatively charged π-system, will give a crystal with herringbone packing structure **7A** in the solid structure. The eclipsed **8B** and staggered **8C** π-stack will yield packing structure **7B**. Of the three local interactions, **8B** is of highest energy because the π-systems repel each other.



8A

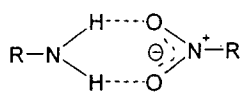
8B

8C

Theoretical studies on the origin of the energetic differences between the types **8A-C** have been carried out. They conclude that the van der Waals ($1/r^6$) attractive forces are favourable for all three configurations, but based on only the $1/r^6$ term, either **8B** or **8C** should be favoured. However, the electrostatic term is net attractive for **8A** but net repulsive for **8B** and **8C**, and the total energy makes the T-shape **8A** the lower energy structure.[24,25] The staggered π-stack **8C** is close in energy to the T-shape **8A,** so it should be a good alternative if the T-shape is not sterically feasible.[25] Although these phenyl-phenyl interactions are weaker than traditional hydrogen bonds they are the dominant influence on the packing arrangements of aromatic molecules.

1.3.2 Interactions involving the nitro group

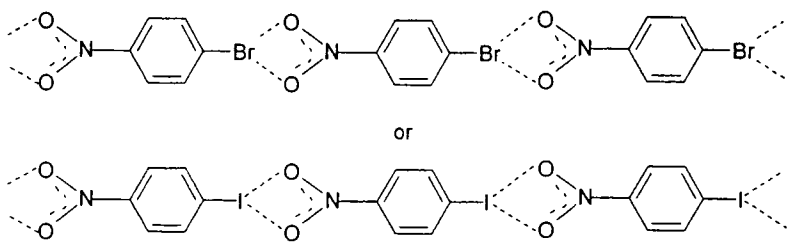
Traditional OH---O and NH---O hydrogen bonds are important intermolecular interactions. They are strong (with bond enthalpies up to 40 kJ/mol) and directional, which makes them ideal for encouraging planarity in crystal structures. One example of an H-bonded supramolecular synthon is the one between an NH_2 donor and the NO_2 acceptor (**9**).



9

10

If a hydrogen bond donor-acceptor pair can be thought of as a Brønsted acid-base interaction, then the carbon-halogen bond can be thought of as a Lewis acid-base interaction. As shown by the quinoidal part of the resonance structure **10**. Therefore halogen atoms can influence packing through this intermolecular interaction, as shown by **11**.[26] The bromine interaction with the nitro group is much weaker than the iodine analogue and may not be strong enough to influence the packing.



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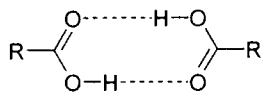
1.3.3 Carboxylic acid interactions

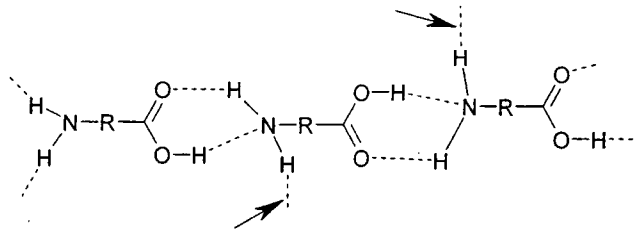
Carboxylic acids provide an example of self-complementary ordering in the solid state.[27] Since each acid moiety is both a hydrogen bond donor and acceptor, the dimerization shown by **12** is seen. This leads to single-synthon supramolecular structures.



12

Donor-acceptor compounds can also utilize the carboxylic acid moiety, for example when a molecule incorporates both the acid and an amine e.g. **13**. This also

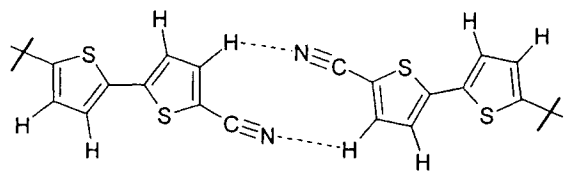
allows for the possibility of a three-dimensional structure by the additional hydrogen bonds indicated by the arrows in **13**.



13

1.3.4 The nitrile-aromatic hydrogen bond interaction

Nitrile groups are quite polar and contain a directional lone pair on the nitrogen. Hydrogens sigma bonded to carbons are slightly positive and are a common target for nitrile groups. Also, the nitrile group is small enough to allow a close interaction in the solid-state. Crystal structures with this type of interaction tend to enforce coplanarity of consecutive oligomeric units by forming ribbon-like arrays of nitrile-aromatic hydrogen interactions, e.g. **14**. As a result, dicyanobenzene[28] and dicyanooligothiophenes[29] adopt the slipped π-stack rather than a herringbone structure.



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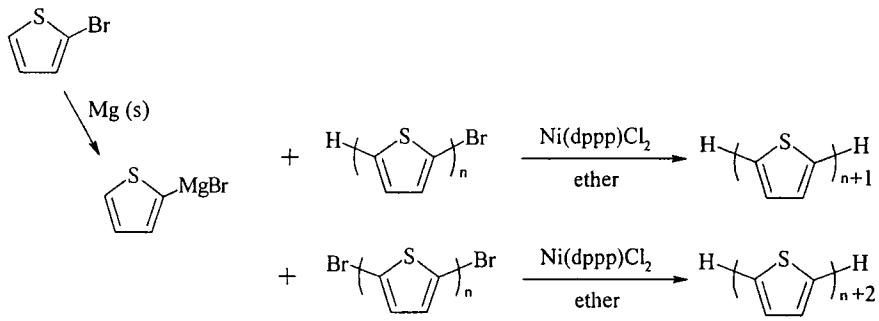
Chapter 2

Synthetic Techniques

In this chapter I will outline synthetic routes to the target oligothiophenes. I will also introduce some of the theory behind the methods and why they have been chosen for our thiophene compounds.

2.1 Coupling Reactions

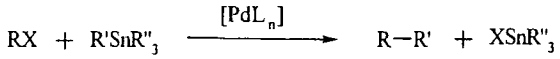
Oligothiophenes, T_2, T_3, and T_4 can be synthesized via the Kumada[30,31,32] (Grignard) reactions shown in Scheme 1 or by the Stille coupling[33] shown in Scheme 2. A third method, the Suzuki coupling, is known but less common.[34] We will be only investigating the Kumada method for synthesizing the unsubstitued oligothiophenes, whereas both the Kumada and Stille coupling methods will be investigated for the substituted oligothiophenes. We will not be looking into the Suzuki coupling in this thesis.



Scheme 1

The Kumada method is useful as it is easy to eliminate byproducts, uses non-toxic reagents, and uses a relatively cheap nickel-based catalyst. Unfortunately, it is not compatible with many functional groups. The Stille coupling (Scheme 2) is useful because it is preformed under mild conditions, has good functional group tolerance, and

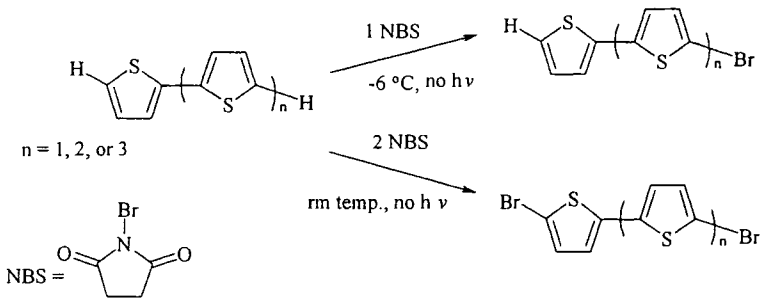
can give asymmetrically substituted products. Unfortunately, the tin byproducts are sometimes difficult to remove and are toxic. Also, the palladium catalyst is expensive. It is also stereospecific and regioselective, giving high yields.[33]



Scheme 2

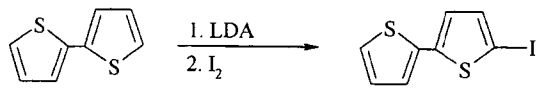
2.2 Halogenations

Brominations are most effectively carried out with NBS (Scheme 3). Both THF and DMF solvents can be used. DMF was used when the compounds were not soluble in THF. THF is preferred as it is easier to remove in the purification step. All of these reactions were performed in the dark to encourage the electrophilic reaction which is selective for the most reactive site (α to the sulphur) and to reduce the chance of a radical reaction, which would not be selective. Recrystallized NBS was used when the Br_2 impurity would be an issue (i.e. in mono-bromination reactions)



Scheme 3

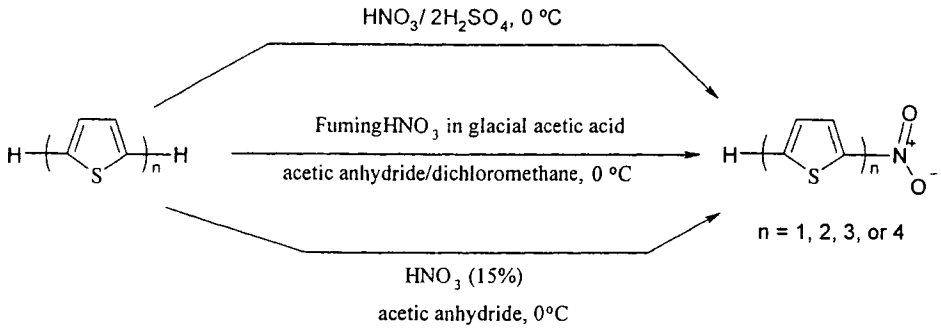
Iodinations can be affected by reacting I_2 with a carbanion (Scheme 4).[35] When the deprotonating reagent LDA is not suitable, e.g. in the presence of our functional group, NO_2, iodination using the relatively expensive NIS can be done. Such iodinations are performed in much the same way as the brominations (see Scheme 3), with THF as solvent. Alternatively, DMF can be used if there is a solubility issue. The NIS can be used as received as it does not appear to suffer photochemical degradation to the same extent as NBS.



Scheme 4

2.3 Nitrations

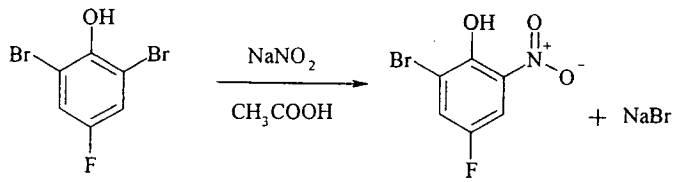
Some nitrothiophenes are known, but their synthesis is patented in a process with little experimental data reported.[15] We needed to develop a reliable method to generate multi-gram amounts. There are many ways to attach a NO_2^+ group to a thiophene ring, some of which are detailed here: (i) the standard textbook nitration[36] using a 1 HNO_3/ 2 H_2SO_4 solution, (ii) the fuming nitric acid nitration,[37] and (iii) the neat nitric acid nitration (Scheme 5). Since the 2- and 5- positions are the most reactive in thiophenes, the electrophilic replacement of an α-hydrogen for a NO_2^+ is expected to occur preferentially at those sites.



Scheme 5

For reactive compounds like phenols and pyrroles, nitration with HNO_3/H_2SO_4 is too harsh and results in oxidation of these substrates. Such compounds can be readily nitrated with HNO_3 alone. Literature preparations suggest that improved yields occur when using fuming nitric acid in glacial acetic acid with acetic anhydride/ dichloromethane as solvent,[37] rather than in neat nitric acid.

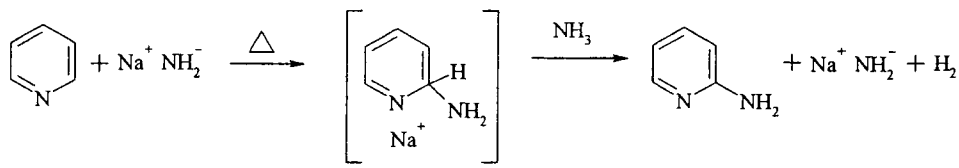
A final approach to nitration is the Zincke nitration,[38] which is applicable to substituted (activated) aromatic rings. The Zincke nitration involves the use of a nitrite-salt, $NaNO_2$ or KNO_2, and was first performed in 1900 when Zincke nitrated a halogenated-phenol (Scheme 6).



Scheme 6

2.4 Aminations

We decided to investigate two types of aminations for our compounds; the Chichibabin reaction[39] and the Gabriel reaction.[40] The original Chichibabin reaction involved the amination of pyridine by sodium amide, see Scheme 7. The aromatic ring was reactive enough to undergo nucleophilic substitution and replace the hydride ion. The thiophene ring is even more electron-rich and reactive than pyridine. The nitrogen is not only resonance activating (donating) like sulphur, but is also inductively withdrawing, which may help stabilize the transition state. When halogenated thiophenes are reacted, rearrangement of the bromine and amine groups to the 3-position occurs, which is undesirable. Therefore we will attempt the reaction with unhalogenated thiophenes.[41] The literature workup in NH_3 was deemed unfeasible due to the difficulty in obtaining NH_3, so water was used instead.

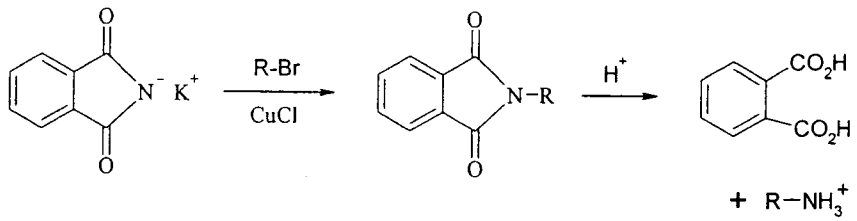


Scheme 7

It is not possible to attach an amine on a thiophene itself because the ring is too electron-rich. However, it is expected that with either Br or NO_2 as a substituent this would sufficiently stabilize the product and thus make the reaction possible.

The Gabriel synthesis involves using potassium phthalimide to attach an ammonium group (Scheme 8). Advantages of the Gabriel synthesis[40] are: (i) there is no secondary or tertiary amine contamination of the primary amine (ii) it has a very wide

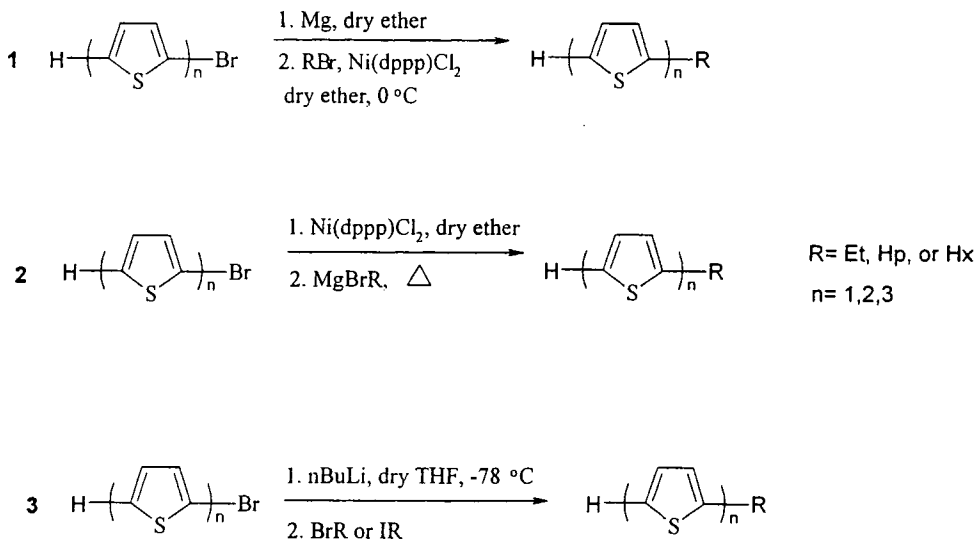
tolerance for many functional groups, and (iii) the conditions are mild for both steps. High yields for the primary amine are generally obtainable. Cuprous chloride was used in a 1:1 molar ratio with the potassium phthalimide. It is thought that the reaction follows a free radical mechanism. This is supported by the ability to isolate phthalimide itself from the reaction mixture. A number of aromatic systems bearing halogen substituents and capable of creating electron delocalization in the ring (*e.g.* $-NO_2$, -CN) have been seen to be favourable for the Gabriel synthesis. The work by Gibson et al.[40] found that their N-thienylphthalimides would not survive the hydrolysis and usually decompose *inter alia* to formaldehyde and ammonia. We expect that oligothiophenes, being less reactive than thiophene itself, would fair better in the reaction.



