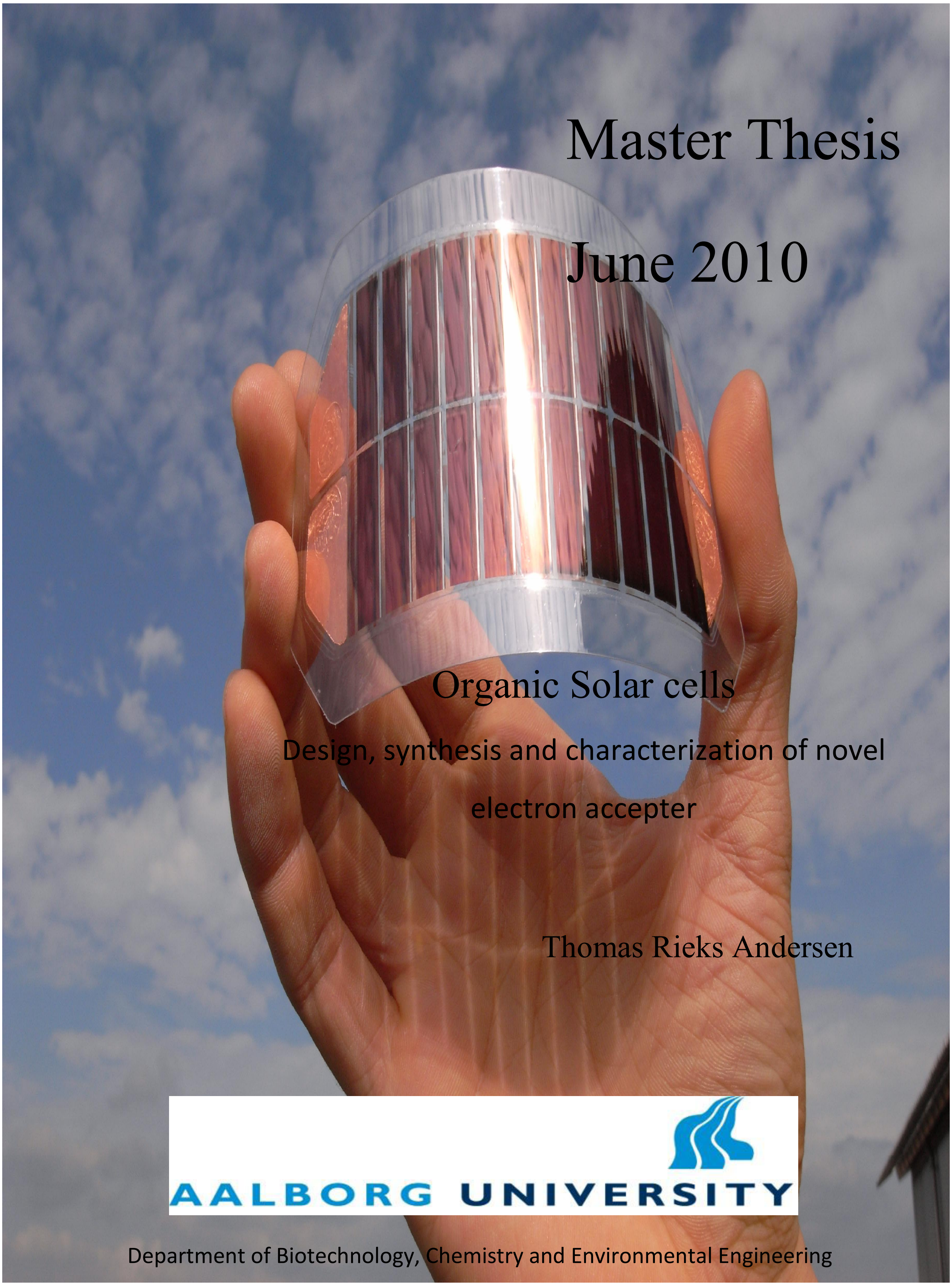

# Master Thesis

June 2010

# Organic Solar cells

## Design, synthesis and characterization of novel electron accepter

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## Title

Organic Solar Cells –
Design, synthesis and
characterization of novel
electron accepter

## Theme
Organic synthesis

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## Semester
K9K-K10K

## Project period
September 1st 2009 to June 15th 2010

Thomas Rieks Andersen

Number of copies 3

Number of pages 66

Number of appendices 3

## Abstract

This master thesis had the intent to develop a low band gap novel electron accepter oligomer with improved electron transport and acceptance properties. By adding electron withdrawing groups onto thiophenes linked to a known electron accepter core selected on the basis of band gaps of already prepared molecules as well as the position of the LUMO level in order to maximize solar cells performance.

N,N’-bis(2,2’-octyldodecyl)-naphthalene-1,8,4,5-bis(dicarboximide) and 3,3’dinitro-2,2’-dithiophene were chosen as the electron accepter core and side chain respectively. The end molecule could not be synthesized due to problem with the formation of 2-octyldodecyl-1-amine and Stille coupling reagent.

N,N’-bisoctyl-2,6-dithiophenenaphthalene-1,8,4,5-bis(dicarboximide) was obtained by Stille coupling. Its properties were tested with UV/vis spectroscopy and in organic solar cells with Poly(3-hexylthiophene) as electron donor. An efficiency of 0.084 % was obtained, the device was annealed which let to a decrease in efficiency to 0.055%.

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Sektion for Kemi

## Titel

Organiske Solceller –
Design, syntese og karakterisering
Af ny elektronaccepter

## Tema
Organisk syntese

## Kandidatstuderende
Thomas Rieks Andersen

## Vejleder
Donghong Yu

## Semester
K9K-K10K

## Projekt periode
1. September 2009 til 15. Juni 2010

Thomas Rieks Andersen

Oplagsantal 3

Sideantal 66

Bilagsantal 3

## Synopsis

Dette speciale havde til hensigt at udvikle en lav band gap ny elektron accepter oligomer med forbedret elektrontransport og -accepter egenskaber. Ved at påsætte elektron tiltrækkende grupper på thiophen påsat en allerede kendt elektron accepter kerne valgt på basis af band gaps af kendte molekyler også ud fra LUMO niveauet placering for at maksimere sol cellens præstation.

N,N’-bis(2,2’-octyldodecyl)-naphthalen-1,8,4,5-bis(dicarboximid) og 3,3’dinitro-2,2’-dithiophen var valgt som elektron accepter kernen and side kæderne respektivt. Slut molekylet kunne ikke blive syntetiseret på grnd af problemer med dannelsen af 2-octyldodecyl-1-amin og Stille koblings reagent.

N,N’-bisoctyl-2,6-dithiophenenaphthalen-1,8,4,5-bis(dicarboximid) blev fremskaffet ved Stille kobling. Dets egenskaber blev testet ved UV/vis spektroskopi og i en organisk sol celle med Poly(3-hexylthiophene) som elektron donor. En effektivitet på 0.084% blev opnået, apparaterne blev annealet, hvilket medførte et fald i effektivitet til to 0.055%.

# Preface

The picture on the cover is from www.exposolar.org.

This thesis is written on the basis of work done at the Faculty of Engineering, Science, and Medicine at Aalborg University in the period from September 2008 to June 2009 under the guidance of associate professor Donghong Yu, and at the Changchun Institute of Applied Chemistry Chinese Academy of Sciences under the supervision of Hui Tong and Hy Song.

The thesis is divided into a main part and an appendix, in the main part there will be found a short introduction to organic solar cell and motivation for them, an experimental part, results and discussion, and a conclusion of the synthesis and purification of the oligomer and its characterization.

I would like to thank my supervisor Donghong Yu for his direction, assistance, and guidance during this thesis, but also Hy song for his assistance in the laboratory during my time in the people's republic of China.

Furthermore I would like to thank:

- Shoa Yang and Lee Ying, Changchun Institute of Applied Chemistry Chinese Academy of Sciences, for taken their time to show me around and helping me getting settled in Changchun.
- Jan Alstrup, National Laboratory for Sustainable Energy, Risø DTU, for solar cell device manufacturing and testing.
- Anne Flensborg and Thorbjørn Terndrup Nielsen, section of chemistry, Aalborg University, for assistance and sparring in the laboratory.

# Table of Content

# 1. Introduction

In the last decade much political initiative have been taken to shift the world energy production from fossil fuels such as gas, oil, and coal, to renewable energy sources including wind energy, water turbines, photovoltaic cells etc. [Ren, 2009]. Renewable energy is perceived as a possible solution to lower the emission of green house gases, because it is generally either carbon dioxide free or neutral, and suitable for ensuring future energy supply.

Solar energy is by far the renewable energy sources with the greatest potential (cf. Table 1) up to thousands of times of the world consumption of energy [EIA, 2009].

| World consumption | Wind | Geothermal | Solar |
|---|---|---|---|
| 15 TW | 870 TW | 32 TW | 86,000 TW |

**Table 1: Energy available to be harvested for different renewable energies and the world energy consumption.**

Despite the great potential the prevalence of solar energy is very small, only 0.05 % of the world energy consumption is generated by solar energy [REN, 2009]. This is due to the high price for 1 kWh in comparison with other renewable energy sources (cf. Figure 1). The commercial available solar cells are generally inorganic solar cells based on silica crystals,which are expensive in production, because of high production temperatures [Braga et al., 2008], and therefore is the power outlet comparable expensive.

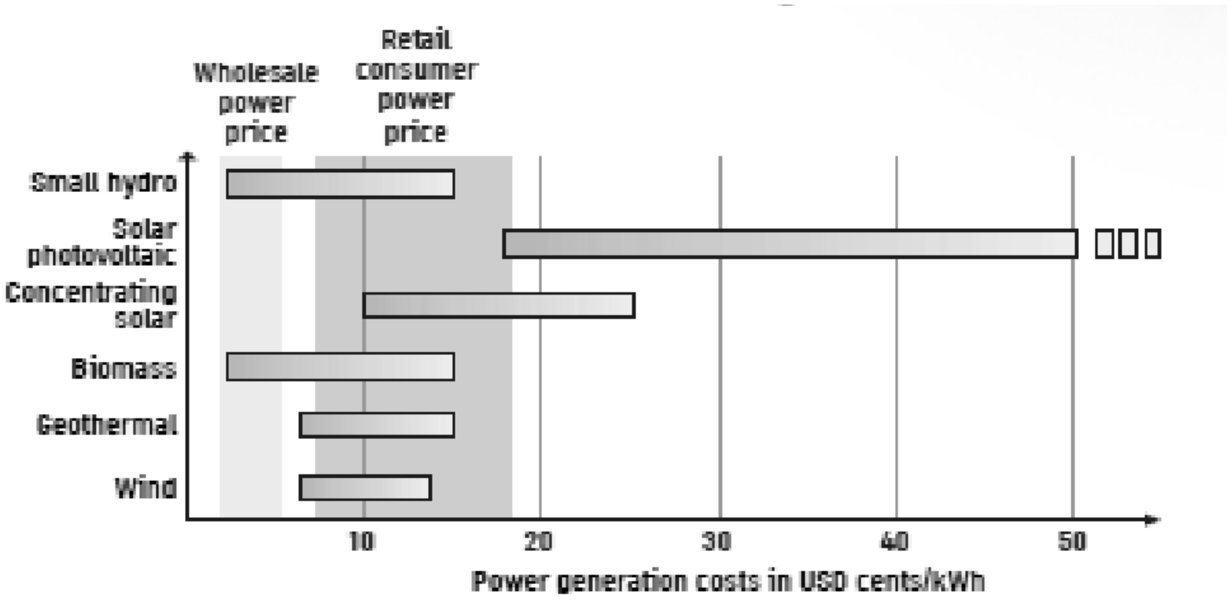

**Figure 1: Price in US Dollar cents pr. KWh [IEA, 2007].**

Organic based photovoltaic devises are in these years an area with extensive research as an inexpensive renewable energy source [Bundgaard & Krebs, 2007]. They are made from larger organic molecules or polymers, which are soluble in organic solvents and thereby easier to process. Their largest drawbacks are their low efficiency and lifetime [Gai et al., 2009].

## 1.1. The aim of the thesis

The aim of this project will be to address the efficiency problems for organic photovoltaic cells. A detailed description on how the solar cells works will be given in which the important parameters will be outlined. From this a possible solution will be suggested. A model system will be prepared and tested.

# 2. Organic photovoltaic devices

Organic photovoltaic devices have a planar layered structure consisting of a photon absorbing layer sandwiched between two electrodes. One of them being transparent allowing photons to pass into the absorbing layer, commonly used for this purpose is indium tin oxide. The other electrode is usually a low working metal, a metal from which electrons are easily withdrawn, often aluminum, calcium, or magnesium (cf. Figure 2). [Spanggaard & Krebs, 2004]

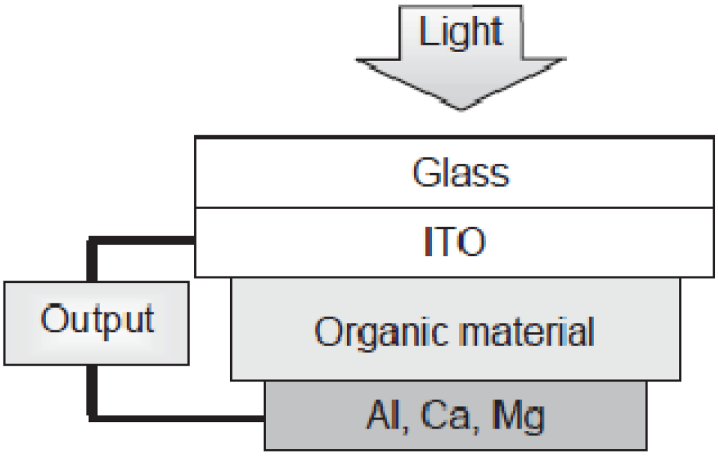

**Figure 2: Presentation of an organic photovoltaic device. The organic material is being sandwiched in between two electrodes indium tin oxide and a low working metal aluminum calcium or magnesium with a substrate of glass on top. [Spanggaard & Krebs, 2004]**

When a photon is absorbed in the active layer, an excitation of an electron occurs. It will be excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). This excitation leave's an empty electron spot in the HOMO also known as a hole. The excitated electron and hole is forming a neutral state called an exciton. In an OPV the exciton must be dissociated to free carriers to produce electricity [Kroon et al., 2008]. After dissociation the electron and hole will move to the different electrodes (cf. Figure 3). Where the electron will go through an external circuit to recombine with the hole on the electrode within this travel the excess energy is drained [Bundgaard & Krebs, 2007]. For dissociation to occur in an OPV, a strong electric field is needed. This can be either externally or internally introduced as an applied electric field or interfaces respectively [Günes et al., 2007]. The interface is formed by an electron accepting and electron donating material. Here the exciton will be split up due to difference in the ionization potential between the accepter and the donor [Armstrong et al. 2009].

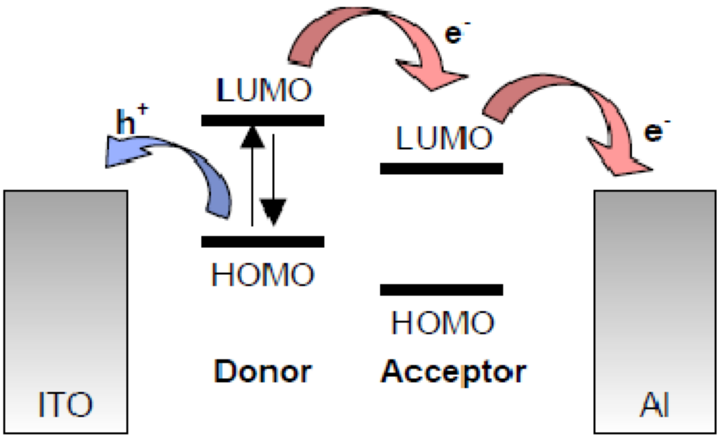

**Figure 3: Exciton dissociation at the interface between a donor accepter material, the electron goes from the donor to the accepter materials where as the hole stay in the donor, and they are transported to their respective electrodes. [Spanggaard & Krebs, 2004]**

The electron and hole in the exciton can recombine, this is when the excited electron “falls” back into the hole, which limits the life time of the exciton. When this occurs the energy is released and cannot be utilized for electricity. This lowers the exciton diffusion length to no longer than 1-10 nm [Kroon et al., 2008]. Therefore OPVs are oftenthe bulk heterojunction type. There consist of a homogeneous mixture of accepter- and donor materials in the active layer to ensure as large an interface area as possible [Hoppo et al., 2004].

For a material to act as an electron accepter, it needs to have a lower LUMO level than that of the donor. A potential difference of 0.3 eV has been found essential for exciton dissociation [Kroon et al., 2008]. The most commonly used electron accepters for OPV are soluble fullerene derivatives, especially [6,6]-phenyl- butyric acid methyl ester (PCBM) (cf. Figure 4). They have impressive electron transport and acceptance properties. Their largest drawback is poor absorption of photon in the visible and near infrared range [Koeppe & Sariciftci, 2006]. Organic molecules and inorganic crystals can also be used [Hoppe & Sariciftci, 2007].

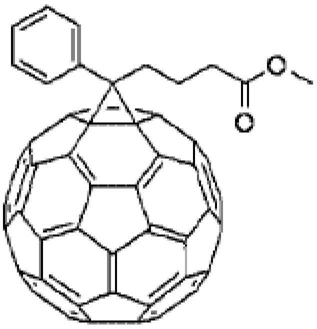

Figure 4: [C61]PCBM. One of the most commonly used electron accepter for OPV.

The efficiency of an OPV is measured as power conversion efficiency (PCE), which has the formula:

$$PCE\ (\%) = \frac{FF \times V_{OC} \times I_{SC}}{P_{in}}$$

$I_{SC}$ is the short circuit current, $V_{OC}$ is the open circuit voltage, FF is the fill factor, and $P_{in}$ is the power applied into the system [Armstrong et al., 2009].

The short circuit current is the maximum current, which can run through the device. It is a value for the amount photon absorption in the active layer [Kroon et al., 2008] and the dissociation of the formed excitons [Armstrong et al., 2009]. This can be improved by lowering the band gap, so more photons will have efficient energy to excite the electron in the active layer [kippelen et al., 2008]. This will also ensure a better match with the photon flux from the sun (Figure 5). The band gap is the difference in energy between the HOMO and LUMO of the material. $I_{SC}$ might also be improved by increasing the thickness of the active layer so as many photons as possible get absorbed [Dennler et al., 2009], and by increasing the offset between LUMO levels of the donor and the accepter [Armstrong et al., 2009].