Scheme 8

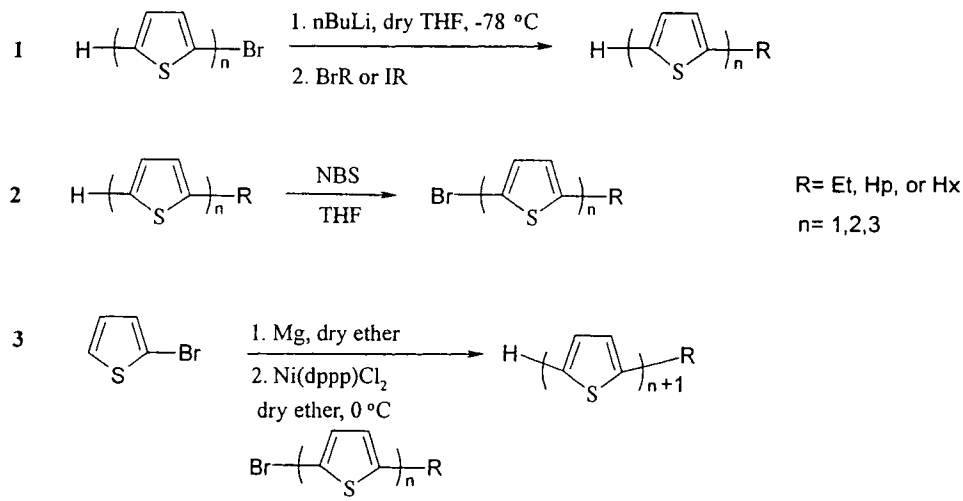
2.5 Alkylations

It has been shown in the literature that oligothiophenes with straight-chain alkyl end-groups are good OLED materials.[37,42] Therefore, we decided to investigate the formation of such compounds. Three possible methods to make alkyl products are: the Kumada coupling, use of commercial Grignard reagents, and a lithiation method (Scheme 9).



Scheme 9

A complementary route to attaching longer alkyl groups via the Kamada coupling is by making the alkyl-thiophene and coupling it to TMgBr, as shown in Scheme 10. This may be less harsh then trying to alkylate the oligothiophenes. This reaction is well known and is not expected to decompose the alkyl-group.



Scheme 10

Chapter 3

Results and Discussion

3.1 Synthetic Results

3.1.1 Synthesis of T_n

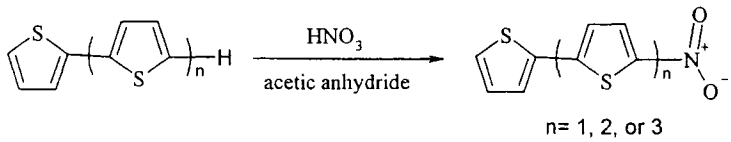
The synthesis of T_2, T_3, and T_4 are standard syntheses and worked with typical yields (34-91%).[30,31,32]

3.1.2 Synthesis of Br_2T_n and BrT_n

The synthesis of Br_2T_2 and Br_2T_3 are standard syntheses and worked with typical yields (70-75%).[43] The synthesis of BrT_2 and BrT_3 were adapted from standard syntheses, i.e. the reaction was done in the freezer at -3 °C instead of at room temperature, and worked with typical yields (70-80%).[43]

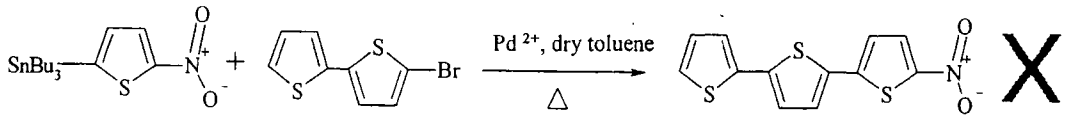
3.1.3 Synthesis of T_nNO_2 (n = 1, 2, 3 and 4)

In preparing nitrated products we must choose a nitration that will not oxidize the ring and will mono-nitrate if we control the stoichiometry. We had the most success with neat nitric acid (Scheme 11). The reactions worked quite well with yields ranging from 31% to 93%. The T_4NO_2 was not fully spectroscopically characterized due to solubility issues, but the mass spectrum did indicate that it had formed.



Scheme 11

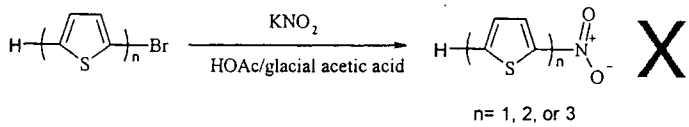
We also tried coupling BrT_2 and Bu_3SnTNO_2, as shown in Scheme 12, but this had only limited success mainly due to the difficulty in synthesizing pure BrT_2.



Scheme 12

The nitration using 1:2 HNO_3:H_2SO_4 solution did not work, and only oxidized the thiophene sulphur, producing a black sludge. The fuming nitric acid nitration yielded some product, but with yields from 2-22 %, this was far from satisfactory.

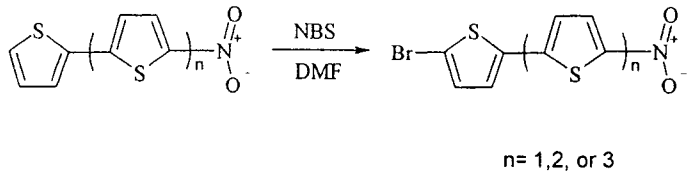
The Zincke nitration, a fourth way to synthesize T_nNO_2 was found to be unfeasible, as shown in Scheme 13.[38] We expect thiophene compounds are too electron-rich for the reaction to work. Insolubility of the reagents was also a source of difficulty.



Scheme 13

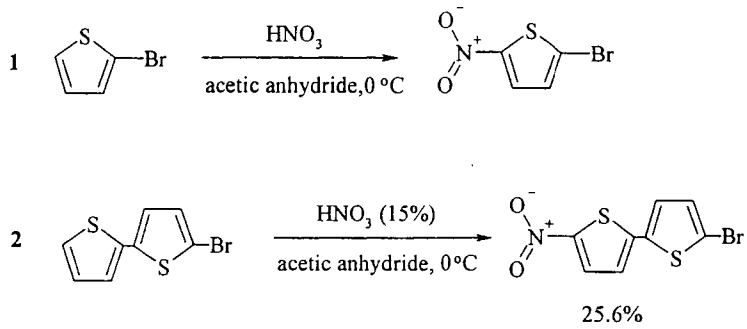
3.1.4 Synthesis of BrT_nNO_2 (n = 2, 3 and 4)

Our NBS brominations gave good yields (70-90%) and worked well even with the EW NO_2 group attached to the ring, as shown in Scheme 14. The BrT_4NO_2 could not be characterized by ^1H NMR spectroscopy due to solubility issues, but the mass spectrum did indicate that it had been formed in a mixture with T_4NO_2, $T_4(NO_2)_2$, and BrT_4NO_2. We have attempted to separate the components by sublimation and fractional recrystallization, but the low solubility makes this difficult as well.



Scheme 14

We have also tried to prepare a brominated product by nitrating brominated oligomers. When this reaction was attempted mixed products formed, which included de-brominated products. Because the halogen replacement was unpredictable, we decided that it was best to halogentate our compounds after nitration (see section 3.1.3), except in the case of TBr which nitrated well while maintaining the bromo group (see Scheme 15). There was an additional problem in preparing NO_2T_2Br this way because of the difficulty in synthesizing BrT_2, which is a low-melting point solid.[43] Unfortunately, we could not make any NO_2T_2Br via any other route, so we had to be satisfied with the low yield and difficult synthesis.

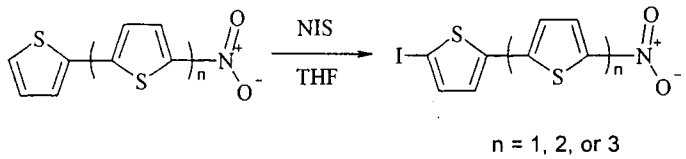


Scheme 15

3.1.5 Synthesis of IT_nNO_2 (n = 2, 3 and 4)

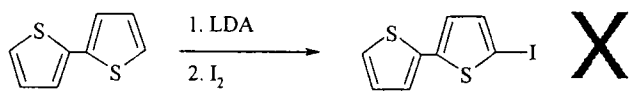
Iodinations with NIS were fairly successful (Scheme 16). This seems to be the best method to iodinate substituted oligothiophenes. It is the least harsh and does not affect the sometimes reactive end-groups. The yields were good (65-74%). The IT_4NO_2

was not characterized fully due to its low solubility, but the mass spectrum did indicate that it had been formed. Also, IT_2NO_2 was also not fully characterized as we have been unable to purify it. The ^1H NMR spectrum indicated a mixture of products, although the mass spectrum and the ^1H NMR spectrum indicate that the product had been formed. Unlike the NBS bromination reactions, which were stirred overnight and worked up in the morning, the NIS iodinations had to be stirred for considerably longer times to ensure that the reaction went to completion. When left for a sufficient amount of time (days to weeks), the desired product is pure, and very little starting material was seen in the ^1H NMR spectrum. Once formed, the products are stable, so the reaction must be slow kinetically.



Scheme 16

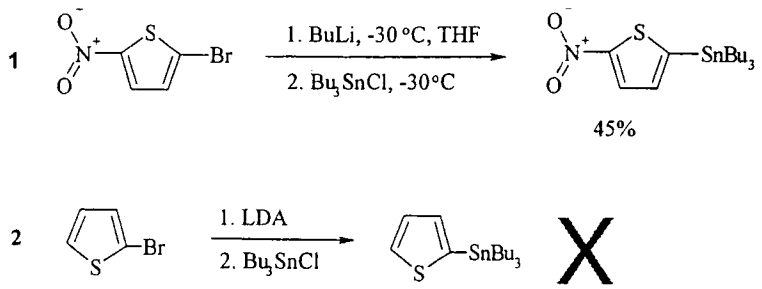
A second iodination method, shown in Scheme 17, was unsuccessful. Deprotonation with LDA does not seem to work well with our thiophene compounds. We only tried this reaction once and then decided that NIS was the better way to go since the LDA reaction is time-intensive.



Scheme 17

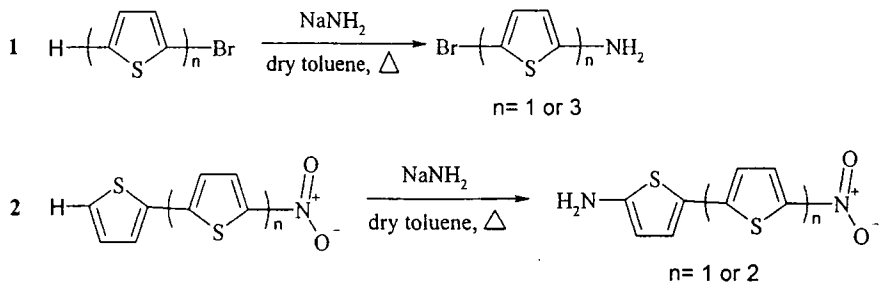
3.1.6 Attempted synthesis of $NO_2T_nNH_2$ (n = 2, 3 and 4)

Our planned route to $NO_2T_nNH_2$ required the creation of an aminated portion and a nitrated portion that could then be coupled together. The nitrated portion required the formation of NO_2TSnBu_3. We tried this reaction two ways, i.e. by using BuLi or LDA to lithiate the halogen site and then to replace the Li with Bu_3SnCl. We found that these reactions were very unreliable and did not always work (Scheme 18). The LDA reaction never produced any product. When the BuLi reaction worked it was in 45% yield (Scheme 18), but at other times the reaction failed completely.



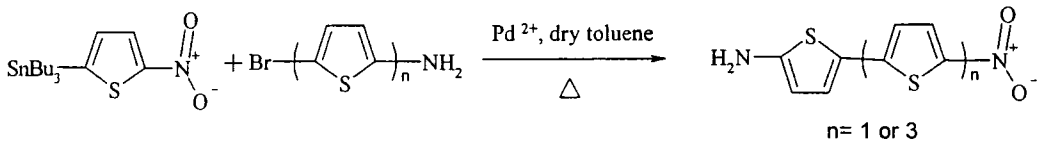
Scheme 18

The aminated portion was created using the Chichibabin[39] reaction which appeared at first to work well (IR spectra of the crude product indicated an N-H peak). However, when purified by sublimation, the NH_2 group was decomposed by the heat. We also tried first nitrating and then aminating, in the hope that the EWG would help the reaction. However, this reaction did not work. Scheme 19 outlines the aminations that were explored using this method.



Scheme 19

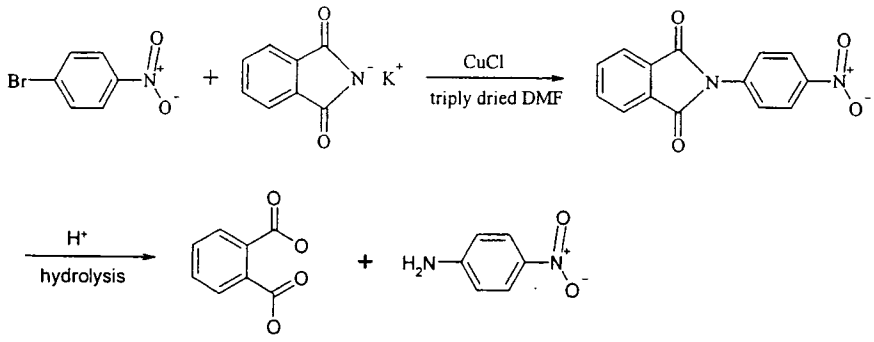
When we tried to use the Stille coupling reaction (using the crude T_nNH_2) to make our various amino/nitro products, crude yields were 66-80%. Again, however, purification through sublimation decomposed the amino group even though it appeared in their IR spectra before sublimation. The method of reaction is laid out in Scheme 20.



Pd $^{2+}$ = bis(triphenylphosphine)-palladium(II)

Scheme 20

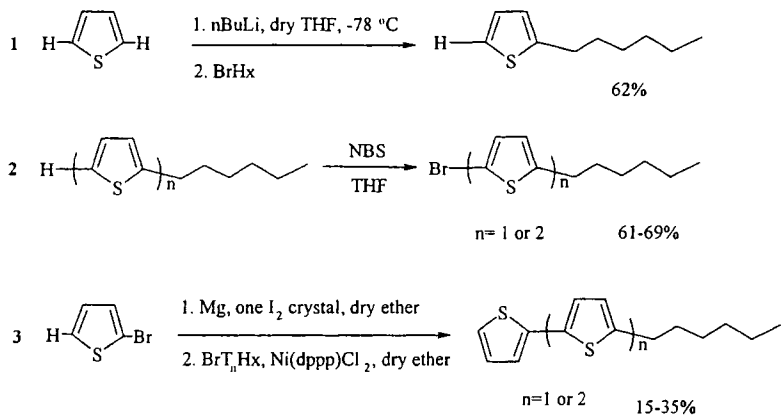
With the failure of the Chichibabin reaction, we moved to another method of amination. We modeled the Gabriel synthesis (outlined in Scheme 21) with 1-bromo-4-nitrobenzene, to see how easy it was to perform and whether it would be applicable to our compounds. The reaction did not work well even on our model compound, perhaps due to the fact that not all the reagents dissolved in toluene (the oligothiophenes would not be soluble in the solvents used in the original paper). As the model reaction did not work, we did not feel it was prudent to waste our synthesized nitrooligothiophenes on this method.



Scheme 21

3.1.7 Synthesis of T_nHx (n = 1, 2 and 3)

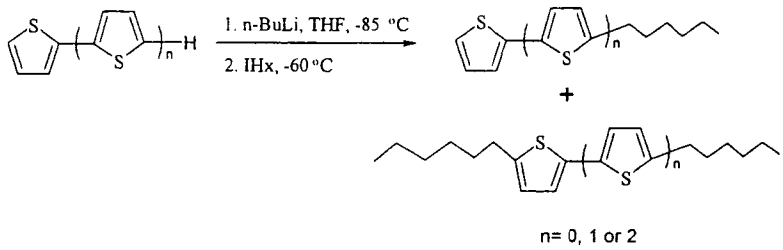
We had the most success with an adaption of the literature synthesis,[42] adding thienylmagnesium bromide to hexylbromide. To add more thiophene rings, we added TMgBr to the bromo-hexylated oligomer (section 3.1.8). This route was chosen because we were afraid of decomposing or isomerizing the hexyl group if we were to make it into a Grignard reagent. Further, the solubility of HxT_2Br in ether is low. This method worked with moderate yields after distillation, as shown in Scheme 22.