The open circuit voltage is the potential when the current is zero. The maximum $V_{OC}$ is found to be the difference between the HOMO level of the donor and the LUMO level of the accepter molecules. [Kippelen et al., 2008]

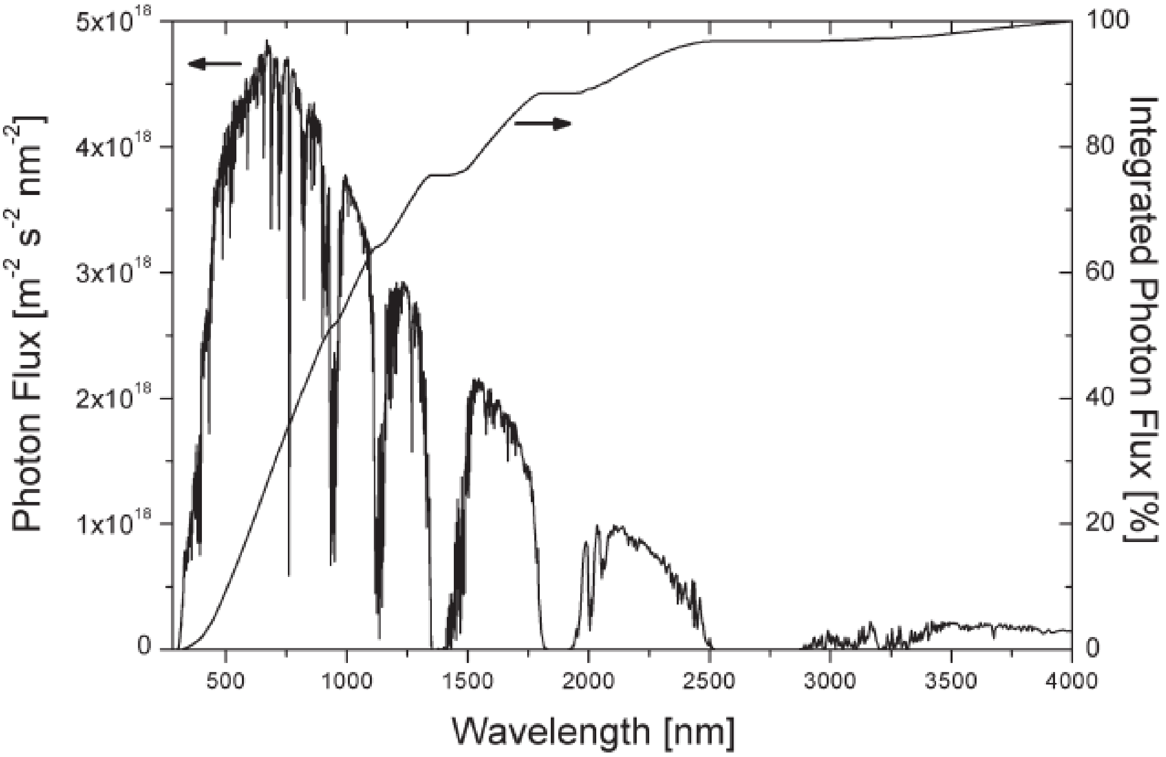

**Figure 5: The Photon Flux as a function of the wavelength (left) and Integrated Photon Flux as a function of wavelength (right). [Kroon et al., 2008]**

The fill factor is determined by the number of the photo-generated charge carriers that actually reach the electrode [Hoppe et al., 2004]. It is depending on how balanced charge carrier transport is and the exciton recombination properties of the materials [Kroon et al., 2008]. It can be influenced negatively by disorder and impurities [Kippelen et al., 2008]. This is due to a decrease in the hole transport which then causes unbalanced transport and hereby a buildup of space charge can occur. Also too thick an active layer can have a bad influence the FF, due to larger probability of recombining [Kroon et al., 2008] [Hoppe et al., 2004].

To make an efficient OPV, it is therefore necessary to determine the perfect band gap and the optimal active layer thickness. The band gap needs to be small in order obtain a large $I_{SC}$, but when it is lowered the $V_{OC}$ is decreasing. Therefore it is necessary to compromise to find the optimal band gap according to [Kroon et al., 2008] it is 1.4 eV, where [Kippelen et al., 2008] claims it is 1.6 eV. At 1.4 eV photon with a wavelength below 886 nm can get absorbed whereas at 1.6 eV only photon with a wave length below 775 nm can be absorbed. The optimal thickness of the active layer is also difficult to determine, a thick layer will ensure large absorption of photons thus increasing the short circuit current. But the long length to the electrode will also cause recombination of electrons and holes, thereby lowering the FF [Coakley & McGehee, 2004]. The layer thickness should be around 100 nm depending on the accepter [Günes et al., 2007]. In addition to the design of the active layer, it is also necessary to add protective layers between the electrodes and the active layer. Between the ITO electrode and the active layer a layer of poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PPS) is widely used to protect the active layer against indium diffusing into it and it also serves as a electron blocking layer [Spanggard & Krebs, 2004]. Between the metal electrode and the active layer, there often deposited a thin LiF, MgO, or Sm, to keep metal from diffusing into the active layer and react with vinyl group disrupting the conjugation [Spanggaard & Krebs, 2004].

Another important aspect for making efficient OPVs, especially with the bulk heterojunction type, is controlling the morphology of the active layer. This is due to occurrence of isolated regions of donor or accepter (cf. Figure 6), which will lead to charge build up and recombining of electrons and holes. [Coakley & McGehee, 2004]

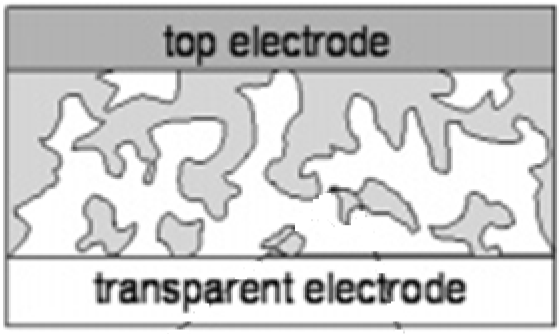

**Figure 6: Example of phase separation within a bulk heterojunction organic photovoltaic device. Grey areas represent the electron accepter and white areas are the donor. There are some areas which has contact with the wrong electrode and areas which has no contact at all. [Coakley & McGehee, 2004]**

To achieve optimal charge carrier transport, it is widely believe that the morphology should be a distribution of phases like in Figure 7.

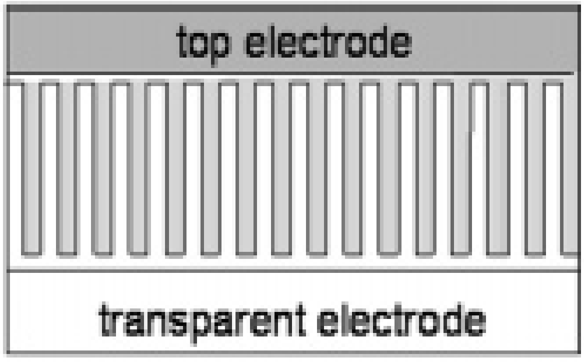

**Figure 7: Optimized active layer. No phase separation, all electron accepters are in contact with the anode and all electron donor molecules are in contact with the cathode. [Coakley & Mcgehee, 2004]**

Different attempts have been made to control the morphology. The most investigated controlling method is annealing of the active layer [Clarke & Durrant, 2009] [Bertho et al., 2009]. Alternative methods have also been developed, among them are addition of additive and spin coating from a mixture including a non-solvents [Lee et al., 2009] [Moule & Meerholz, 2009]. But also introducing alkyl chains to the molecule will increase the film forming ability and thereby order of the film.

The PCE can be determined experimentally from an I-V curve produced under artificial sun light,which is called air mass (AM). In northern Europe and North America AM1.5 spectrum is used, it corresponds to the solar spectrum reacting these parts of the world with sun 45° above the horizon [Kroon et al., 2007]. From the I-V curve (cf. Figure 8), $V_{OC}$ and $I_{SC}$ can be determined directly as the crossing with the 1.-axis and the 2.-axis respectively, the FF can be calculated as a function of $V_{OC}$ and $I_{SC}$ from the formula:

$$FF = \frac{I_{MMP} * V_{MMP}}{I_{SC} * V_{OC}}$$

There $I_{MMP}$ and $V_{MMP}$ are the current and voltage at the point with the maximum power.

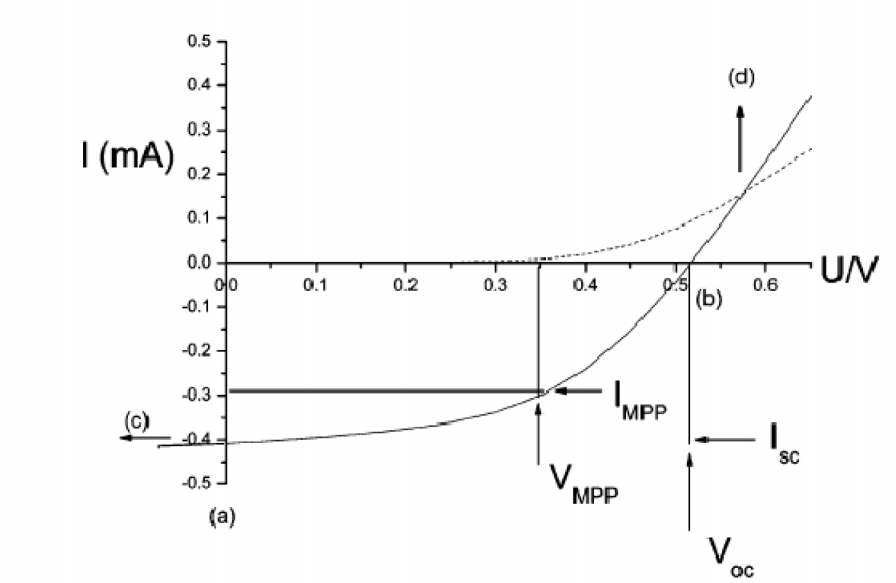

**Figure 8: I-V curve, the intersection from the curve with the 1. and 2.-axis is the $V_{OC}$ and $I_{SC}$ respectively. The $I_{MMP}$ and $V_{MMP}$ are determined from the point with the maximum product between I and V. [Günes et al., 2007]**

## 2.1. *Project plan*

The aim for this project will be to produce a novel electron accepter and investigating its properties in an organic photovoltaic cell (OPV). Little research has been done in finding novel organic materials suitable for electron accepter in OPV. N-type materials can be produced by incorporating strong electron accepting and transporting parts into oligomers or as repeating unit of polymers. One of the more commonly used electron accepting parts is perylenedicarboximide (PDI) often with both alkyl and thiophene based side chains [Huang et al., 2009] [Chen et al., 2005] [Mikroyannidis et al., 2009]. The PDI based electron accepters are in general inexpensive, thermal stability, have good electron accepting properties, and small band gaps in the area of 1.6 eV [Hou et al., 2008] [Yan et al., 2009][Zhan et al., 2007]. Another group of potential electron accepters are based on naphthalene-bis(dicarboximide)(NDI). They have similar structures to PDI, but only little studies have been performed regarding their possible use in OPV. Despite [Yan et al., 2009] reporting them as having better electron transport properties than PDI. They do however not surpass PCBM in terms of transport and acceptance properties [Chen et al., 2008][Nakamura et al., 2005]. This difference can be decreased by incorporating a strong electron withdrawing group on the thiophene linked to NDI, thereby making them electron accepting and transporting [Zaumseil & Sirringhaus, 2007]. Among the most electron withdrawing groups are nitro, cyano, fluorinated molecules, and carboxylic acid [Schwok et al., 1990] [Li et al., 2007]. A PDI accepter with fluoroalkylated side chains have been prepared by [Li et al., 2007], it did however not show an improvement in electron transporting compared with PDI with pure alkyl side chains supposibly due to poor packing. According to [Schwok et al., 1990] nitro groups are more electron withdrawing than cyano groups, which make it interesting to incorporate nitrothiophene side chains to NDI (cf. Figure 9). This will ensure light absorption from the thiophene rings but should still improve the electron transport and acceptance.

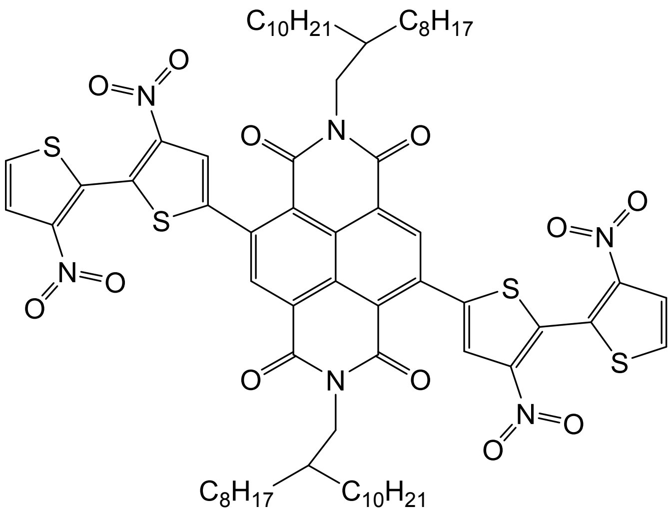

Figure 9: N,N'-bis(2-octyldodecyl)-2,6-di(3,3'-dinitro-2,2'-dithiophene)naphthalene-1,4,5,8-bis(dicarboximide).

[Chen et al., 2008] has reported the optical band gap, for a copolymer polymer based on NDI linked together by dithiophene units, to be 1.45 eV. Whereas the similar copolymer based on PDI has a band gap of 1.65 eV. The NDI and PDI monomers have a band gap of 3 eV and 2.4 eV respectively. [Chen et al., 2005] reports a decreasing band gap by increasing length of the thiophenes chain on PDI. From 2.4 eV to 1.97 eV with a thiophene chain of one unit, whereas a dithiophene chain gives a band gap of 1.73 eV determined optically. The same tendency should be seen with NDI as the core molecule. [Chou et al., 2009] has modulated the band gap of polythiophene to be 2.05 eV, and poly(3-nitrothiophene) as 2.34 eV. Due to these previous prepared molecules and modulations, the band gad for N,N'-bis(2-octyldodecyl)-2,6-di(3,3'-dinitro-2,2'-dithiophene)naphthalene-1,4,5,8-bis(dicarboximide)( NDI2OD-T-3-$NO_2$) should be in the area of 1.9 - 2 eV.

In this project the focus will be on synthesizing and purifying the monomers and the later coupling to obtain NDI2OD-T-3-$NO_2$. The optical and electrical properties of the oligomer will then be tested.

# 3. Experimental

Chemicals were purchased from a range of suppliers of which a detailed list can be seen in Appendix A. DMF and Toluene was dried with 4 Å molecular sieves that have been activated for 2 hours at 600 ˚C. THF dried with sodium lumps and distilled under $N_2$ before use. N-bromosuccinimide (NBS) was recrystallized from water before use. Copper for Ullmann synthesis was activated before use, activation can be found in Appendix C. The rest of the chemicals were used as received.

The molecules where characterized by NMR and elementary analysis, their NMR spectra can be found in Appendix B.

$^1H$ and $^{13}C$ NMR was performed on a Bruker DRX600 NMR spectrometer operating at a field strength of 14.1 T, equipped with a triple-axis gradient TXI (H/C/N) probe. Topspin 2.0 was used for acquisition and data processing.

## 3.1. Synthesis

The accepter oligomer was synthesized in 11 main steps as shown in Figure 10. Each step is described and explained in the following section.

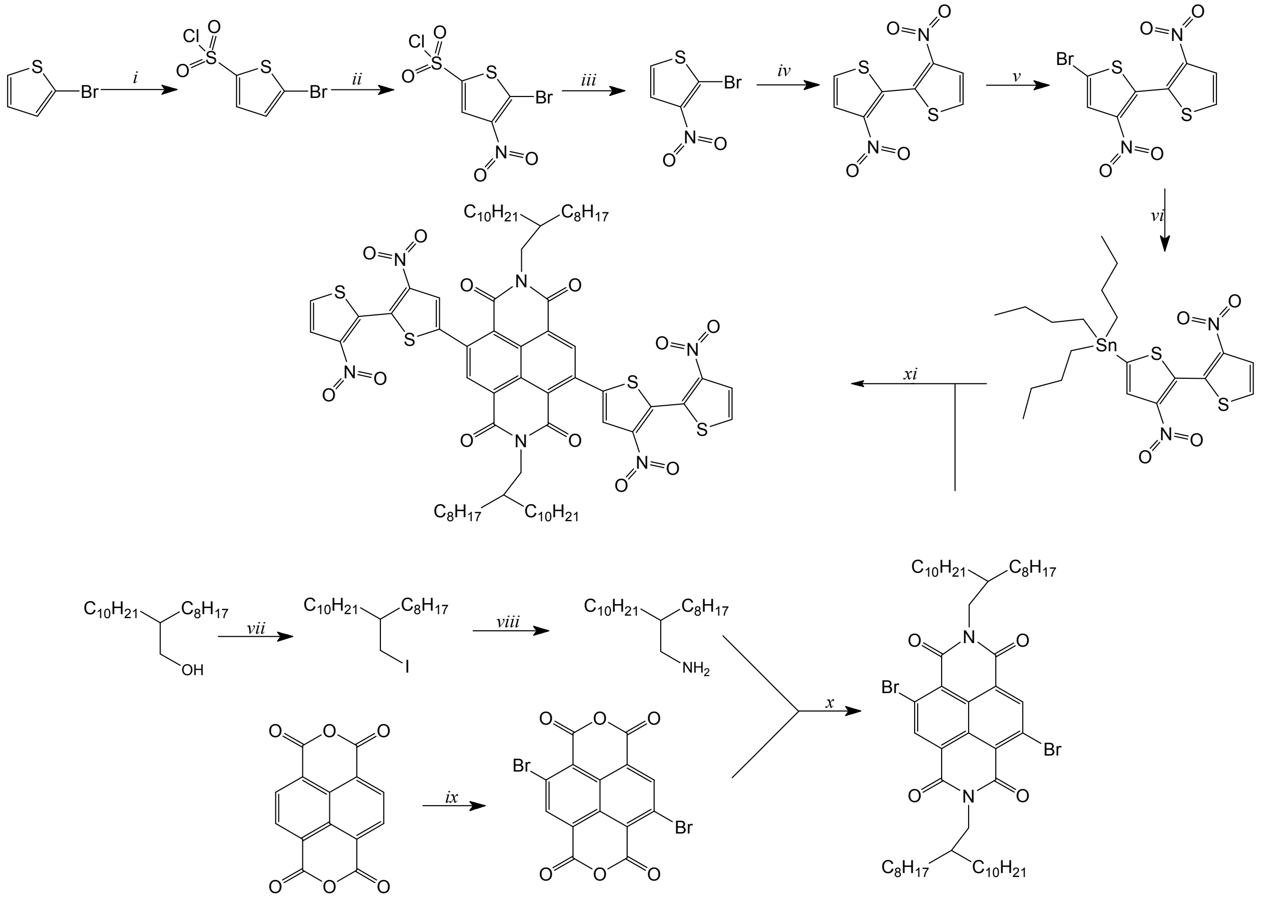

**Figure 10: The route of synthesis for N,N'-bis(2,2'-octyldodecyl)-2,6-di(3,3'-dinitro-2,2'-dithiophene)naphthalene-1,8,4,5-bis(dicarboximide).** ***i)*** **DMF $SO_2Cl_2$ 96 °C,** ***ii)*** **fuming $HNO_3$,** ***iii)*** **$H_2O$ reflux, diluted $H_2SO_4$ distillation,** ***iv)*** **Cu/xylene, reflux,** ***v)*** **NBS/trifluoroacetic acid /$H_2SO_4$,** ***vi)*** **phenyllithium/tributyltin chloride, -78 °C,** ***vii)*** **iodine/triphenylphosphine/imidazole, 0 °C , r.t. ,** ***viii)*** **potassium phthalimide hydrazine hydrate, 25 °C,** ***ix)*** **DBI/fuming $H_2SO_4$,85 °C,** ***x)*** **1-methyl-2-pyrrilidone/ glacial acetic acid,85 °C,** ***xi)*** **$Pd(PPh_3)_4$/Toluene 100 °C.**