Scheme 22

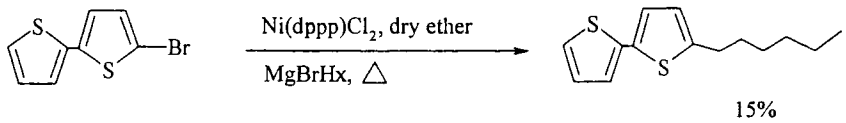
We attempted a number of less successful routes as well. Initially, we tried our hexylations with hexyliodide (because of availability). However, the fact that iodine is a

far more labile group caused a significant amount of di-hexylated product to be formed (see Scheme 23).



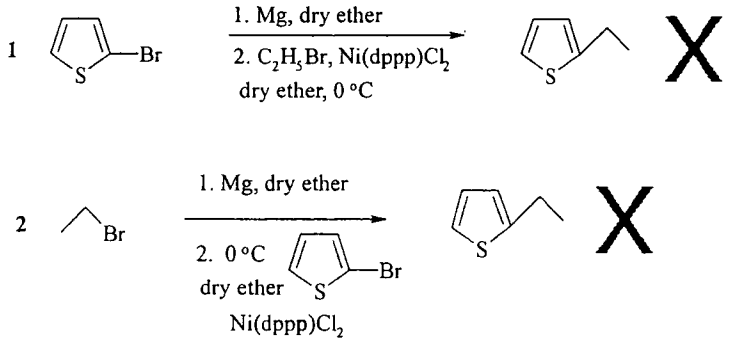
Scheme 23

We also tried using commercial hexylmagnesium bromide, but the difficulty in making BrT_2 limited its utility (see Scheme 24).



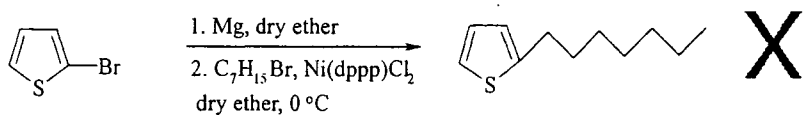
Scheme 24

We also tried to prepare short-chain compounds using the methods shown in Scheme 25. Neither method was successful as indicated by ^1H NMR spectroscopy. This may have been due to difficulty in isolating the low-boiling point product.



Scheme 25

Our one attempt to attach a heptyl group on BrT failed, as indicated by ^{1}H NMR spectroscopy (see Scheme 26).

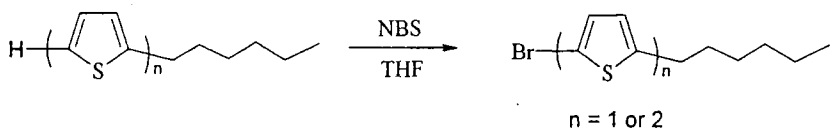


Scheme 26

None of the reactions to synthesize $T_nC_2H_5$ or $T_nC_7H_{15}$ were optimized because they were abandoned after the success in synthesizing the hexylated derivative.

3.1.8 Synthesis of BrT_nHx (n = 1 and 2)

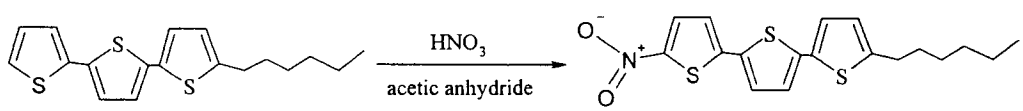
The brominations of the hexyl-compounds (Scheme 27) worked fairly well with good yields (60-70%).



Scheme 27

3.1.9 Synthesis of NO_2T_nHx (n = 3)

We nitrated T_3Hx according to the neat nitric acid method (described in section 3.1.3). We were able to sublime the red solid, but the low melting points of the product and its byproducts have so far hampered efforts at purification.



Scheme 28

3.2 Spectroscopic Data

3.2.1 UV-Visible Spectra

To determine the effect of substitution on the oligothiophenes, we investigated a bithiophene and a terthiophene series. Solutions were all 1×10^{-5} *M* in toluene.

In the bithiophene series (Figure 4) we see a large bathochromic shift upon attachment of the nitro group due to the increase in conjugation. The spectrum does not change significantly when a bromo group is attached, as the bromo group has no effect on conjugation. The bathochromic shift indicates a shift to lower energy or longer wavelength, meaning the HOMO and LUMO are closer in energy.

In the terthiophene series (Figures 5 and 6) we see the same effect as for the bithiophene series. The spectrum of T_3 does not change when a bromo or iodo group is added, but when a nitro group is added a large bathochromic shift is seen. This again indicates that the addition of a halogen group has little effect on conjugation length of the compound. The maximum wavelength of absorptions are consistent with those found by Garcia et al.[14] for T_3, T_3NO_2, T_3Br_2 and BrT_3NO_2.

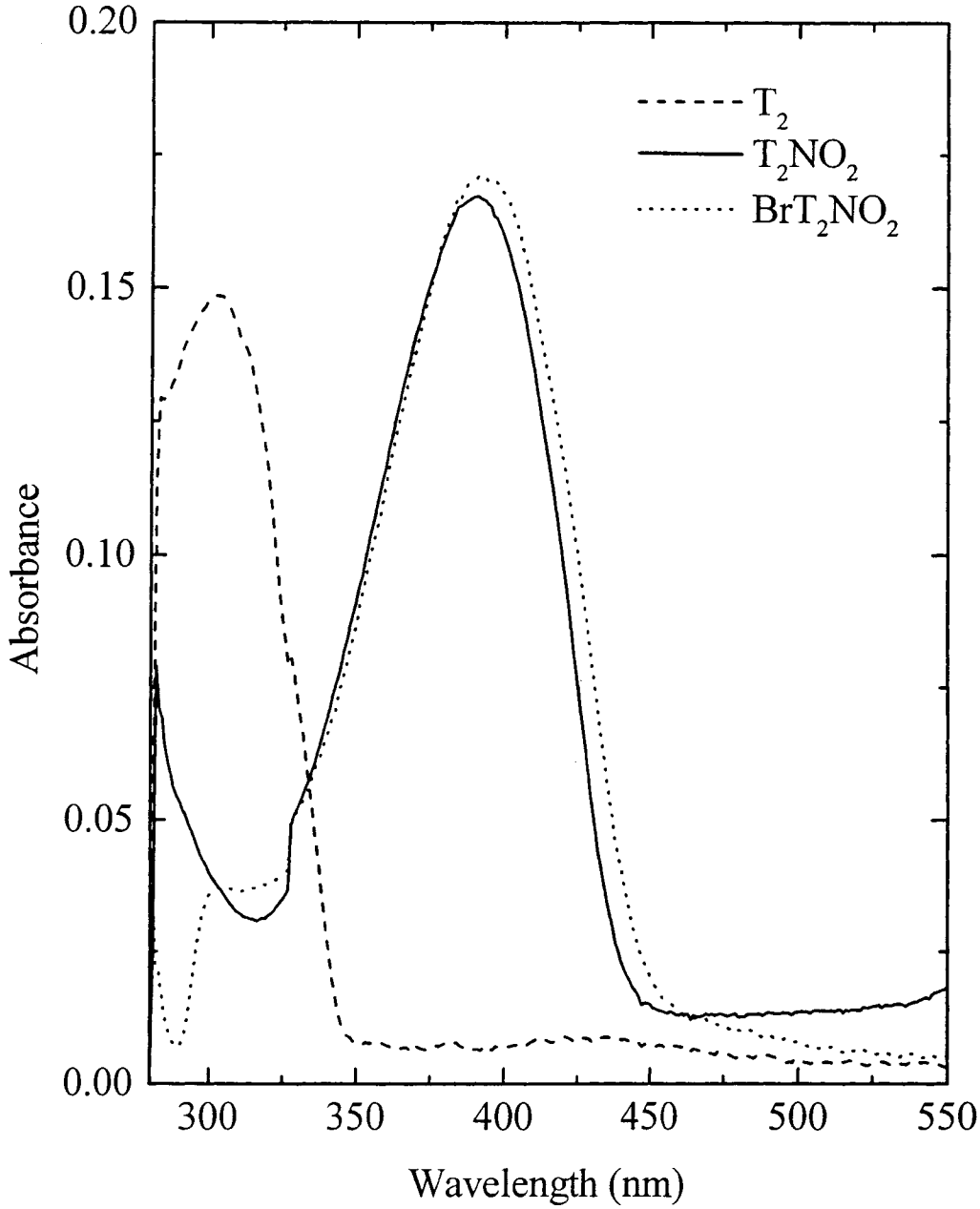


Figure 4: UV-Vis spectra of the bithiophene series

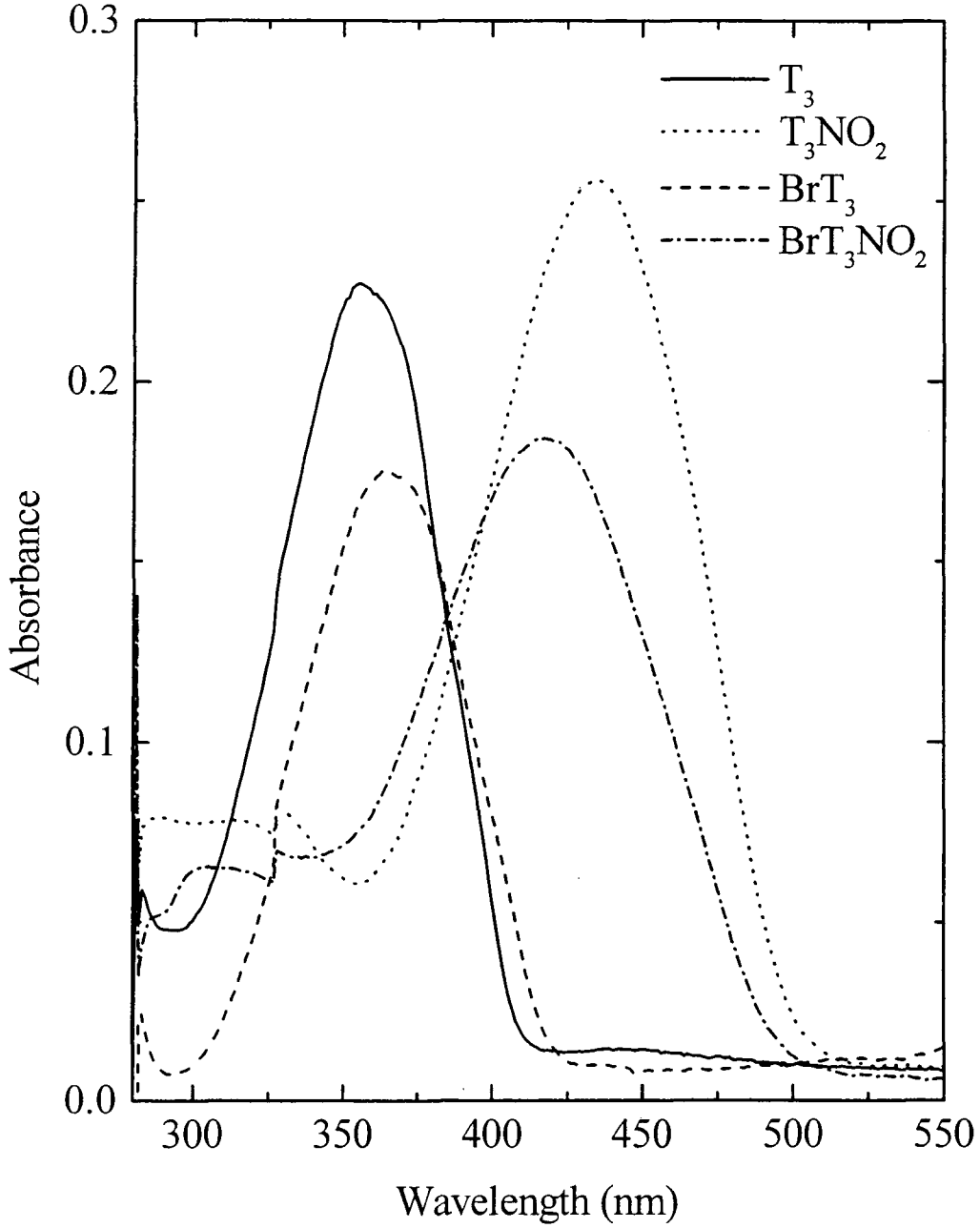


Figure 5: UV-Vis spectra of the terthiophene series

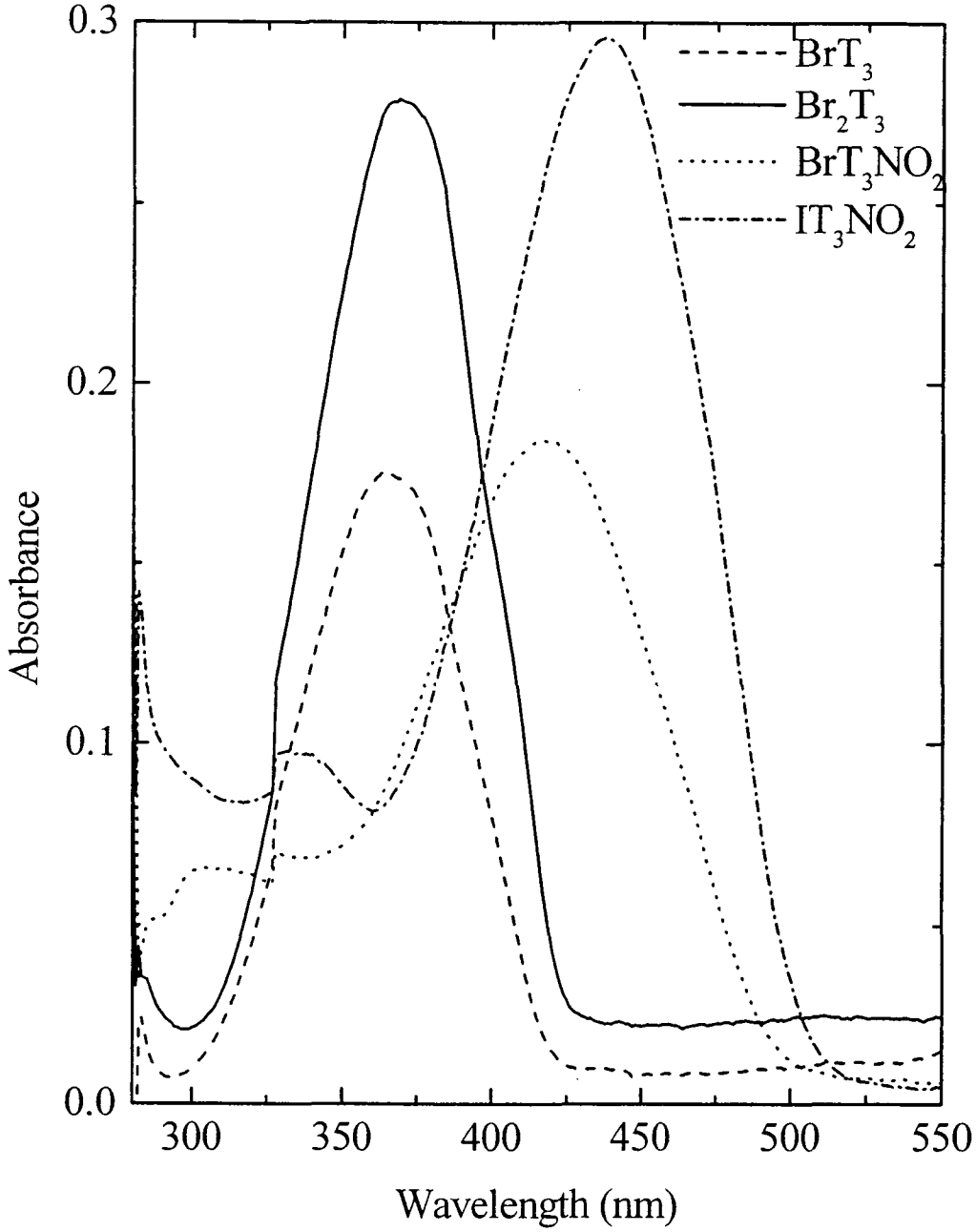


Figure 6: UV-Vis spectra of the halogen-terthiophene series

3.2.2 Fluorescence data

Both fluorescence and phosphorescence (section 3.2.3) spectroscopy were used to characterize the bi- and terthiophene series. Fluorescence is the radiation that is emitted during a transition between electronic states of the same spin or multiplicity. The fluorescence measurements were run on the same samples as used for the UV-Vis spectra.