### 3.1.1. Synthesis of 5-bromothiophene-2-sulfonyl chloride

#### Reaction mechanism

5-bromothiophene-2-sulfonylchloride was synthesized via chlorosulfonation of 2-bromothiophene. First DMF and sulfonyl chloride formed a complex through a vilsmeier haack reaction like mechanicm [Kojtscheff et al., 1966] (cf. Figure 11), a dislocation of nitrogen's lone pair removes the double bond to the oxygen which then attacks the sulfur atom and forms a sulfur oxygen bond and an chlorine ion function as leaving group (A) [Clayden et al., 2001]. The chlorine ion then attacks the former carbonyl carbon and the carbon oxygen bond is broken (B), internal rearrangement occurs and sulfur trioxide is formed (C), which is a good sulfonation agent

[Kojtscheff et al., 1966]. Thiophene attacks sulfur trioxide in a nuclephilic attack and an arenium intermediate is formed (C) rearrangement occurs which lead to the formation of a sulfonation group (E). The sulfonation group was then attacked by chlorine ion lone pair and the oxygen group function as the leaving group (F) [March & Smith, 2007].

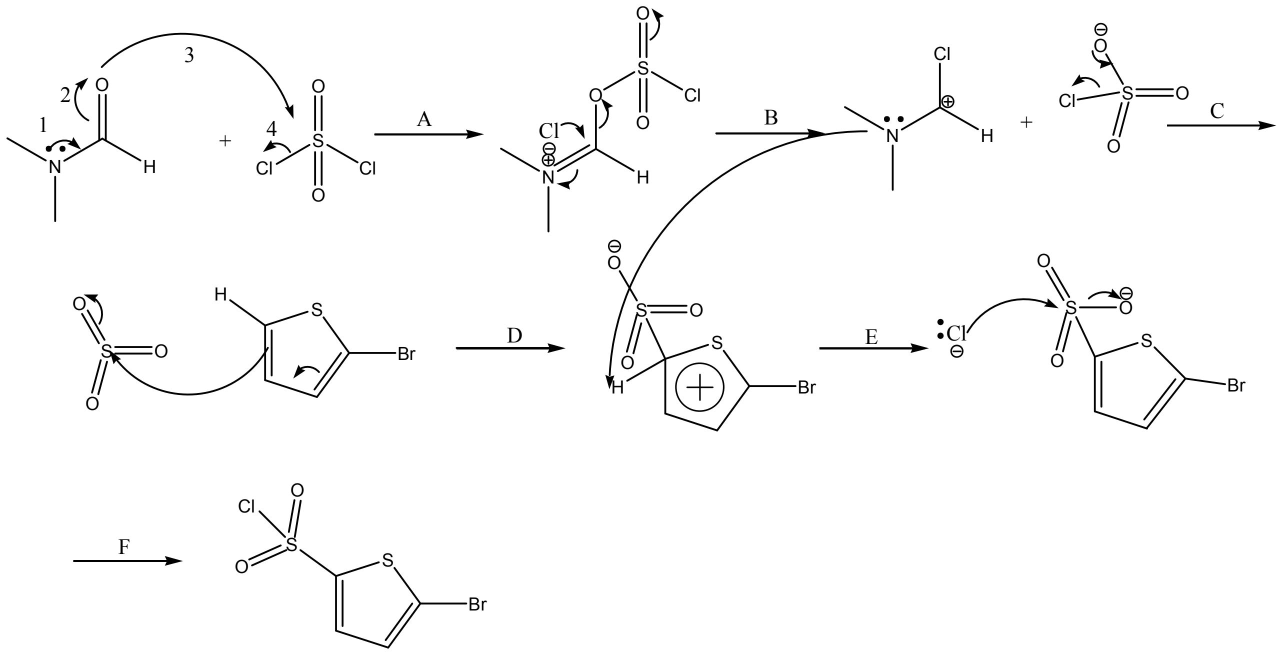

Figure 11: The mechanism for clorosulfonation of 2-bromothiophene.

## Procedure

15.4 mL (25.7 g, 0.191 mol) of $SO_2Cl_2$ was added to 14.8 mL (14.1 g, 0.192 mol) of DMF on an ice bath and stirred for an hour to form a hygroscopic solid. 24 g (0.147 mol) of 2-bromothiphene was added and the temperature was raised to 96 ˚C. After an hour the brown reaction mixture was cool to room temperature and poured into ice water, extracted with chloroform and washed with water, 5 % $NaHCO_3$, and water, then dried over $Na_2SO_4$. The solvent was removed and the resulting brownish green residue was vacuum distilled to yield 25.2 g (0.096 mol, 65.3%) impure yellow solid used for next step of reaction without further purification.

$^1$H NMR ($CDCl_3$): $\delta = 7.7$ (d, 1H), 7.2 (d, 1H)

## 3.1.2. Synthesis of 5-bromo-4-nitrothiophene-2-sulfonyl chloride

### Reaction mechanism

5-bromo-4-nitrothiophene-2-sulfonyl chloride was obtained by nitration of 5-bromothiophene-2-sulfonyl chloride. The nitration can by dividered into two steps, in the first step nitric acid react with another nitric acid molecule to form a positively charge nitronium ion which afterward will be attacked by the nucleplilic aromatic thiophene ring to form an arenium ion intermediate. Which get deprotonated by an attack from $NO_3^-$ and nitric acid molecules is regenerated (cf. Figure 12).

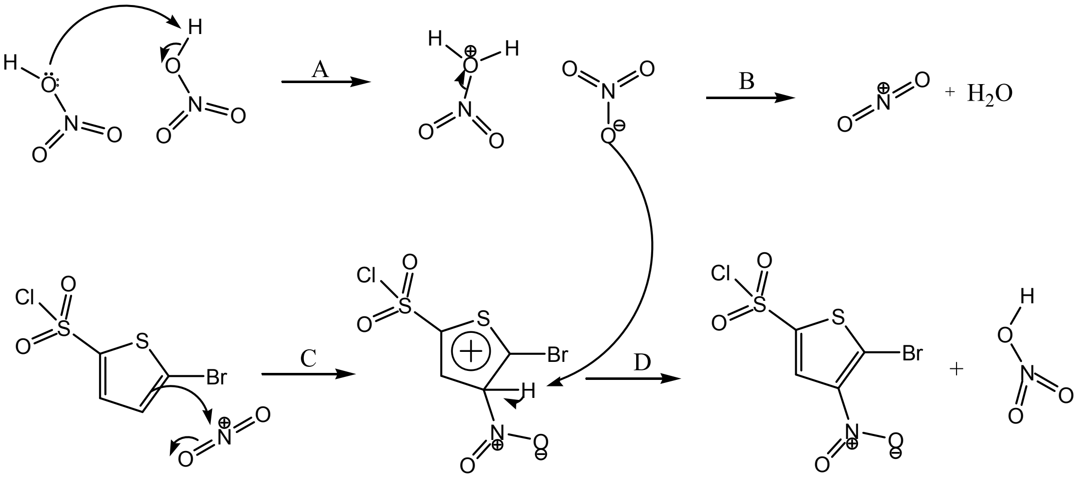

**Figure 12: Nitration of 5-bromothiophene-2-sulfonyl chloride. Reaction between two nitric acid molecules (A) gives a nitronium ion due to dehydration (B). The aromatic ring attack nitronium ion to form an arenium ion intermediate (C) which reacts $NO_3^-$ to yield 5-bromo-4-nitrothiophene-2-sulfonyl chloride and one of nitric acid molecules are regenerated.**

### Procedure

5.05 g (0.0193 mol) of 5-bromothiophene-2-sulfonyl chloride was added gradually to 25.0 mL of fuming $HNO_3$ on an ice bath. After addition the reaction mixture was heated to room temperature for 2 hours. Then the reaction was stopped by pouring the mixture into ice water, the white precipitate was filtered off and recrystallized from hexane yielding 2.02 g (6.59 mmol, 34.1 %) of colorless needle-like crystals.

$^1H$ NMR ($CDCl_3$): $\delta = 8.28$ (s, 1H )

## 3.1.3. Synthesis of 2-bromo-3-nitrothiophene

### Reaction mechanism

2-bromo-3-nitrothiophene is obtained by a two step reaction (cf. Figure 13). In the first step chloride is substituted by a hydroxy group  so it become a surfonylic acid via a nuclephilic attack, by the lone pair electrons in oxygen atom from water, on the sulfur atom from the sulfonyl chloride group, and a hydrochloric acid molecule is formed [Clayden et al., 2001].  In the second step the aromatic ring makes a nuclephilic attack on hydrogen in hydronium and it substitutes the sulfonylic acid [Smith & March, 2007].