In the bithiophene series (Table 1) the attachment of a nitro group has little effect on the fluorescence, while the addition of the bromo group to T_2NO_2 causes a significant increase in the wavelength of fluorescence. There is a significant solvatochromic shift for T_2NO_2 on moving from toluene to chloroform, which often indicates a difference in polarity between the ground state and the excited state. This is often seen in materials with NLO properties.[44]

Table 1: Bithiophene series fluorescence emission data

Compound	λ(nm)	Intensity
T_2 (toluene)	329	34
T_2NO_2 (toluene)	330	41
BrT_2NO_2 (toluene)	441	30
T_2NO_2 ($CHCl_3$)	395	20

The maximum wavelength of emissions were consistent with those found by Garcia et al.[14] for T_3, T_3NO_2, T_3Br_2 and BrT_3NO_2. In the terthiophene series (Table 2) the attachment of a nitro group to T_3 does cause a shift in the fluorescence spectrum, while attachment of a bromo group to T_3 causes a negligible shift. Interestingly, attachment of a second bromo group to BrT_3 does not cause a shift, nor is BrT_3NO_2 different from T_3NO_2. It seems that the bromo group has an effect on its own, but when a nitro group is

also attached the effect appears minimized. The solvent dependence is also seen as in the bithiophene series, highlighting the need to use the same solvent for all species when comparing linear optical properties.

Table 2: Terthiophene-series fluorescence emission data

Compound	λ(nm)	Intensity
T_3 (toluene)	433	78
T_3NO_2 (toluene)	522	71
BrT_3 (toluene)	438	27
Br_2T_3 (toluene)	450	29
BrT_3NO_2 (toluene)	517	135
IT_3NO_2 (toluene)	526	65
T_3NO_2 ($CHCl_3$)	577	64

3.2.3 Phosphorescence data

Phosphorescence is very similar to fluorescence except it is the radiation emitted in a transition between electronic states of different multiplicities. It is a spin-forbidden transition, and therefore has a longer lifetime then fluorescence under the same conditions (solvent, temperature, etc.). Phosphorescence is usually at a lower frequency than that of fluorescence. In detecting phosphorescence, the source has to be turned on then turned off, and the subsequent emission recorded. This emission may only last for a microsecond or less, so cooling the system under liquid nitrogen helps in the detection of the emission. Unfortunately, this means that the solvent freezes and may affect the emission much differently than in the fluorescence experiment (i.e. these measurements are on glassy phases). The phosphorescence measurements were run on the same samples as used for the UV-Vis and fluorescence spectra.

In the bithiophene series (Table 3), the only compound that is phosphorescent is BrT_2NO_2; the addition of only a nitro or a bromo group has no effect. Presumably, a charge-transfer state in BrT_2NO_2 is involved, which would not exist in either T_2 or T_2NO_2.

Table 3: Bithiophene-series phosphorescence emission data

Compound	λ(nm)	Intensity
T_2 (toluene)	-	-
T_2NO_2 (toluene)	-	-
BrT_2NO_2 (toluene)	426	18

- indicates no observed phosphorescence

In the same way, only the heterodisubstituted BrT_3NO_2 and IT_3NO_2 phosphoresce in the terthiophene series (Table 4). The data implies that the identity of the halogen does not matter, since the phosphorescence of BrT_3NO_2 and IT_3NO_2 are virtually the same.

Table 4: Terthiophene-series phosphorescence emission data

Compound	λ(nm)	Intensity
T_3 (toluene)	-	-
T_3NO_2 (toluene)	-	-
BrT_3 (toluene)	-	-
Br_2T_3 (toluene)	-	-
BrT_3NO_2 (toluene)	428	20
IT_3NO_2 (toluene)	425	14

- indicates no observed phosphorescence

Unfortunately, we cannot fully explain these spectroscopic data without theoretical calculations to determine the nature of the orbitals involved. These calculations will be done in future studies and are beyond the scope of this thesis.

3.3 Electrical conductivity and susceptibility data

For a complete description of the apparatus and the methodology see Sears et al.[45] An LCR impedance bridge is used to measure the complex admittance of the powdered samples prepared for this thesis. The meter is computer controlled and records both the real component (conductance) and the imaginary component (susceptance) as a function of frequency. A schematic of the electrode system used in the measurements is shown in Figure 7, where the sample is packed into the space between the electrodes e_1 and e_2 and subjected to an AC signal of two volts.

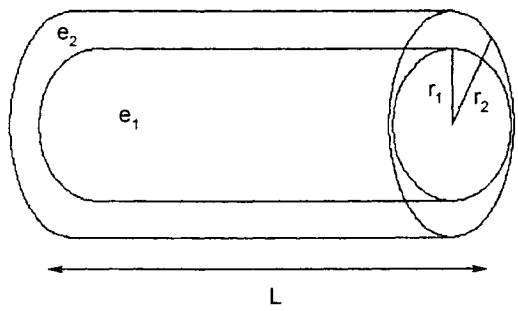


Figure 7: A schematic of the sample chamber used in the conductivity tests

The admittance is converted into conductivity and susceptibility based on the geometry of the chamber. The conductivity indicates how mobile the electrons are in the material, and is converted from conductance with the following equation:

$$\sigma = [\ln(r_2/r_1)/ 2\pi L]\times G = 5.80 \times G$$

where G = conductance, r_2 = outer radius, r_1 = inner radius, and L = length of the cylinder in metres. The susceptibility indicates how polarizable the material is, i.e. how strongly

the molecule is polarized in an electric field. Susceptibility is converted from susceptance by the following equation:

$$\chi = (B/\omega C_o) - 1$$

where ω = angular frequency of the driving voltage, C_o = air capacitance (the capacitance of the apparatus with no sample in it), and B = susceptance. In the above equations, G and B have been corrected for stray effects.

The conductivity and susceptibility were measured on the terthiophene series. The power law dependence of the four conductivity vs. frequency curves, shown in Figure 8, indicate that T_3, T_3NO_2, BrT_3, and BrT_3NO_2 are all dielectric materials. Although all four have very low conductivity, it is clear that T_3 and T_3NO_2 are the least conducting and BrT_3 and BrT_3NO_2 are the most conducting. Therefore, the effect of adding a halogen group is greater than that of adding a nitro group. This means that increasing the conjugation length increases the conductivity at high frequency. It is interesting to note that you get a change in slope when you add a nitro group, but not when you add a bromo group. This change in slope is associated with a uniform increase in conductivity. From Figure 9 it is clear that changing the halogen (from Br to I) has little effect on conductivity. Also, the addition of a second bromo group produces very little change in the conductivity (Figure 10). Therefore, addition of more than one bromo group is not necessarily beneficial.

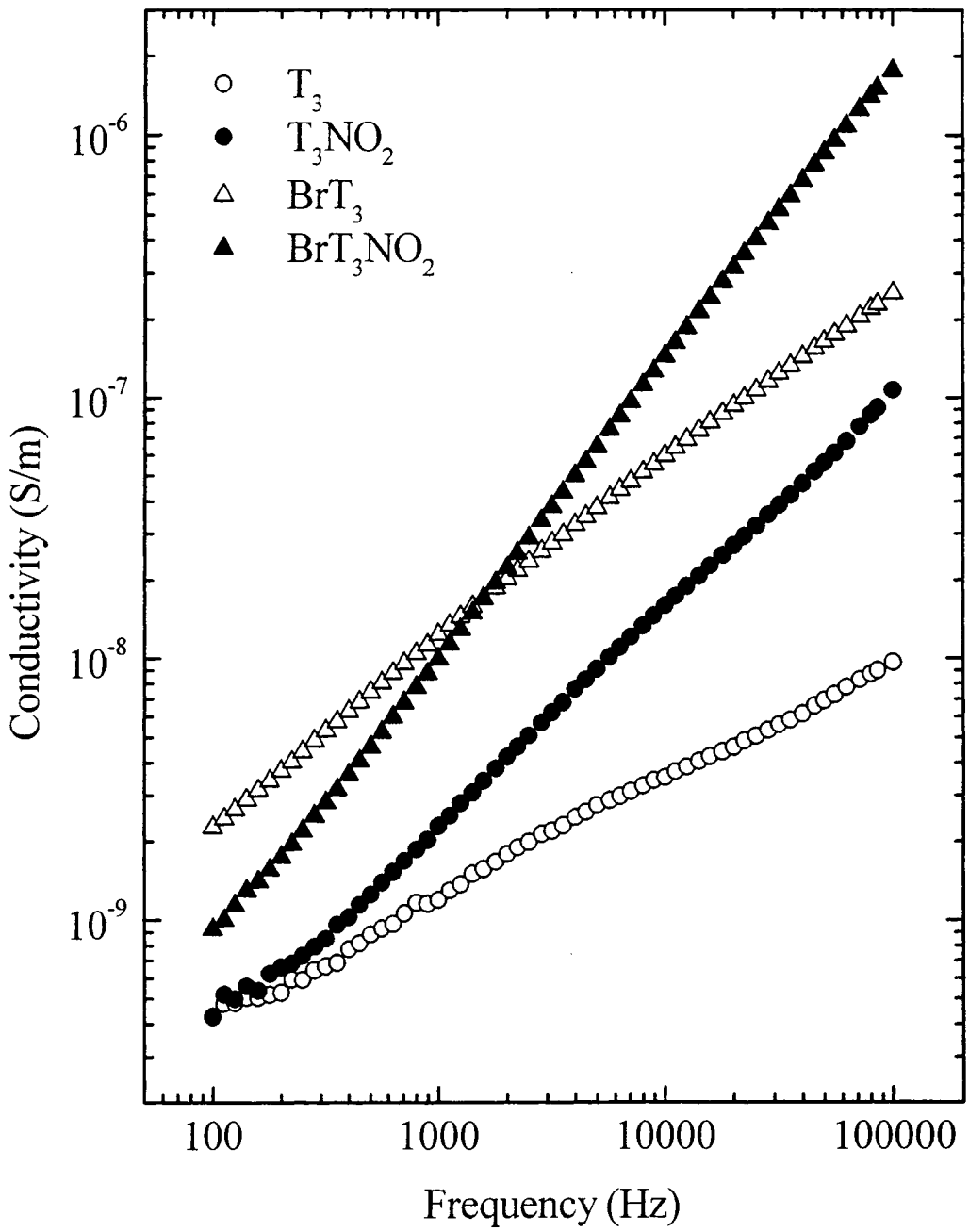


Figure 8: Conductivity vs. frequency graph of the terthiophene-series

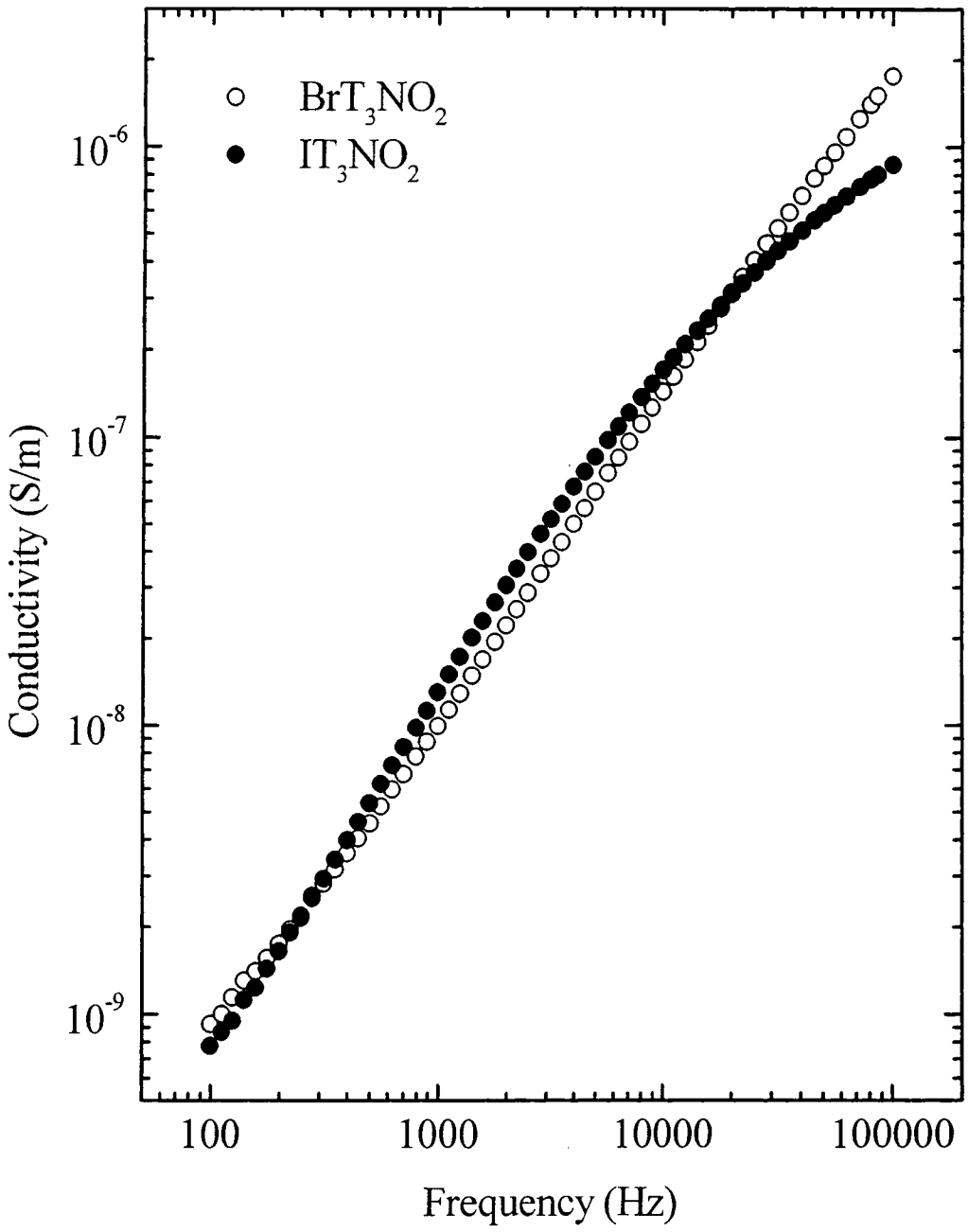


Figure 9: Conductivity vs. frequency graph of BrT_3NO_2 and IT_3NO_2

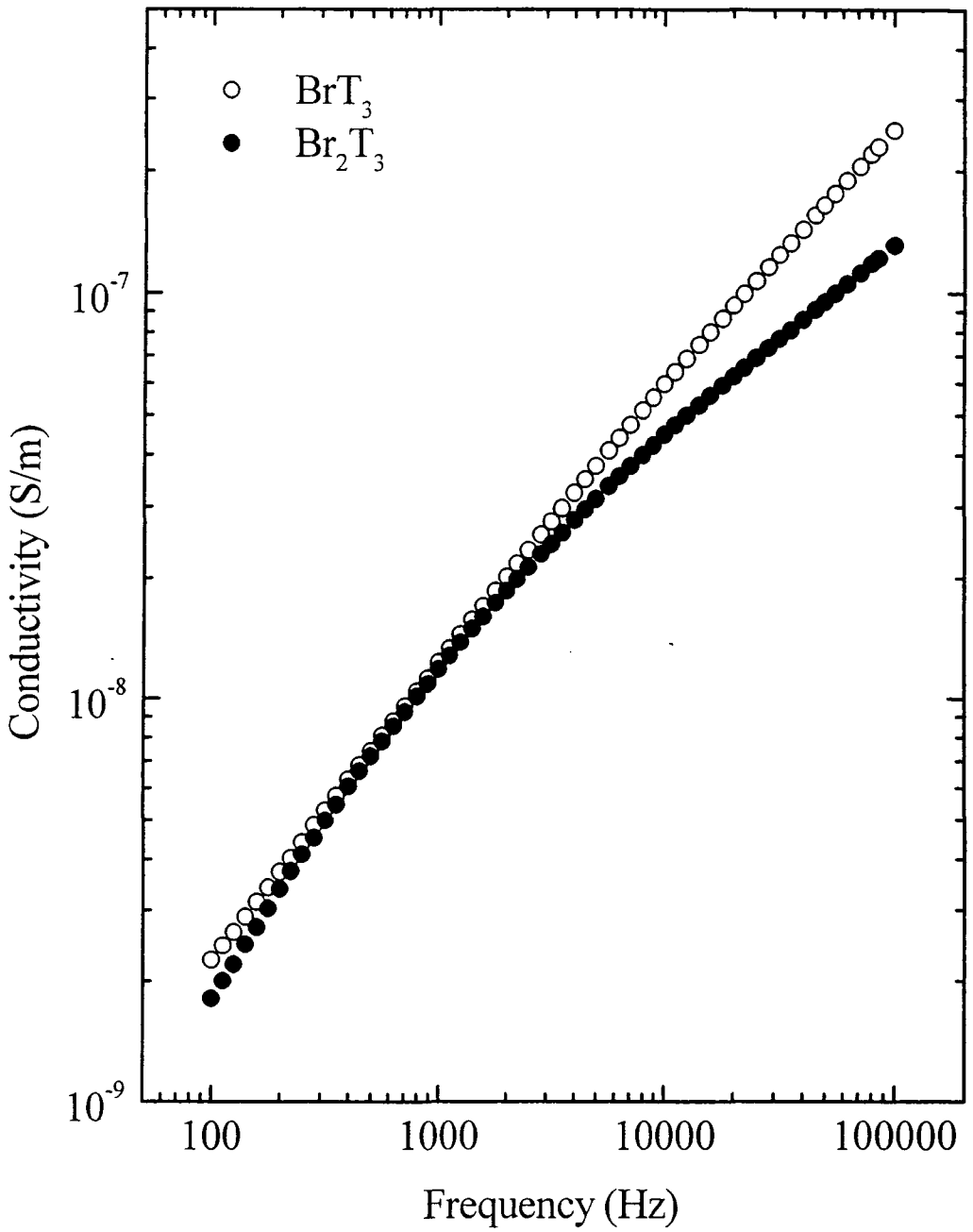


Figure 10: Conductivity vs. frequency graph of BrT_3 and Br_2T_3

Figure 11 shows the susceptibility vs. frequency curves for the four terthiophene samples, as in Figure 8. We see that BrT_3NO_2 is more easily polarized than T_3, T_3NO_2 and BrT_3. Interestingly, the addition of an iodo group rather than a bromo group does not change the susceptibility as significantly (Figure 12). It is not obvious why the susceptibility of BrT_3NO_2 is so much higher than IT_3NO_2. My conjecture is that since Br is smaller and more electronegative than I (2.93 vs. 2.66), the molecule has a stronger permanent dipole moment and polarization occurs through molecular rotation (induced by the AC current). In Figure 9, there is very little difference in the conductivity of BrT_3NO_2 and IT_3NO_2. This indicates that susceptibility seems halogen controlled whereas conductivity appears to be related to both the nitro and the halogen groups. It is interesting that in the susceptibility curves of Figure 13, the susceptibility of Br_2T_3 is slightly greater than that of BrT_3. Perhaps having two end-groups instead of one improves susceptibility.

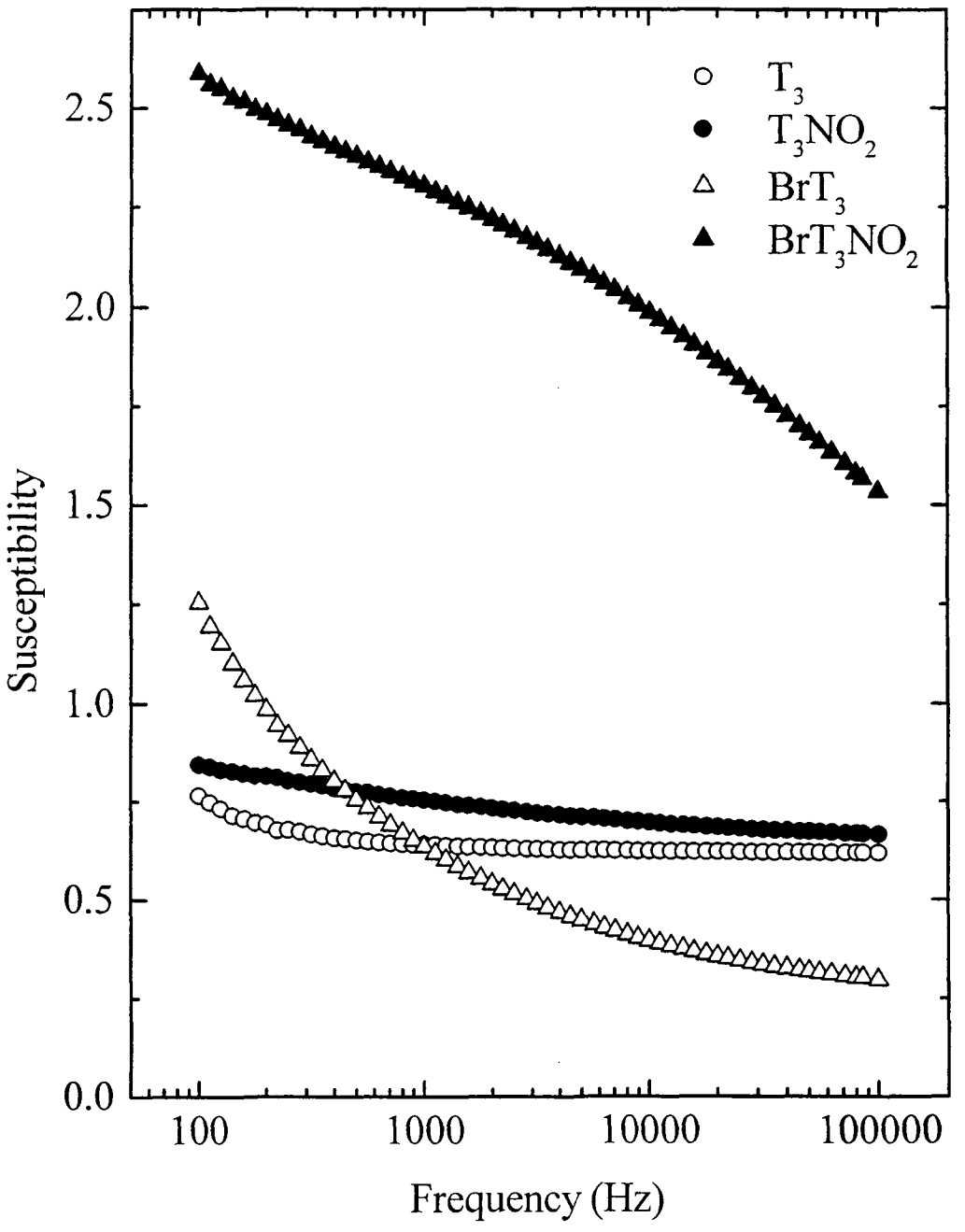


Figure 11: Susceptibility vs. frequency graph of the terthiophene-series

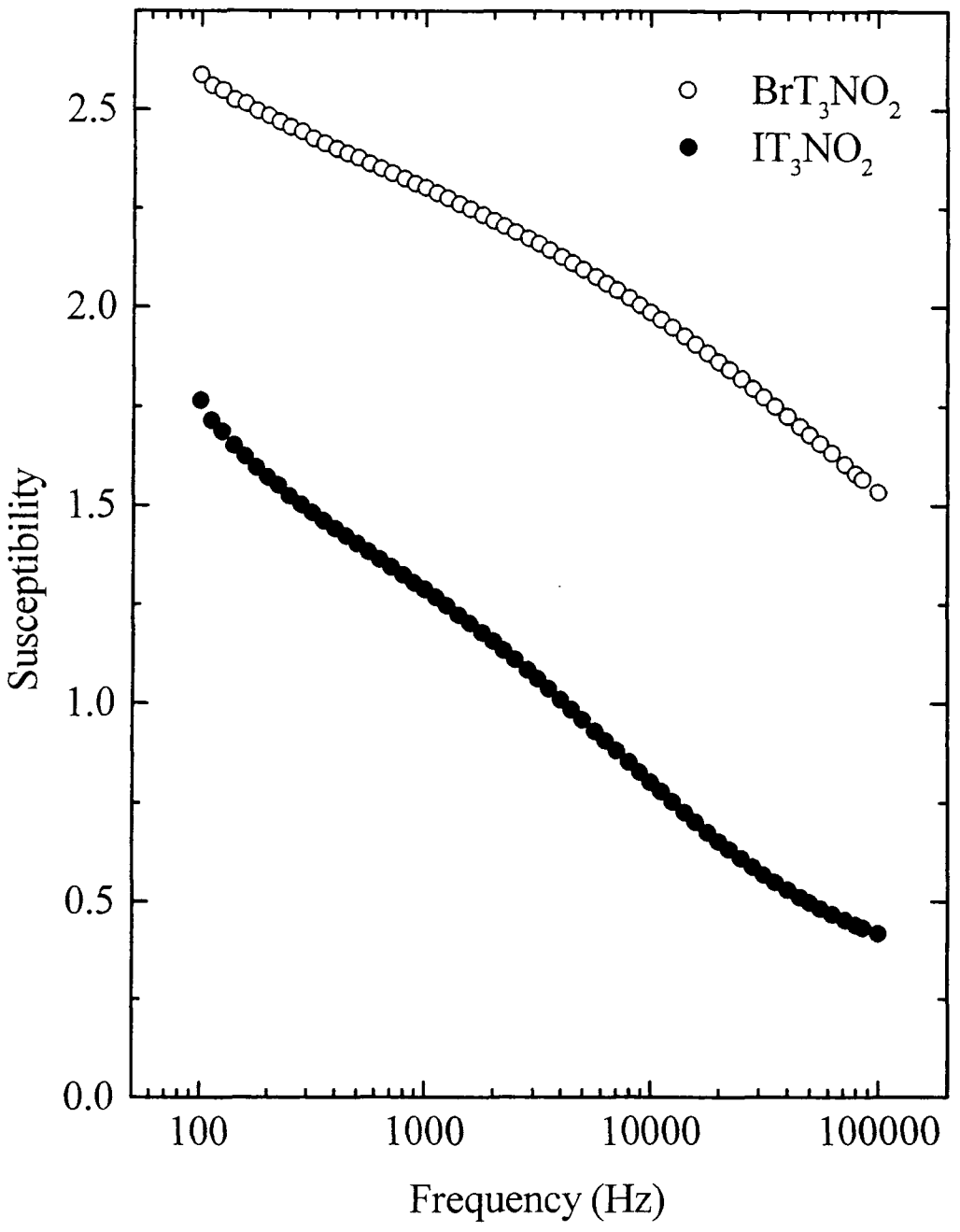


Figure 12: Susceptibility vs. frequency graph of BrT_3NO_2 and IT_3NO_2

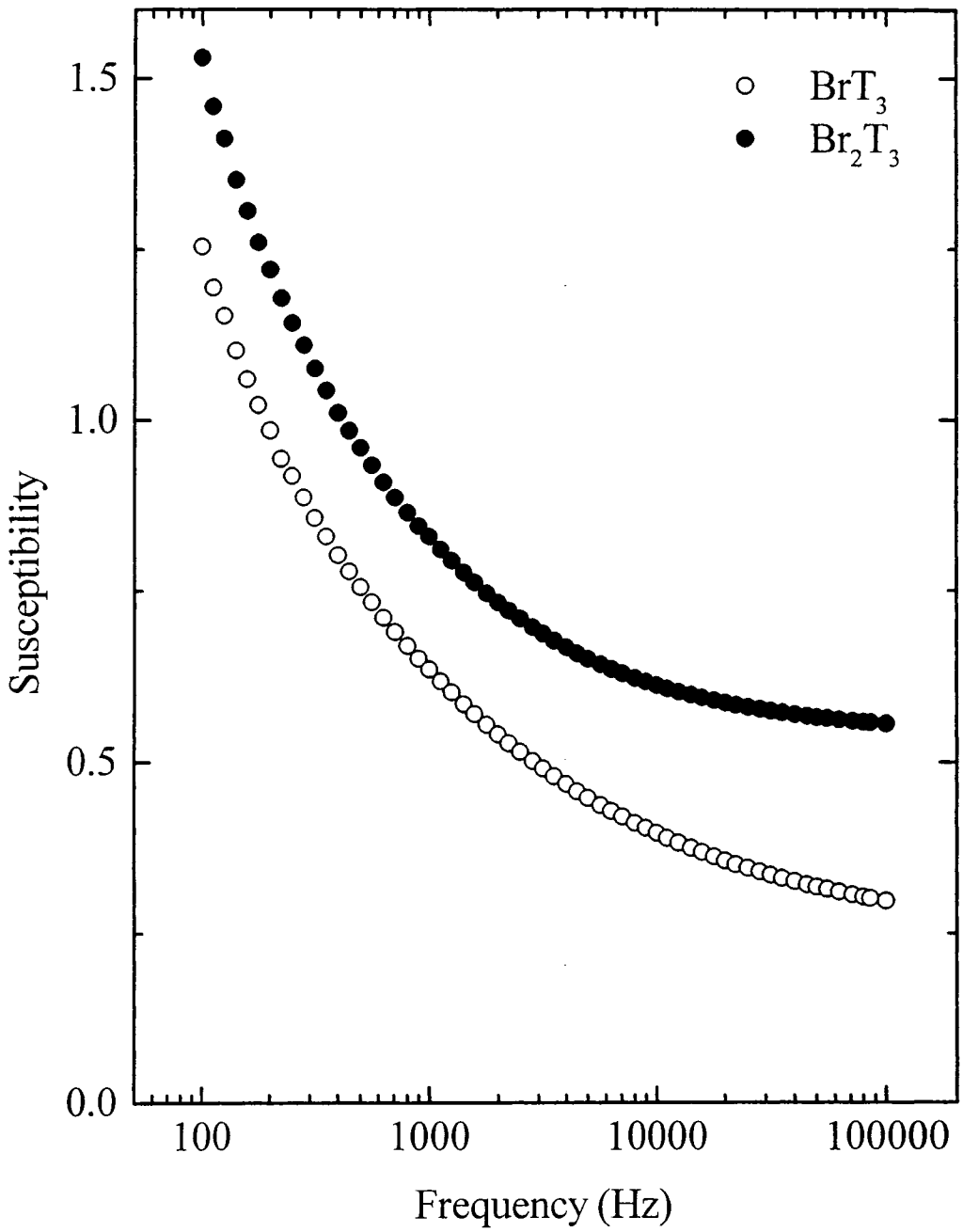


Figure 13: Susceptibility vs. frequency graph of BrT_3 and Br_2T_3

3.4 Summary

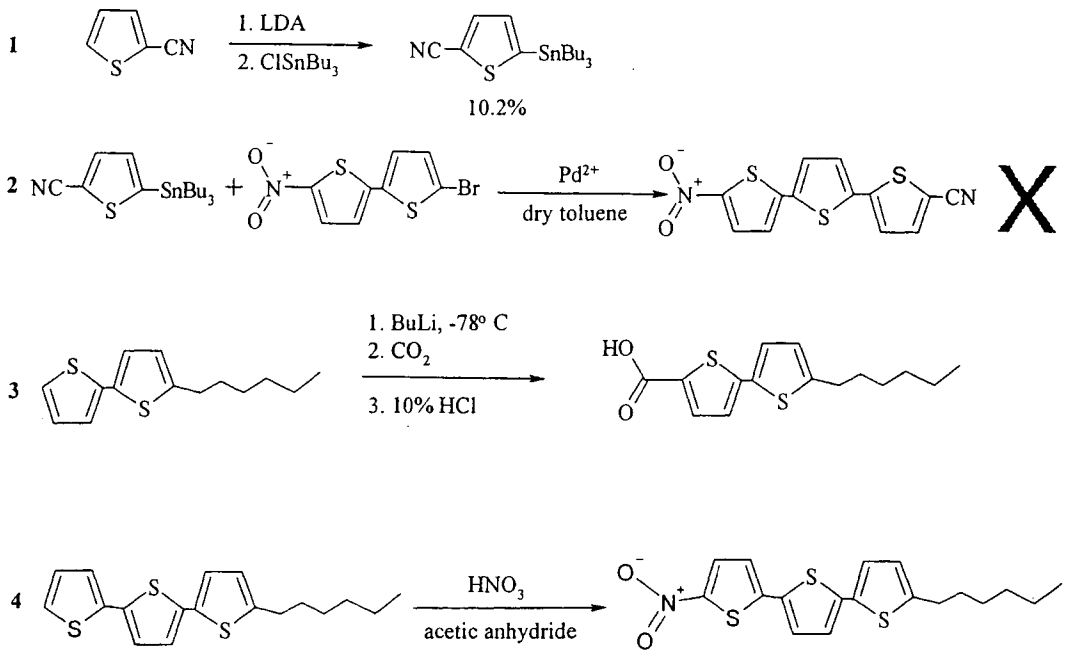
The following compounds were synthesized and fully characterized: T_2NO_2, BrT_2NO_2, T_3NO_2, BrT_3NO_2, and IT_3NO_2. The following compounds were also synthesized, but only partially characterized: NH_2T_3Br, $NH_2T_4NO_2$, T_2Hx, T_3Hx, HxT_3NO_2 and $COOHT_2Hx$.