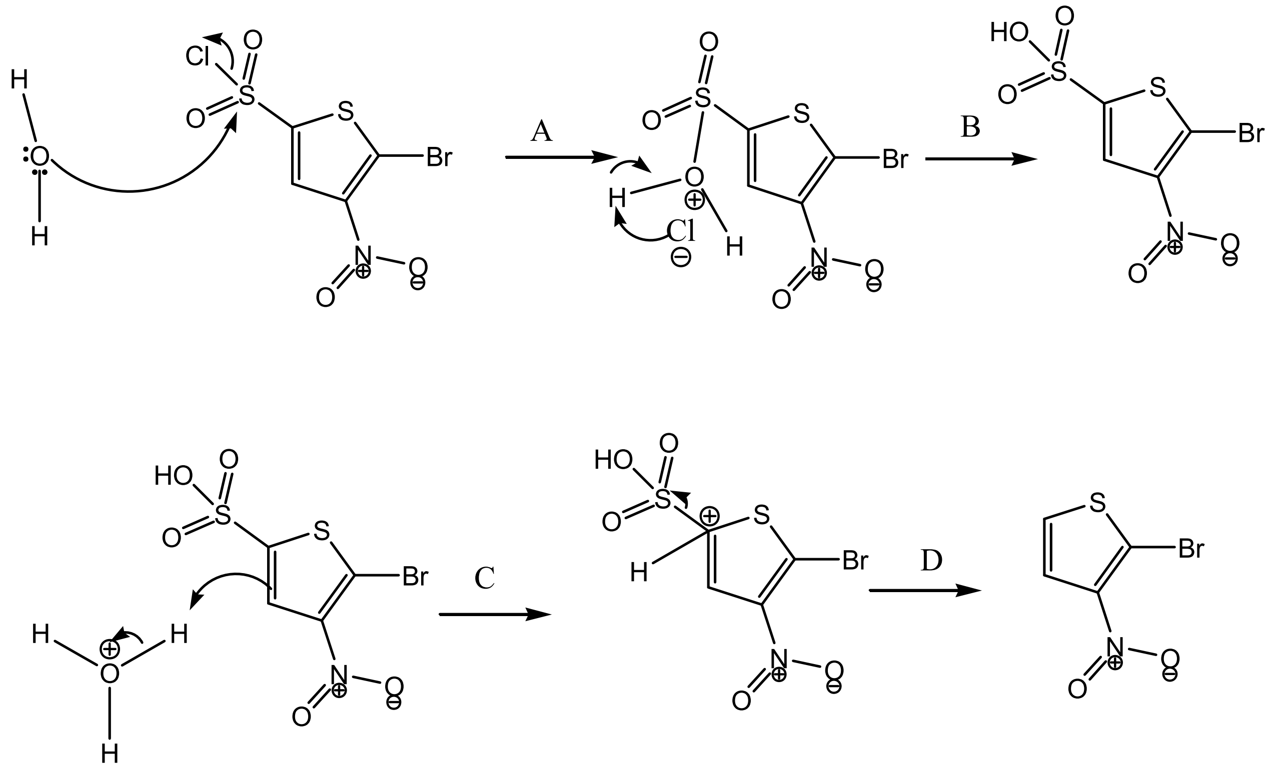

Figure 13: Desulfonation of 5-bromo-4-nitrothiophene-2-sulfonyl chloride in a two step reaction. Lone pair from oxygen in $H_2O$ attacks the sulfur atom in sulfonyl chloride (A), deprotonation occurs and sulfonylic acid is formed(B). Hydronium is attacked by thiophene and an arenium ion intermediate is formed, lone pair from oxygen in $H_2O$ attacks the sulfur in sulfonylic acid and 2-bromo-3-nitrothiphene is formed.

### Procedure

4.60 g (0.0150 mol) of 5-bromo-4-nitrothiophene-2-sulfonylchloride added to 64.4 mL of water and refluxed for 4 hours, poured into diluted sulfuric acid (41.4 mL 94-96 % $H_2SO_4$ and 50.6 mL $H_2O$)

and distilled at 160 ˚C with addition of water every half an hour, the white solid was recrystallized from hexane yielding 2.672 g (0.0128 mol, 85.6%) of colorless needle-like products.

$^1$H NMR ($CDCl_3$): δ = 7.56 (d, 1H), 7.30 (d, 1H)

### 3.1.4. Preparation of 3,3´-dinitro-2,2´-dithiophene

Two different methods was tried out to obtain 3,3´-dinitro-2,2´-dithiophene, they will be descript below.

#### Reaction mechanism

The reaction mechanism is shown in Figure 14 although the exact mechanisms for this direct aryl halides coupling is not completely known. It is however known that the presence of such a reductant as alcohols is very important. [Wang et al., 2005]. In this situation [Mukhopadhyay et al., 2003] believes that the PEG polymer function as a reductant due to the hydroxyl group on the end groups. [Wang et al., 2005] is doubting this function of PEG because they have been making multitable reaction cycles with addition of new aryl halides that gives them 6 times more possible products than using the PEG proposed by [Mukhopadhyay et al., 2003].

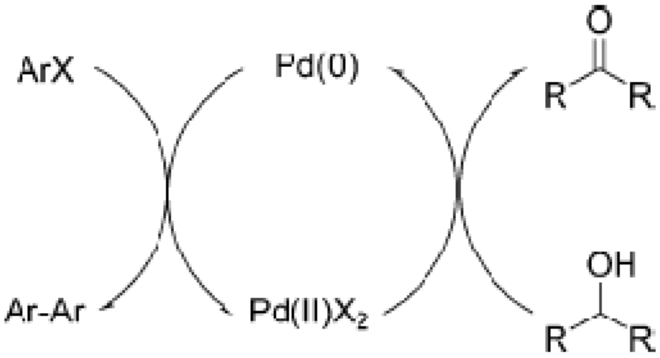

Figure 14: Catalytic circle for the homocoupling with a palladium catalyst using alcohol group as reductant.

In Figure 15 actual reaction scheme is shown.

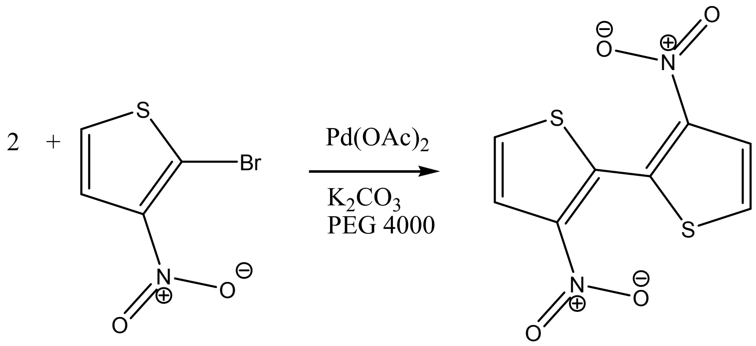

**Figure 15: Homocoupling of 2-bromo-3-nitrothiophene to yield 3,3'-dinitro-2,2'-dithiophene by Ullmann coupling.**

## Procedure

2-bromo-3-nitrothiophene (0.115 g, 0.551 mmol) was added to a reaction flask together with Palladium(II)acetate (0.0079 g, 0.0351 mmol), $K_2CO_3$ (0.0759 g, 0.550 mmol), PEG 4000 (0.573 g), under $N_2$ atmosphere and heated to 120˚ C. Thereaction was monitored with TLC tests, after 16 hours the mixture was cooled to room temperature, black solids was purified by column chromatography with DCM/Hexane (1:2) as eluent. To yield, only small amount of 3,3′-dinitro-2,2′-dithiophene was obtained.

## Reaction mechanism

3,3′-dinitro-2,2′-dithiophene was obtained by Ullmann coupling of 2-bromo-3-nitrothiophene. According to [Smith and March, 2007], the mechanism is not fully known but it is believed to be a two step reaction as seen in Figure 16. First, an oxidation and addition occur (A) with the addition of copper to 2-bromo-3-nitrothiophene. Second, an additional copper reacts with the bromine ion to form 2-copper-3-nitrothiophene (B), which reacts with another 2-bromo-3-nitrothiophene in which an oxidation and addition occurs (C).Lastly, a reduction and elimination occurs to form 3,3'-dinitro-2,2'-dithiophene (D).