The UV-Vis spectra of the nitro- and halo-derivatives indicated that the addition of a nitro group caused a bathochromic shift whereas the addition of a halogen group had little effect. The fluorescence data for the bithiophene series showed that the attachment of a nitro group has little effect, while the addition of a bromo group causes a shift to longer wavelength of fluorescence. The fluorescence data for the terthiophene series showed that an attachment of a single bromo or nitro group caused an shift to longer wavelength of fluorescence, but the attachment of a second end-group has minimal effect, regardless of the identity of the group (halogen or nitro). The phosphorescence data showed that oligothiophenes with only a nitro group or bromo group alone were not phosphorescent but the attachment of both a halogen and a nitro group gives a phosphorescent compound. Further, the identity of the halogen does not matter since the spectra of BrT_3NO_2 and IT_3NO_2 are virtually the same.

Conductivity increases with the attachment of either a nitro group or a halogen. The identity of the halogen (Br or I) does not appear to matter. On the other hand, the susceptibility is halogen controlled. The susceptibility of BrT_3NO_2 is much greater than IT_3NO_2.

3.5 Future Work

In the future we will expand the hexyl- and nitro-series by adding different end groups. The synthesis of NO_2T_3Hx, NO_2T_3CN and $COOHT_3Hx$ has already been attempted, and we are in the process of improving the reactions and purifying the products (see Scheme 29). We may look into making HxT_3CN and $COHT_3Hx$. We may in the future investigate better methods of purification since this seemed to be the biggest challenge in this thesis. We used a rough pump (10^{-2} torr) with the tube oven to sublime our products at lower temperatures to avoid decomposition; use of a differential pump could be used to reduce the pressure by two orders of magnitude and further reduce the temperature required to sublime our heat sensitive products.



Scheme 29

Also, we intend on extending the current series with more thiophene groups, e.g. BrT_5NO_2, IT_5NO_2, NO_2T_4Hx, NO_2T_5Hx, etc.

Chapter 4

Experimental

T_2,[32] T_3,[30] T_4,[31] T_2Br,[43] T_3Br,[43] T_2Br_2[43] and T_3Br_2[43] were all synthesized according to standard literature methods. All reactions were performed under nitrogen unless otherwise stated. See Appendix 2 for lists of chemicals used as received and those that were further purified. See Appendix 3 for instrumentation information.

Preparation of 2,2'-bithiophene, T_2. This compound was prepared by the literature route,[32] but is included here as an example of a typical Kumada synthesis Over the course of an hour, 25.5 g (156 mmol) of TBr in 50 mL of dry ether was added dropwise to 4.53 g (186 mmol) of Mg turnings in 50 mL of dry ether at 0 °C. The reaction was initiated with a small amount of TBr and a crystal of iodine. The solution was warmed to room temperature and stirred for a further 3 hours, after which time it was added via cannula to a solution of 25.5 g (156 mmol) of TBr and 0.53 g (0.98 mmol) of Ni(dppp)Cl_2 in 50 mL dry ether at 0 °C. This solution was left stirring overnight at room temperature. The next day the solution was poured into 200 mL of a saturated NH_4Cl solution. The solution was extracted with ether (3×100 mL), the ether was rotary evaporated (removed under the reduced pressure of a rotary evaporator), and the brown oil vacuum distilled, giving a yield of 23.5 g (91%). The mpt. was identical with the commercially available product (32-33 °C).

Preparation of 2,2':5',2"-terthiophene, T_3. This compound was prepared by the literature (Kumada) route.[30] The orange powder was purified by recrystallization from hexanes, 8.91 g (34%). The mpt. was identical with the commercially available product (93-95 °C).

Preparation of 2,2':5'.2":5",2"'-quaterthiophene, T_4. This compound was previously made by a different route.[31] Over the course of one hour, 27.0 g (166 mmol) of TBr in 50 mL of dry ether was added dropwise to 4.03 g (166 mmol) of Mg turnings in 50 mL of dry ether at 0 °C. The reaction was initiated with a small amount of TBr and a crystal of iodine. The solution was warmed to room temperature and stirred for a further 3 hours, after which time it was added via cannula to a solution of 10.76 g (33 mmol) of T_2Br_2, and 0.42 g (0.77 mmol) of Ni(dppp)Cl_2 in 50 mL dry ether at 0 °C. This solution was left stirring overnight at room temperature. The next day the solution was poured into 200 mL of a saturated NH_4Cl solution, and the precipitate vacuum filtered to yield an orange powder, which was recrystallized from chlorobenzene, giving a yield of 5.37 g (49%). The mpt. was consistent with the literature value (215-216 °C).

Preparation of 5,5'-dibromo-2,2'-bithiophene, Br_2T_2. This compound was prepared by the literature route.[43] In the dark, 23.97 g (144 mmol) of T_2 was dissolved in 200 mL DMF. To this stirred solution 67.05 g (377 mmol) recrystallized NBS was added, portionwise over the course of several hours. The mixture was stirred overnight. The solution was poured into distilled water, vacuum filtered, washed with ethanol, and air dried. Typical yields were in excess of 75 %. The product was recrystallized in ethanol prior to further use. The mpt. was consistent with the literature value (145 °C).

Preparation of 5,5'-dibromo-2,2'-terthiophene, Br_2T_3. This compound was prepared by the literature route (as per T_2Br_2).[43] Typical yields were in excess of 70 %. The product was recrystallized in 2:1 toluene:hexane prior to further use. The mpt. was consistent with the literature value (156-157 °C).

Preparation of 5-bromo-2,2'-bithiophene, BrT_2. This procedure was adapted from the published route.[43] In 100 mL THF, 4.08 g (25 mmol) T_2 was dissolved and then cooled to -3 °C in a freezer. NBS (4.78 g, 27 mmol) was added portionwise, with shaking, to the T_2 solution, after which the flask was returned to the freezer. The addition took several hours. The solution was rotary evaporated in the morning to yield a pale green solid. The solid was melted and vacuum distilled to yield a pale yellow solid (4.79 g, 80%). The mpt. was consistent with the literature value (30-33 °C).

Preparation of 5-bromo-2,2':5',2''-terthiophene, BrT_3. This procedure was adapted from the published route.[43] In 200 mL DMF, 5.72 g (23 mmol) T_3 was dissolved and then cooled to -3 °C in a freezer. NBS (4.36 g, 24 mmol) was added portionwise, with shaking, to the T_3 solution. After each addition, the flask was returned to the freezer. The addition took several hours in total. After this time 200 mL distilled water was added to the solution. The precipitate was vacuum filtered, washed with ethanol, and then recrystallized in 1:2 toluene:hexanes. The precipitate was vacuum filtered and air-dried to yield a golden-yellow powder. Typical yields were in excess of 70%. The mpt. was consistent with the literature value (136-137 °C).

Preparation of 2-bromo-5-nitrothiophene, $BrTNO_2$. In 20 mL acetic anhydride 4.42 g (27 mmol) TBr was added, then 3.30 g (52 mmol) HNO_3 (90% excess) was added dropwise while the solution was stirred in an ice bath. The solution turned dark red. It was then added to 100 mL saturated sodium bicarbonate solution and extracted with dichloromethane (3×100 mL). The organic layer was dried over magnesium sulphate and the dichloromethane was rotary evaporated. The subsequent brown oil was purified by vacuum distillation which yielded 3.58 g (64%). ^1H NMR (δ, d_6-DMSO): 6.82 (d, J_{AB}

5.0 Hz, 1H), 6.28 (d, J_{AB} 5.0 Hz, 1H) ppm. Mass spectrum: *m/e* 209 (M^+, 65%), 177 ($[M-O_2]^+$, 36%), 161 ($[M-NO_2]^+$, 10%), 151 ($[M-CNO_2]^+$, 100%).

Preparation of 5-nitro-2,2'-bithiophene, T_2NO_2. To 50 mL acetic anhydride, 2.20 g (35 mmol) of HNO_3 (15% excess) was added, then 5.01 g (30 mmol) T_2 was added dropwise while stirring in an ice bath. The solution turned brown-black; it was added to 100 mL saturated sodium bicarbonate solution and extracted with dichloromethane (3×100 mL). The organic layer was dried over magnesium sulphate and the dichloromethane was rotary evaporated. The subsequent brown oil was purified by vacuum distillation which yielded an orange liquid that turned to a solid upon cooling, 3.75 g (58.9%). Subsequently, the product was sublimed *in vacuo* using a tube oven, which produced a yellow powder, mpt. 105.4-108.1 °C. ^{1}H NMR (δ, d_6-DMSO): 8.12 (d, J_{AB} 3.5 Hz, 1H), 7.81 (d, J_{AB1} 5.0 Hz, 1H), 7.71 (d, J_{AB2} 2.5 Hz, 1H), 7.45 (d, J_{AB3} 4.5 Hz, 1H), 7.21 (t, J_{AB4} 6 Hz, 1H) ppm. Mass spectrum: *m/e* 211 (M^+, 75%), 181 ($[M-NO]^+$, 10%), 165 ($[M-NO_2]^+$, 7%), 153 ($[M-CNO_2]^+$, 9%), 121 ($[M-SCNO_2]^+$, 100%), 108 ($[M-SC_2NO_2]^+$, 11%), 69 (26%), 46 ($[M-SC_4H_3]^+$, 15%). Anal. Calcd for $C_8H_5NO_2S_2$: C, 45.48; H, 2.39; N, 6.63 %. Found: C, 44.34; H, 2.49; N, 6.37 %.

Preparation of 5-bromo-5'-nitro-2,2'-bithiophene, BrT_2NO_2. In 25 mL acetic anhydride 4.79 g (20 mmol) T_2Br was dissolved, then 1.50 g (24 mmol) of HNO_3 (15% excess) was dissolved in 20 mL acetic anhydride, which was in an ice bath. Then dropwise, while stirring, the acid solution was added to the T_2Br solution. The mustard-yellow solution was added to 100 mL saturated sodium bicarbonate solution and extracted with dichloromethane (3×100 mL). A very fine precipitate appeared, so the dichloromethane was rotary evaporated without drying over magnesium sulphate. The

powder was recrystallized in ethanol. It yielded a yellow powder, which was then sublimed using a pot sublimer. It was further purified by sublimation *in vacuo* using a tube oven (1.45 g, 25.6 %), mpt. 189.4-193.3 °C. ^{1}H NMR (δ, d_6-DMSO): 8.12 (d, J_{AB} 4.0 Hz, 1H), 7.56 (d, J_{AB1} 4.0 Hz, 1H), 7.45 (d, J_{AB2} 4.5 Hz, 1H), 7.36 (d, J_{AB3} 4.0 Hz, 1H) ppm. Mass spectrum: *m/e* 291 (M^+, 98%), 261 ($[M-NO]^+$, 26%), 245 ($[M-NO_2]^+$, 23%), 233 ($[M-CNO_2]^+$, 12%), 201 ($[M-SCNO_2]^+$, 100%), 164 (53%). Anal. Calcd for $C_8H_4BrNO_2S_2$: C, 33.12; H, 1.38; N, 4.83 %. Found: C, 32.75; H, 1.62; N, 4.51 %.

Attempted preparation of 5-iodo-5'-nitro-2,2'-bithiophene, IT_2NO_2. T_2NO_2 (1.79 g, 8.5 mmol) was dissolved in 100 mL THF. While stirring, in the dark, NIS (2.05 g, 9 mmol) was added slowly, a portion every ten minutes, then the solution was left to stir overnight. Then 100 mL of distilled water was added, extracted with dichloromethane (3×100 mL). The organic layer was dried over magnesium sulphate and the dichloromethane was rotary evaporated. The subsequent powder was then purified using a pot sublimer to yield a yellow-orange powder (1.8562 g, 65%). The ^{1}H NMR spectrum indicated a mixture of products. It could not be purified enough for analysis although the mass-spectrum indicated that some IT_2NO_2 was produced.

Preparation of 5-nitro-2,2':5',2"-terthiophene, T_3NO_2. T_3 (8.75 g, 35 mmol) was dissolved in 100 mL acetic anhydride with heating. Then 2.75 g (44 mmol) HNO_3 (15% excess) was added dropwise while stirring. The brown-black solution was added to 200 mL saturated sodium bicarbonate solution. A red precipitate formed, which was vacuum filtered to yield a red solid. Recrystallization of the solid was attempted in 1:2 toluene:hexanes. No precipitate formed so the toluene/hexanes was rotary evaporated, to yield an orange powder (3.19 g, 31%). Subsequently, the product was sublimed *in vacuo*

in a tube oven, which produced a red powder, mpt. 157-160 °C. ^{1}H NMR (δ, d_6-DMSO): 8.12 (d, J_{AB} 4.5 Hz, 1H), 7.69 (d, J_{AB1} 4.0 Hz, 1H), 7.63 (d, J_{AB2} 6.0 Hz, 1H), 7.46 (d, J_{AB3} 4.5 Hz, 2H), 7.41 (d, J_{AB4} 4.0 Hz, 1H), 7.15 (t, J_{AB5} 4.5 Hz, 1H) ppm. Mass spectrum: *m/e* 293 (M^+, 100%), 263 ($[M\text{-}NO]^+$, 10%), 247 ($[M\text{-}NO_2]^+$, 25%), 235 ($[M\text{-}CNO_2]^+$, 7%), 203 (87%). Anal. Calcd for $C_{12}H_7NO_2S_3$: C, 49.13; H, 2.40; N, 4.77 %. Found: C, 48.33; H, 2.61; N, 4.61 %.

Preparation of 5-bromo-5''-nitro-2,2':5',2"-terthiophene, BrT_3NO_2. T_3NO_2 (0.78 g, 2.7 mmol) was dissolved in 100 mL DMF. While stirring, in the dark, NBS (1.84 g, 10 mmol) was added slowly, a portion every ten minutes, and the solution was left to stir overnight. In the morning, 200 mL of distilled water was added and a red solid precipitated, which was vacuum filtered. The red solid was then recrystallized from toluene. The mpt. was determined to be 171.9-174.9 °C. Mass spectrum: *m/e* 373 (M^+, 100%), 343 ($[M\text{-}NO]^+$, 12%), 327 ($[M\text{-}NO_2]^+$, 27%), 283 ($[M\text{-}SCNO_2]^+$, 73%), 145 (33%). Anal. Calcd for $C_{12}H_6BrNO_2S_3$: C, 38.72; H, 1.62; N, 3.76 %. Found: C, 37.90; H, 1.85; N, 3.22 %. Low solubility in all common solvents prevented an analysis by ^{1}H NMR spectroscopy.

Preparation of 5-iodo-5''-nitro-2,2':5',2"-terthiophene, IT_3NO_2. T_3NO_2 (3.19 g, 11 mmol) was dissolved in 250 mL DMF. While stirring in the dark, NIS (2.48 g, 11 mmol) was added slowly, a portion every ten minutes, and the solution was left stirring for three weeks. 200 mL of distilled water was added and a red solid precipitated, which was vacuum filtered to yield a red-orange powder (0.27 g, 70%). The red-orange solid was then sublimed *in vacuo* using a tube oven. The mpt. was determined to be 232.4-233.2 °C. ^{1}H NMR (δ, $CDCl_3$): 7.86 (d, J_{AB} 4.5 Hz, 1H), 7.26 (d, J_{AB1} 3.0 Hz, 1H), 7.20 (d, J_{AB2}

4.0 Hz, 1H), 7.09 (d, J_{AB3} 4.0 Hz, 1H), 7.07 (d, J_{AB4} 4.0 Hz, 1H), 6.91 (d, J_{AB5} 4.0 Hz, 1H) ppm. Mass spectrum: *m/e* 419 (M^+, 100%), 389 ($[M-O]^+$, 5%), 373 ($[M-NO_2]^+$, 23%), 329 (40%), 293 ($[M-I]^+$, 11%), 248 ($[M-NO_2I$, 7%). Anal. Calcd for $C_{12}H_6INO_2S_3$: C, 34.38; H, 1.44; N, 3.34 %. Found: C, 34.50; H, 1.65; N, 3.11 %.