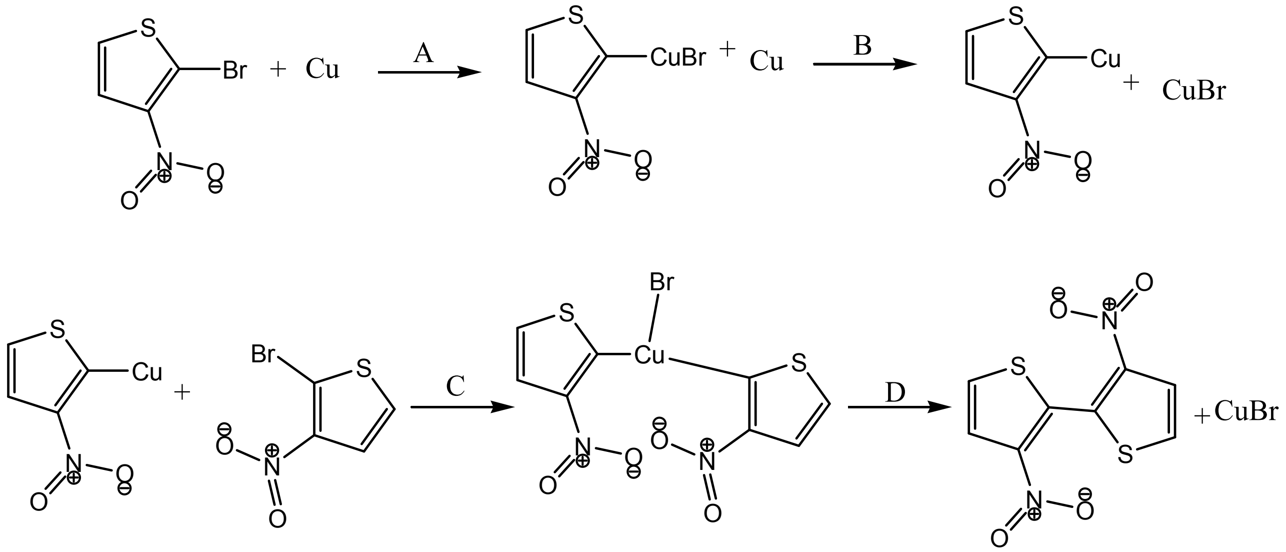

Figure 16: Synthesis of 3,3´-dinitro-2,2´-dithiophene by Ullmann reaction. A, an oxidation and addition-; B, an additional Cu substrates the bromine ion; C an oxidation and addition_; and D, a reduction and elimination.

## Procedure

1.328 g (6.38 mmol) of 2-bromo-3-nitrothiophene and 1.339 g (21.1 mmol) activated copper was added to 17 mL of xylene, and refluxed for 12 hours. Afterwards, the suspension was filtered, the filtrate was washed with boiling xylene, solvents were removed under vacuum resulting in a yellowish solid, following a recrystallizaion from benzene/ethanol (1:4) mixture yielding 0.557 g (2.18 mmol, 68.3%) yellow-green solid.

$^1$H NMR ($CDCl_3$): $\delta = 7.74$ (d, 2H), 7.47 (d, 2H)

## 3.1.5. Preparation of 5-bromo-3,3´-dinitro-2,2´-dithiophene

Two different methods was tried out to obtain 5-bromo-3,3´-dinitro-2,2´-dithiophene, which will be descript below.

## Reaction mechanism

5-bromo-3,3´-dinitro-2,2´-dithiophene was synthesized by electrophilic bromination with $KBrO_3$ and acid as a catalyst, reaction mechanism is illustrated in Figure 17. The first step is the formation of a positive bromine ion [Harrison et al., 1981] [Gilow & Ridd, 1973]. The positive bromine ion is then attacked by the nuclephilic aromatic ring to give a carbocation and an arenium ion is formed,

$HSO_3^-$ attack the hydrogen and 5-bromo-3,3′-dinitro-2,2′-dithiopheneis formed [Smith & March, 2007].

$$6\ H_2SO_4 + BrO_3^- + 5\ Br^- \longrightarrow 3\ Br_2 + 3\ H_2O + 6\ HSO_3^-$$

$$Br_2 + H_2O \longrightarrow H^+ + Br^- + HOBr$$

$$HOBr + H^+ \longrightarrow H_2\overset{\oplus}{O}Br \longrightarrow H_2O + Br^+$$

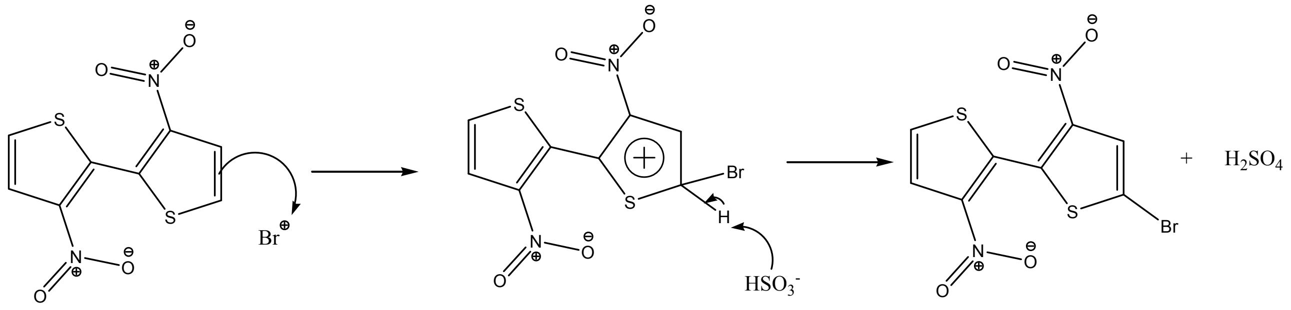

Figure 17: Monobromation of 3,3’-dinitro-2,2’-dithiophene with a bromine ion.

## Procedure

1.72 mL $H_2SO_4$ was added to 1.72 mL $H_2O$, 0.0552 g (0.215 mmol) of 3,3′-dinitro-2,2′-dithiophene was added and stirred for 0,5 hours, afterwards 0.0377 g (0.226 mmol) $KBrO_3$ was added and the temperature raised to 30°C for 3,5 hours, Ater filtration, the yellow solid was washed twice with $H_2O$. Reaction checked by TLC, only little amount had reacted.

## Reaction mechanism

5-bromo-3,3′-dinitro-2,2′-dithiophene was synthesized by a free radical bromination with NBS, the reaction mechanism [smith & March, 2007] can be seen in Figure 18.

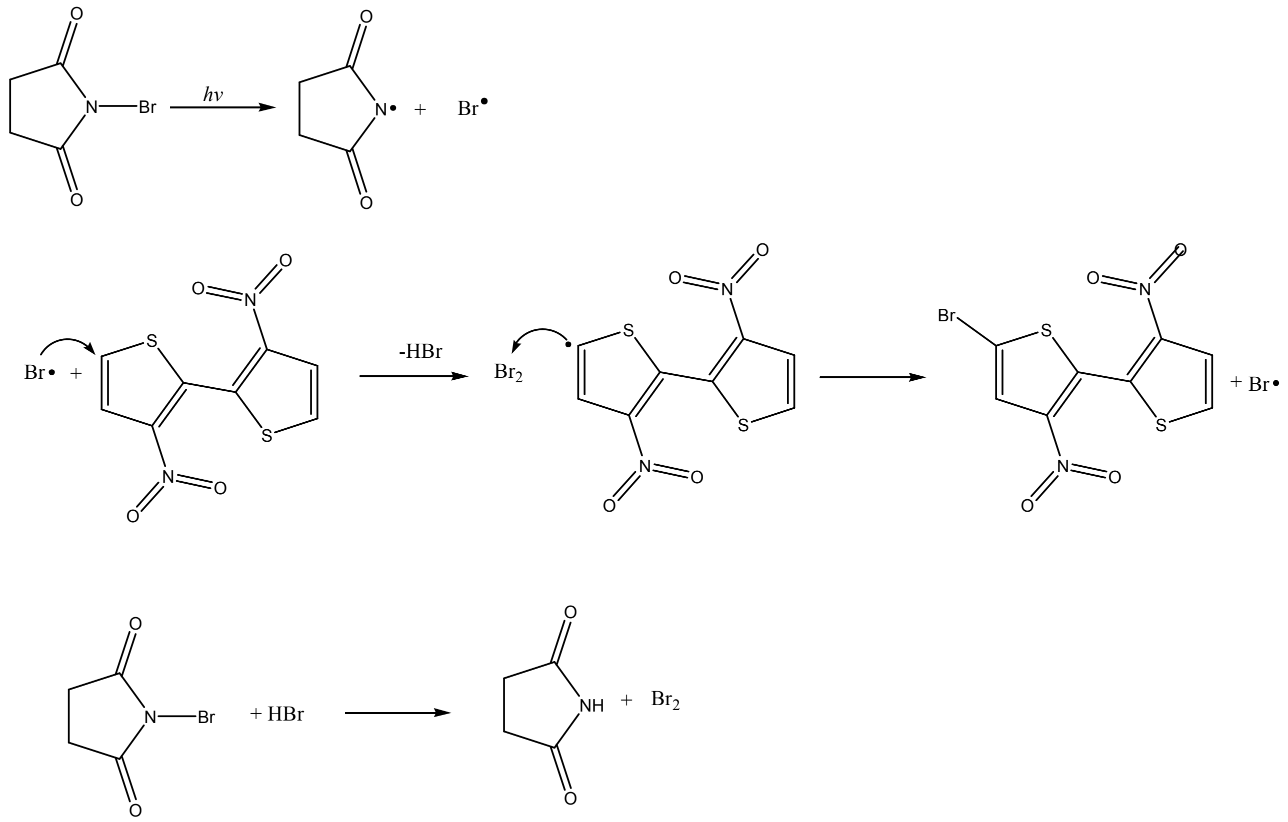

**Figure 18: Reaction mechanism for free radical bromination with NBS.**

## Procedure

0.361 g (1.41 mmol) of 3,3′-dinitro-2,2′-dithiophene was added to 10 mL of trifluoroacetic acid under stirring on a ice bath. After an hour, 2 mL of $H_2SO_4$ was added, than 0.283 g (1.59 mmol) of NBS was added. After half an hour, the ice bath was removed, the mixture reacted for additional half an hour, poured into water, extracted with DCM, dried over $Na_2SO_4$, purified by silica column with EA/Pentane (1:10) as eluent, yielding 0,195 g (0.582 mmol, 41.3%) of yellow solids.