Attempted preparation of 5-nitro-2,2':5'.2":5",2"'-quaterthiophene, T_4NO_2. T_4 (5.31 g, 16 mmol) was dissolved in 100 mL acetic anhydride. 1.38 g (22 mmol) HNO_3 (15% excess) was added dropwise while stirring at reflux. The red solution was then added to 200 mL saturated sodium bicarbonate solution. A red precipitate formed, and the reaction mixture was vacuum filtered to yield a red solid. The powder was recrystallized from chlorobenzene and the precipitate vacuum filtered to yield a red powder (3.47 g, 57.5%). It could not be purified enough for analysis although the mass spectrum indicated that some T_4NO_2 was produced. Low solubility in all common solvents prevented an analysis by ^1H NMR spectroscopy.

Attempted preparation of 5-bromo-5"'-nitro-2,2':5'.2":5",2"'-quaterthiophene, BrT_4NO_2. T_4NO_2 (1.73 g, 4.6 mmol) was dissolved in 250 mL DMF. While stirring in the dark, NBS (1.11 g, 6.2 mmol) was added slowly, a portion every ten minutes, then the solution was left to stir overnight. In the morning, 200 mL of distilled water was added and a red solid precipitated, which was vacuum filtered to give a burgundy solid (1.61g, 77%). It could not be purified enough for analysis though the mass spectrum indicated that some BrT_4NO_2 was produced. Low solubility in all common solvents prevented an analysis by ^1H NMR spectroscopy.

Attempted preparation of 5-iodo-5'''-nitro-2,2':5'.2":5",2"'-quaterthiophene, IT_4NO_2. T_4NO_2 (1.61 g, 4.3 mmol) was dissolved in 250 mL DMF. While stirring, in the dark, NIS (1.35 g, 6 mmol) was added slowly, a portion every ten minutes, and the solution was left to stir overnight. In the morning, 200 mL of distilled water was added and a red solid precipitated, which was vacuum filtered to yield a red-orange powder (1.59 g, 74%). It could not be purified enough for analysis although the mass-spectrum indicated that some IT_4NO_2 was produced. Low solubility in all common solvents prevented analysis by ^1H NMR spectroscopy.

Preparation of 2-nitro-5-(tributyltin)thiophene, NO_2TSnBu_3. $BrTNO_2$ (3.58 g, 17 mmol) was dissolved in 100 mL dry THF and the solution cooled to -30 °C. Then 1.54 g (24 mmol) of BuLi was added via syringe maintaining the temperature at -30 °C. The solution was stirred at -30 °C for one hour. Next 8.21 g (25 mmol) Bu_3SnCl was added via syringe at -30 °C, and the reaction was warmed to room temperature and stirred overnight. The resulting black solution was poured into 100 mL of distilled water and extracted with ether (3×100 mL). The organic layer was then dried over magnesium sulphate and the ether was rotary evaporated. The resulting black oil was purified by vacuum distillation, which yielded 3.24 g of golden brown oil (45%). ^1H NMR (δ, $CDCl_3$): 7.19 (d, J_{AB} 3.0 Hz, 1H), 6.98 (d, J_{AB} 3.0 Hz, 1H), 1.60 (m, 2H), 1.40 (m, 2H), 1.20 (m, 2H), 0.98 (m, 3H) ppm.

Attempted preparation of 2-amino-5-bromothiophene, NH_2TBr. TBr (5.0 g, 31 mmol) and $NaNH_2$ (1.72 g, 44 mmol) were dissolved in 30 mL dry toluene. The solution was refluxed for three hours, and the resulting brown solution was left to stir overnight at room temperature. The solution was then poured into 100 mL of distilled water, and

extracted with ether (3×100 mL). The organic layer was dried over magnesium sulphate and the ether was rotary evaporated. The subsequent brown oil was then distilled using vacuum distillation, yielding 0.731 g (13.4%) of a clear liquid. The product was used without further characterization or purification.

Preparation of 5-amino-5"-bromo-2,2':5',2"-terthiophene, NH_2T_3Br. In 30 mL of dry toluene 3.04 g (9.3 mmol) BrT_3 and 0.58 g (15 mmol) $NaNH_2$ (62% excess) was dissolved. The orange solution was refluxed for 2 hours, after which time it turned dark brown with a yellow tinge. It was left stirring overnight at room temperature. In the morning, the solution had turned mustard yellow. It was poured into 100 mL of distilled water, whereupon a yellow precipitate formed. This precipitate was vacuum filtered and washed with ethanol. The product dried to a dark yellow solid 2.56 g (81%). Infrared spectrum (4000-600 cm^{-1}): 3200 (s, N-H stretch), 1550 (w, N-H bend), 1000 (w) cm^{-1}.

Attempted preparation of 2-amino-2'-nitrobithiophene, $NH_2T_2NO_2$.

Method 1. $Sn(Bu)_3TNO_2$ (1.74 g, 4.13 mmol), NH_2TBr (0.73 g, 4.10 mmol), and $(PPh_3)_2PdCl_2$ (0.13 g, 0.18 mmol) were added together in 60 mL of dry toluene and refluxed for 4 hours. The solution was left stirring overnight and turned red by the morning. The toluene was rotary evaporated to yield a red oil, which was vacuum distilled to give a yellow oil. The yellow oil was purified by column chromatography (silica gel, 50% ether in hexanes). It yielded an orange solid (0.61 g, 32%), in which the IR spectrum showed no NH_2 peak.

Method 2. T_2NO_2 (1.80 g, 8.5 mmol) and $NaNH_2$ (0.53 g 13.5 mmol) were dissolved in 30 mL of dry toluene. The solution was then refluxed for 2 hours, and left stirring overnight at room temperature. In the morning, the brown-green-yellow solution

was added to 100 mL of distilled water, and extracted with ether (3×100 mL). The organic layer was dried over magnesium sulphate and the ether was rotary evaporated. The subsequent oil was then vacuum distilled to produce an orange liquid that solidified upon cooling. Pot sublimation was attempted to purify the product, but it decomposed to an intractable black solid. The ^{1}H NMR spectrum and the mass spectrum indicated that the reaction was unsuccessful.

Attempted preparation of 5-amino-5'-nitro-2,2':5',2"-terthiophene, $NH_2T_3NO_2$. T_3NO_2 (11.78 g, 40 mmol) and $NaNH_2$ (5.24 g, 13 mmol) were dissolved in 100 mL of dry toluene. The solution was then refluxed for 2 hours, and left stirring overnight at room temperature. In the morning, the maroon solution (with green fluorescence) was added to 100 mL of distilled water. A maroon precipitate formed, which was vacuum filtered. The subsequent powder was sublimed *in vacuo* using a tube oven, which the ^{1}H NMR spectrum showed only yielded T_3NO_2.

Attempted preparation of 5-amino-5"'-nitro-2,2':5'.2":5",2"'-quaterthiophene, $NH_2T_4NO_2$. $Sn(Bu)_3TNO_2$ (3.24 g, 8.0 mmol), BrT_3NH_2 (2.56 g, 8.0 mmol), and $(PPh_3)_2PdCl_2$ (0.23 g, 0.32 mmol) were added together in 60 mL of dry toluene and refluxed. The solution was left stirring overnight, it turned rusty red in the morning. The toluene was rotary evaporated and the subsequent red-orange solid was recrystallized in hexanes to yield an orange powder (2.35 g, 80%), mpt. 106.4-119.9 °C. Infrared spectrum (4000-600 cm^{-1}): 3400 (s, N-H stretch), 1630 (w, N-H bend) cm^{-1}. Mass spectrum: *m/e* 375 ($[M-NH_2]^+$, 10%), 328 ($[M-NO_2-NH_2]^+$, 100%), 283 (25%), 248 (27%), 203 (50%). The mass spectrum indicated that the NH_2 never attached and that the

NH_2 peaks in the IR spectrum may be from inorganic sources, e.g. starting materials. Low solubility in all common solvents prevented analysis by ^1H NMR spectroscopy.

Preparation of 2-hexylthiophene, THx. This compound was previously made by the literature route.[42] Product was purified by vacuum distillation to give a yellow liquid (18.43 g, 62%). ^1H NMR (δ, d_6-DMSO): 7.3 (d, J_{AB} 5.0 Hz, 1H), 6.95 (t, J_{AB1} 3.5 Hz, 1H), 6.85 (d, J_{AB2} 1.0 Hz, 1H), 2.8 (m, 2H), 1.6 (m, 2H), 1.3 (m, 6H), 0.9 (m, 3H) ppm.

Preparation of 2-bromo-5-hexylthiophene, BrTHx. This compound was synthesized by a procedure modified from the literature route.[42] THx (17.88 g, 106 mmol) was dissolved in 200 mL THF. While stirring, in the dark, NBS (20.01 g, 112 mmol) was added slowly, a portion every ten minutes, and the solution was left to stir overnight. In the morning, 200 mL of distilled water was added, the organics extracted into dichloromethane (3×100 mL). The organic layer was dried over magnesium sulphate and the dichloromethane was rotary evaporated. This yielded a yellow oil that was vacuum distilled, to give a yellow liquid (16.06 g, 61%). ^1H NMR (δ, d_6-DMSO): 7.03 (d, J_{AB} 3.5 Hz, 1H), 6.71 (d, J_{AB1} 3.5 Hz, 1H), 2.8 (m, 2H), 1.6 (m, 2H), 1.3 (m, 6H), 0.9 (m, 3H) ppm.

Preparation of 5-hexyl-2,2'-bithiophene, T_2Hx. Over the course of one hour, 12.2 g (75 mmol) of TBr in 50 mL of dry ether was added dropwise to 2.23 g (92 mmol) of Mg turnings in 50 mL of dry ether at 0 °C. The solution was warmed to room temperature and stirred for a further 3 hours, after which time it was added via cannula to a solution of 16.06 g (65 mmol) of BrTHx and 0.55 g (1.01 mmol) of Ni(dppp)Cl_2 in 50 mL dry ether at 0 °C. This solution was left stirring overnight at room temperature. The next day, the solution was poured into 100 mL of a saturated NH_4Cl solution. The solution was

extracted with ether (3×100 mL), the organic layer was dried over magnesium sulphate and the ether was rotary evaporated. The brown oil was vacuum distilled for a yield of 5.69 g (35%). ^{1}H NMR (δ, d_6-DMSO): 7.38 (d, J_{AB} 10 Hz, 1H), 7.13 (d, J_{AB1} 35 Hz, 1H), 7.02 (d, J_{AB2} 10 Hz, 1H), 6.99 (t, J_{AB3} 10 Hz, 1H), 6.71 (d, J_{AB4} 5 Hz, 1H), 2.7 (m, 2H), 1.5 (m, 2H), 1.2 (m, 6H), 0.8 (m, 3H) ppm.

Preparation of 5-bromo-5'-hexyl-2,2'-bithiophene, BrT_2Hx. T_2Hx (4.88 g, 19 mmol) was dissolved in 200 mL THF. While stirring in the dark, NBS (5.10 g, 29 mmol) was added slowly, a portion every ten minutes, and the solution was left to stir overnight. Then 200 mL of distilled water was added, extracted with dichloromethane (3×100 mL), the organic layer was dried over magnesium sulphate and the dichloromethane was rotary evaporated. The brown oil was purified using a silica column with hexanes as the solvent. It yielded 4.45g (69%) of a yellow liquid, which the ^{1}H NMR spectrum showed to be a mixture of product and starting materials. It was used unpurified to make T_3Hx.

Preparation of 5-hexyl-2,2':5',2"-terthiophene, T_3Hx. Over the course of an hour, 3.7 g (23 mmol) of TBr in 25 mL of dry ether was added dropwise to 0.75 g (31 mmol) of Mg turnings in 25 mL of dry ether at 0 °C. The solution was warmed to room temperature and stirred for a further 3 hours. It was then added via cannula to a solution of 4.43 g (13 mmol) of BrT_2Hx and 0.50 g (0.92 mmol) of Ni(dppp)Cl_2 in 30 mL dry ether at 0 °C. This solution was left stirring overnight at room temperature. The next day, the solution was poured into 100 mL of a saturated NH_4Cl solution. The solution was extracted with ether (3×100 mL), the organic layer was dried over magnesium sulphate and the ether was rotary evaporated to yield a black-brown sludgy oil. The oil was purified by column chromatography (silica gel, hexanes), to yield a yellow powder

(0.58 g, 15%), mpt. 57.4- 60.9 °C. ^{1}H NMR (δ, d_6-DMSO): 7.52 (d, J_{AB} 4.0 Hz, 1H), 7.32 (d, J_{AB1} 6.3 Hz, 1H), 7.24 (d, J_{AB2} 4.0 Hz, 1H), 7.17 (d, J_{AB3} 3.5 Hz, 1H), 7.13 (d, J_{AB4} 3.5 Hz, 1H), 7.10 (t, J_{AB4} 4.0 Hz, 1H), 6.82 (d, J_{AB4} 5.0 Hz, 1H), 2.8 (m, 2H), 1.6 (m, 2H), 1.3 (m, 6H), 0.9 (m, 3H) ppm.

Attempted preparation of 5-hexyl-2,2':5',2"-terthiophene, HxT_3NO_2. HxT_3 (6.70 g, 20 mmol) was dissolved in 100 mL acetic anhydride with heating. Then 1.51 g (24 mmol) HNO_3 (15% excess) was added dropwise while stirring. The resulting brown-black solution was added to 100 mL saturated sodium bicarbonate solution. A red precipitate formed, which was vacuum filtered to yield a red solid. The solid was recrystallized in acetonitrile to yield a red solid. Subsequently, the product was sublimed *in vacuo* using a tube oven, which produced a red powder. Mass spectrum: *m/e* 377 (M^+, 66%), 345 ($[M-O_2]^+$, 10%), 332 ($[M-NO_2]^+$, 94%), 306 ($[M-(CH_2)CH_3]^+$, 100%), 261 ($[M-(CH_2)CH_3, NO_2]^+$, 96%).

Preparation of 5-carboxylic acid-5''-hexyl-2,2'-bithiophene, $COOHT_2Hx$. 1.03 g (3.1 mmol) BrT_2Hx was dissolved in 80 mL dry ether, and the solution was cooled down to -78 °C. 2.5 mL (4 mmol) BuLi was added dropwise over 10 minutes, then the reaction was stirred for 2 hours at -70 °C. After gaseous CO_2 was bubbled through the solution for 2 hours, 100 mL of 10% HCl solution was poured into the solution, and the reaction was stirred for a further 30 minutes. The solution was then extracted with ether (3×50 mL), the organic layer was dried over magnesium sulphate, and the ether rotary evaporated to yield a green powder (0.82 g, 90%), mpt. 92.5-99.5 °C. The powder was further sublimed *in vacuo* with a tube oven. ^{1}H NMR (δ, d_6-DMSO): 13.1 (broad), 7.64 (d, J_{AB} 4.0 Hz, 1H), 7.29 (d, J_{AB1} 3.5 Hz, 1H), 7.26 (d, J_{AB2} 4.0 Hz, 1H), 6.86 (d, J_{AB3} 3.5

Hz, 1H), 2.8 (m, 2H), 1.6 (m, 2H), 1.3 (m, 6H), 0.9 (m, 3H) ppm. Mass spectrum: *m/e* 294 (M^+, 35%), 223 ($[C_{10}H_7O_2S_2]^+$, 100%), 179 ($[C_9H_7S_2]^+$, 15%).

Modeling of the Gabriel Synthesis.[40] 1-bromo-4-nitrobenzene (2 g, 9.9 mmol), potassium pthalamide (2.07 g, 11 mmol), and cuprous chloride (0.98 g, 10 mmol) were dissolved in 100 mL dry DMF. The solution was refluxed for three hours and 10 mL of 20% HCl was added to acidify the solution. The reaction was refluxed a further two hours, was then allowed to cool and stirred overnight. The amber solution was then extracted with ether (3×100 mL) and the organic layer dried over magnesium sulphate. The ether was rotary evaporated. It yielded a green powder that was shown to be starting material by ^{1}H NMR spectroscopy.

Preparation of 2-cyano-5-tributyltinthiophene, CNTSnBu$_3$. This procedure was adapted from the published route.[12] LDA was generated *in situ* as follows: 4.8 g (47 mmol) diisopropylamine was dissolved in 100 mL dry THF and cooled to -70 °C, then 29.9 mL (48 mmol) BuLi was added slowly via syringe. The solution was warmed to room temperature to ensure complete reaction then cooled again to -78 °C. 5.2 g (47 mmol) of TCN was added via syringe over 2 minutes and the solution stirred at -70 °C for 1 hour. 15.3 g (47 mmol) of Bu_3SnCl was added via syringe over 5 minutes. The solution was stirred for 30 minutes, then allowed to warm to room temperature and stir overnight. The black solution was poured into 200 mL of distilled water and extracted with ether (3×100 mL). The organic layer was then washed with a brine solution (NaCl and water), dried over magnesium sulphate and the ether was rotary evaporated. The subsequent brown oil was purified by vacuum distillation to yield a brown liquid (1.94 g, 10.2%). The product was used without further characterization or purification.

Attempted preparation of 5-cyano-5'-nitro-2,2':5',2"-terthiophene, CNT_3NO_2. This procedure was adapted from the published route.[12] $Sn(Bu)_3TCN$ (1.94 g, 4.8 mmol), BrT_2NO2 (1.32 g, 4.5 mmol), and $(PPh_3)_2PdCl_2$ (0.20 g, 0.28 mmol) were added together in 60 mL of dry toluene and refluxed for 5 hours. The solution was left stirring overnight at room temperature and it had turned rusty red by the morning. The toluene was rotary evaporated. Recrystallization of the brown-burgandy sludge was attempted in hexanes to yield a yellow liquid which was left to cool. IR spectroscopy revealed that no CN group was present.

Appendices

Appendix 1: Experimental details for alternate syntheses

Attempted preparation of 2-nitrothiophene, TNO_2 (Zincke method). TBr (8.5 g, 52 mmol) and KNO_2 (5.51 g, 65 mmol) were added to 40 mL of glacial acetic acid. After stirring overnight, the yellow solution was added to 100 mL distilled water and extracted with chloroform (3×100 mL). The organic layer was dried over magnesium sulphate and the chloroform rotary evaporated. There was no product in the organic layer.

Attempted preparation of 2-bromo-5-nitrothiophene, $BrTNO_2$. In 10 mL acetic anhydride and 10 mL dichloromethane, 18.7 g (115 mmol) TBr was added. While stirring 3.5 mL of a fuming nitric acid/glacial acetic acid solution (3.5 mL fuming nitric acid in 30 mL glacial acetic acid) was added dropwise while stirring in an ice bath. The yellow solution was left stirring at room temperature for 6 hours, whereupon it turned red-orange. 60 mL distilled water was added to the solution, which was then extracted with dichloromethane (3×100 mL). The organic layer was dried over magnesium sulphate and the dichloromethane was rotary evaporated. The subsequent brown oil was purified by vacuum distillation. The resulting brown liquid smelled strongly of acetic acid. The oil was purified by column chromatography (silica gel, 10% ether in hexanes). This yielded a yellow oil, 0.35 g (1.5%). The ^1H NMR spectrum indicated it was an approximately 1:1 mixture of starting materials and product.

Attempted preparations of 5-nitro-2,2'-bithiophene, T_2NO_2.

Method 1. 2.75 g (44 mmol) HNO_3 was added to a 100 mL round bottom flask in an ice bath, then 7.5 g (77 mmol) H_2SO_4 was added slowly. Next, 3.15 g (13 mmol) T_2 was added dropwise to the solution while stirring. The solution turned black and

solidified. 50 mL distilled water was then added and stirred to break up the solid, then the mixture was extracted with ether (3×100 mL). The organic layer was dried over magnesium sulphate and the ether was rotary evaporated to yield a red-orange liquid and a brown-black solid. Neither of these products were the T_2NO_2, as shown by the ^1H NMR spectrum.

Method 2. In 10 mL acetic anhydride and 10 mL dichloromethane, 1.55 g (9.3 mmol) T_2 was added, then while stirring 3.5 mL of a fuming nitric acid/glacial acetic acid solution (3.5 mL fuming nitric acid in 30 mL glacial acetic acid) was added dropwise at 0 °C. Next 60 mL distilled water was added and stirred at room temperature for 5 minutes. The organic layer was then decanted, dried over magnesium sulphate, and the dichloromethane was rotary evaporated. The solution appeared to have some precipitate in it so it was left in the fridge overnight. In the morning the crystals that formed were vacuum filtered, but they were not T_2NO_2 (by ^1H NMR spectroscopy). The filtrate was extracted with dichloromethane (3×100 mL), dried over magnesium sulphate, and rotary evaporated. The subsequent brown oil was purified by vacuum distillation which yielded a yellow liquid, 0.43 g (21%). The ^1H NMR spectrum indicated this liquid was an approximately 1:1 mixture of starting materials and T_2NO_2.

Method 3 (Zinke method). T_2Br (6.0 g, 24 mmol) and KNO_2 (3.02 g, 35 mmol) were added to 70 mL of glacial acetic acid and the suspension stirred overnight. The green-yellow solution was then added to 100 mL distilled water and extracted with chloroform (3×100 mL). The organic layer was dried over magnesium sulphate and the chloroform was rotary evaporated, yielding a yellow-green solid. However, the ^1H NMR spectrum showed only starting materials.

Attempted preparation of 5-bromo-5'-nitro-2,2'-bithiophene, BrT_2NO_2. T_2NO_2 (3.41 g, 16 mmol) was dissolved in 100 mL DMF. While stirring in the dark, NBS (6.09 g, 34 mmol) was added slowly, a portion every ten minutes, and the solution was left to stir overnight. 200 mL of distilled water was added and a yellow solid precipitated, which was vacuum filtered. The ^1H NMR spectrum and the crystal morphology showed the material to be T_2Br_2.

Attempted preparation of 5-nitro-2,2':5',2"-terthiophene, T_3NO_2.

Method 1. $Sn(Bu)_3TNO_2$ (4.20 g, 9.9 mmol), BrT_2 (2.73 g, 11 mmol), and $(PPh_3)_2PdCl_2$ (0.31 g, 0.45 moles) were added together in 60 mL of dry toluene and refluxed for three hours. The solution was left stirring overnight at room temperature and had turned honey yellow by the morning. The toluene was rotary evaporated to yield a brown-red liquid, and 100 mL sodium bicarbonate solution was added (until basic) to neutralize any acetic acid. The solution was then extracted with ether (3×100 mL), the organic layer was dried over magnesium sulphate, and the ether rotary evaporated, yielding a sludgy brown solid. The solid was then recrystallized from hexanes. The orange precipitate was vacuum filtered to yield an orange powder. The ^1H NMR spectrum contained numerous aromatic peaks, indicating a variety of products.

Method 2 (Zinke method). T_3Br (2.51 g, 7.7 mmol) and KNO_2 (0.76 g, 8.9 mmol) were dissolved in 50 mL of glacial acetic acid and the solution was left stirring overnight. The resulting red solution was added to 100 mL distilled water and extracted with chloroform (3×100 mL). The organic layer was dried over magnesium sulphate and the chloroform was rotary evaporated to yield an orange solid. The ^1H NMR spectrum indicated only starting materials.

Attempted preparation of 2-(tributyltin)thiophene, Bu_3SnT. An LDA solution was made *in situ* by dissolving 7.4 mL (52 mmol) diisopropylamine in 100 mL dry THF, which was cooled to -30 °C. Then 33 mL (53 mmol) BuLi was added slowly via syringe, followed by 8.5 g (52 mmol) 2-bromothiophene via syringe. The solution was allowed to warm to room temperature, re-cooled to -30 °C, and 17 g (52 mmol) of Bu_3SnCl was added via syringe. The reaction was stirred overnight at room temperature. In the morning, the amber solution was poured into 100 mL of distilled water and extracted with ether (3×100 mL). The organic layer was dried over magnesium sulphate and the ether was rotary evaporated. The subsequent brown oil was purified by vacuum distillation. The ^1H NMR spectrum indicated only starting materials.

Attempted preparation of 2-heptylthiophene, THp. Over the course of an hour, 10 g (61 mmol) of TBr in 50 mL of dry ether was added dropwise to 1.5 g (62 mmol) of Mg turnings in 50 mL of dry ether at 0 °C. The reaction was initiated with a small amount of TBr and a crystal of iodine. The solution was warmed to room temperature and stirred for a further 3 hours, after which time it was added via cannula to a solution of 6.62 g (37 mmol) of HpBr and 0.3 g (0.55 mmol) of $Ni(dppp)Cl_2$ in 50 mL dry ether at 0 °C. This solution was left stirring overnight at room temperature. The next day, the solution was poured into 100 mL of a saturated NH_4Cl solution. The solution was extracted with ether (3×100 mL), the organic layer was dried over magnesium sulphate and the ether rotary evaporated. The resulting brown oil was vacuum distilled to yield a yellow liquid. The ^1H NMR spectrum showed that THp had not formed.

Attempted preparation of 2-ethylthiophene, TEt.

Method 1. Over the course of an hour, 5.13 g (31 mmol) of TBr in 50 mL of dry ether was added dropwise to 0.77 g (31 mmol) of Mg turnings in 50 mL of dry ether at 0 °C. The reaction was initiated with a small amount of TBr and a crystal of iodine. The solution was warmed to room temperature and stirred for a further 3 hours. It was then added via cannula to a solution of 3.50 g (32 mmol) of EtBr and 0.31 g (0.58 mmol) of $Ni(dppp)Cl_2$ in 50 mL dry ether at 0 °C. This solution was left stirring overnight at room temperature. The next day, the solution was poured into 100 mL of a saturated NH_4Cl solution. The solution was extracted with ether (3×100 mL), the organic layer was dried over magnesium sulphate and the ether rotary evaporated. Only a few drops of brown oil remained (not enough for ^1H NMR analysis).

Method 2. Over the course of an hour, 15.04 g (138 mmol) of EtBr in 50 mL of dry ether was added dropwise to 3.36 g (138 mmol) of Mg turnings in 50 mL of dry ether at 0 °C. The reaction was initiated with a small amount of the EtBr solution and a crystal of iodine. The solution was warmed to room temperature and stirred for a further 3 hours, after which time it was added via cannula to a solution of 22.44 g (138 mmol) of TBr and 0.40 g (0.74 mmol) of $Ni(dppp)Cl_2$ in 50 mL dry ether at 0 °C. This solution was left stirring overnight at room temperature. The next day, the solution was poured into 500 mL of a saturated NH_4Cl solution. The solution was extracted with ether (3×100 mL), the organic layer dried over magnesium sulphate and the ether rotary evaporated. The subsequent brown oil was vacuum distilled to yield two drops of a yellow liquid. The ^1H NMR spectrum showed only starting materials.

Attempted preparation of 5-hexyl-2,2'-bithiophene, T_2Hx. T_2 (10.31 g, 62 mmol) was dissolved in 130 mL of dry THF, the solution was then cooled to -85 °C, then 39 mL BuLi (62 mmol) was added dropwise over 15 minutes. The solution was then allowed to stir for 45 minutes at -60 °C. Next, 13 g (62 mmol) of HxI was added via syringe and the solution was warmed to room temperature and stirred for another 3 hours. The solution was then poured into 100 mL of distilled water, extracted with ether (3×100 mL), the organic layer dried over magnesium sulphate and the ether rotary evaporated. It yielded a dark green-blue oil that was vacuum distilled, to give a yellow liquid (11.91 g, 77%). The ^1H NMR spectrum showed it to be a mixture of T_2, T_2Hx_2, and T_2Hx (although it appeared to be mostly T_2Hx). ^1H NMR (δ, $CDCl_3$): 7.12 (d, J_{AB} 5 Hz, 1H), 7.07 (d, J_{AB1} 4.5 Hz, 1H), 6.96 (t, J_{AB2} 3.5 Hz, 1H), 6.65 (d, J_{AB3} 3.5 Hz, 1H), 2.7 (m, 2H), 1.7 (m, 2H), 1.3 (m, 6H), 0.9 (m, 3H) ppm.

Attempted preparation of 5-hexyl-2,2':5',2"-terthiophene, T_3Hx. T_3 (5.5 g, 22 mmol) was dissolved in 130 mL of dry THF, the solution was cooled down to -85 °C, then 14 mL BuLi (22 mmol) was added dropwise over 15 minutes. The solution was then allowed to stir for 45 minutes at -60 °C. Then 4.7 g (22 mmol) of HxI was added via syringe and the mustard yellow solution was warmed to room temperature and stirred overnight. In the morning, the clear-brown solution was poured into 100 mL of distilled water, extracted with ether (3×100 mL), and the organic layer dried over magnesium sulphate and the ether rotary evaporated. It yielded a brown oil which was dissolved in hexanes and left overnight to recrystallize. No product precipitated, so the hexanes were rotary evaporated to yield a green-black oil which solidified (7.36 g, 91.7%). The ^1H NMR spectrum showed a mixture of products.

Appendix 2: Starting Materials

A.2.1 Chemicals obtained commercially and used as received

acetic anhydride	Caledon
acetone	Caledon
ammonium chloride	Anachemia
[1,3-Bis(diphenylphosphino)-[propane]dichloronickel(II)	Aldrich
1-bromoethane	Aldrich
1-bromoheptane	Aldrich
1-bromohexane	Aldrich
1-bromo-4-nitrobenzene	Aldrich
2-bromothiophene	Aldrich
butyllithium	Aldrich
carbon dioxide	BOC
chlorobenzene	Caledon
chloroform	Fisher
cuprous chloride	Caledon
2-cyanothiophene	Aldrich
2,5-dibromothiophene	Aldrich
dichlorobis(triphenylphosphine)-palladium(II)	Aldrich
dichloromethane	Caledon
diethyl ether	Caledon
diisopropylamine	Aldrich
d-dimethylsulphoxide	Aldrich

d-chloroform	Aldrich
ethanol	Caledon
fuming nitric acid	Aldrich
glacial acetic acid	Fisher
hexanes	Caledon
hexylmagnesium bromide	Aldrich
hydrochloric acid	Caledon
iodine	Aldrich
1-iodohexane	Aldrich
magnesium sulphate	Caledon
magnesium turnings	Aldrich
N-iodosuccinimide	Aldrich
nitric acid	Anachemia
potassium nitrate	Aldrich
potassium pthalamide	Aldrich
sodium amide	Aldrich
sodium bicarbonate	Malinckrodt
sodium chloride	BDH
sulphuric acid	Anachemia
thiophene	Aldrich
tributyltin chloride	Aldrich

A.2.2 Chemicals obtained commercially and purified

diethyl ether (Caledon anhydrous)- dried with sodium-benzophenone and refluxed under N_2

N-bromosuccinimide (Aldrich)- recrystallized from water

N,N-dimethyformamide (BDH)- dried over Fisher 4A molecular sieves three times

tetrahydrofuran (Caledon)- dried with sodium-benzophenone and refluxed under N_2

toluene (BDH)- dried with sodium and refluxed under N_2

Appendix 3: General procedures and instrumentation

A.3.1 General synthetic procedures

All air-sensitive compounds were handled using standard Schlenk techniques under nitrogen using a double manifold vacuum line (vacuum/nitrogen), which was attached to an Savant VLP200 series rotary vacuum pump. Gradient sublimations were performed on an ATS 3210 series three-zone tube furnace with an ATS 2404 series programmable temperature controller, connected to an Edwards RV8 pump.

A.3.2 Instrumentation, Lakehead University

Melting points were obtained using an Electrothermal Digital Melting Point Apparatus IA9000 series 9100, and are uncorrected. Infrared spectra were recorded using a Perkin-Elmer 1320 Infrared Spectrophotometer with KBr optics, solids were recorded as nujol mulls and liquids recorded neat. ^{1}H NMR spectra were recorded using a Varian Unity Inova 500 MHz spectrometer. Mass spectra were performed using a VG Autospec spectrometer. Elemental CHN analyses were obtained using a 240-XA Analyser by the Lakehead University Instrumentation Laboratory. UV-vis spectra were recorded using a Perkin-Elmer Lambda II spectrometer. Fluorescent and phosphorescent spectra were recorded using a Perkin-Elmer LS 50 B Luminescence spectrometer. All conductivity results were obtained using a Hewlett Packard 4284 A Precision LCR Meter, 20 Hz- 1 MHz.

A.3.3 Collaboration

All the conductivity and susceptibility measurements were performed by Professor W.M. Sears, Department of Physics Lakehead University.

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