$^1$H NMR ($CDCl_3$): $\delta = 7.75$ (d, 1H), 7.73 (s, 1H), 7.50 (d, 1H)

### 3.1.6. Preparation of 3,3′-dinitro-2,2′-dithiophene-5-tributyl stannyl chloride

#### Reaction mechanism

5-(tributyl stannyl)-3,3′-dinitro-2,2′-dithiophene was obtained by transmetalation of 5-lithio-3,3′-dinitro-2,2′-dithiophene with tributyltin chloride. 5-lithio-3,3′-dinitro-2,2′-dithiophene was prepared by halogen-lithium exchange of 5-bromo-3,3′-dinitro-2,2′-dithiophene with phenyllithium. The reaction mechanism for this exchange is subject for some discussion according to [Western, 2004]. It may vary between single electron transfer and anionic atom transfer depending on the substrate structure, solvent, and temperature. The transmetalation is however well known the partially negative α-carbon attacks the partially positive tin atom with the chloride ion as a leaving group [Smith & March, 2007] (cf. Figure 19).

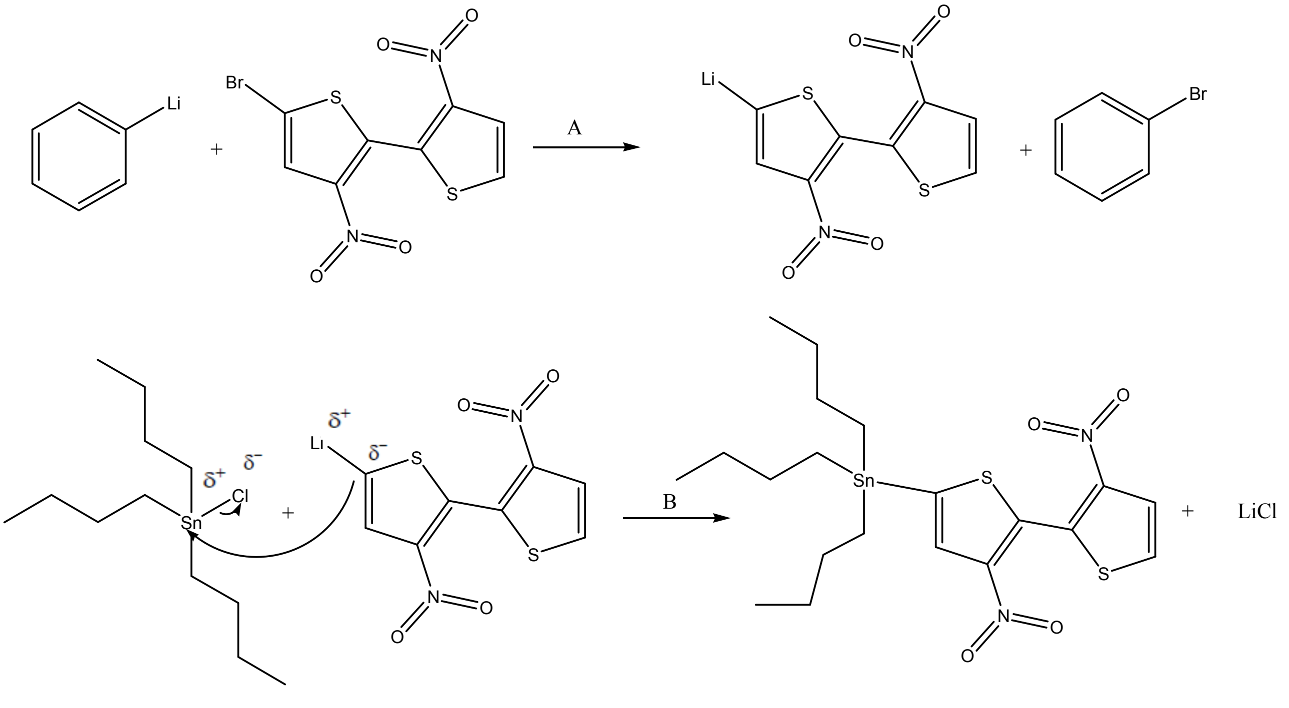

Figure 19: 5-(tributyl stannyl)-3,3′-dinitro-2,2′-dithiophene was formed by a transmetalation of 5-lithio-3,3’-dinitro-2,2’-dithiophene (B). 5-lithio-3,3’-dinitro-2,2’-dithiophene was formed by lithium – halogen exchange.

#### Procedure

Tert-butyllithium (0.25 mL, 0.625 mmol) was added dropwise to a solution of bromobenzene (0.07 mL, 0.666 mmol) in THF at -78 ˚C reacted for 1 hour. Afterwards the temperature was lowered to -110 ˚C and a solution of 5-bromo-3,3′-dinitro-2,2′-dithiophene (0.180 g, 0.537 mmol) in 6 mL THF was added. After 1 hour tributyltin chloride (0.2 mL, 0.742 mmol ) was added and reacted for 1 hour at -110 ˚C and heated to room temperature slowly, and left overnight. Reaction mixture was taken up in DCM, washed 3 times with water, 5 % $NaHCO_3$, and water, dried over $Na_2SO_4$ and purified by silica column with Pentane/ethyl acetate 10:1, only reactant was isolated according to TLC.

### 3.1.7. Preparation of 2-(tribuyl stannyl)-thiophene

The reaction mechanism and procedure is the same as in 3.1.6.

Resulting in impure product but used without further purification.

$^1H$ NMR ($CDCl_3$): $\delta$ = 7.7 (d, 1H), 7.3 (t, 1H), 7.2 (d, 1H), 1.6 (m, 16H), 1.35 (m, 17H), 0.9 (m, 27H)

### 3.1.8. Preparation of 2,6-dibromonaphthalene-1,8,4,5-tetracarboxy-dianhydride

Four different methods was tried out to obtain 2,6-dibromonaphthalene-1,8,4,5-tetracarboxy-dianhydride, which will be descript below.

#### Reaction mechanism

2,6-dibromonaphthalene-1,4,5,8-tetracarboxydianhydride was obtained by electrophilic aromatic substitution bromination with bromine (cf. Figure 20). First the electron rich aromatic structure attacks the electrophile bromonium cation resulting in the formation of a carbon bromine bond and an arenium ion intermediate. The aromatic structure is recovered by reaction between the anion bromide and hydrogen.

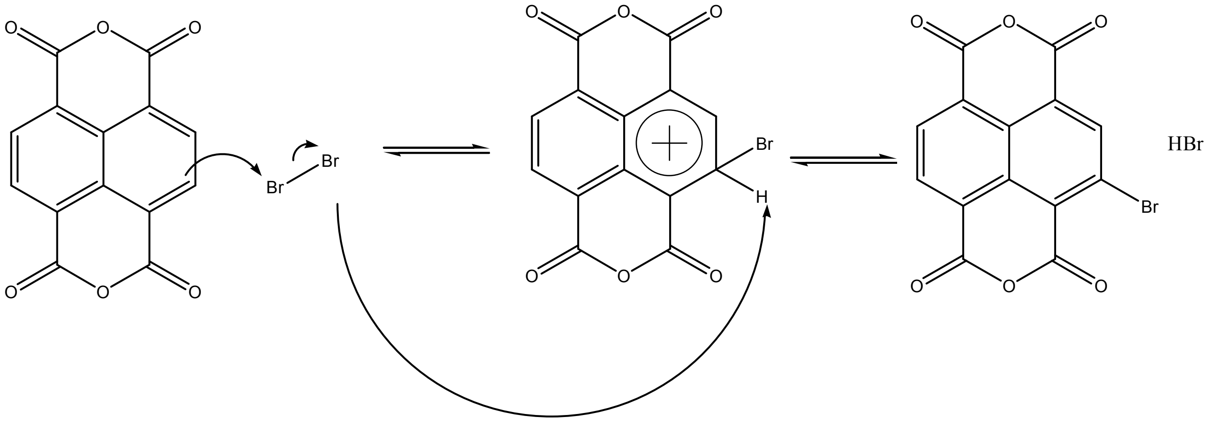

Figure 20: Electrophilic aromatic substitution of 1,8,4,5-tetracarboxydianhydride with bromine.

## Procedure

0.292 g of 1,8,4,5-Naphthalenetetracarboxylic dianhydride (NDA) was mixed with oleum for 3 hours under $N_2$, then 0.02 g of iodine was added and reacted for 1 hour. 2.4 mL of bromine was added drop wise over 10 min, temperature was raised to 90 ˚C, and react for 22 hours. Reaction mixture cooled to room temperature, poured into ice water, filtered, and wash with water and methanol. The product was dried under vacuum to yield clude product of reactant and monobrominated.

## Reaction mechanism

2,6-dibromonaphthalene-1,8,4,5-tetracarboxydianhydride was attempted to synthesis by a free radical bromination with NBS in DMSO and oleum, the reaction mechanism is as in Section 3.1.5.

## Procedure

NDA (0.307 g, 1.14 mmol) was dissolved in DMSO and NBS (0.444 g, 2.49 mmol) was added during 5 min.. Let to react at room temperature for 5 hours under $N_2$, reaction checked by TCL, no reaction occurred.

## Procedure

NDA (0.303, 1.13 mmol) was added to 10 mL vigorously stirred oleum under $N_2$ at 55 ˚C for 2 hours. 0.42 g NBS (2.35 mmol) dissolved in 7 mL oleum was added and the temperature was raised to 85 ˚C. After 44 hours the reaction mixture was cooled to room temperature and poured onto ice, the precipitation was filtered off washed with water and methanol twice. Resulting in 0.223 g but according to NMR mostly reactant.

### Reaction mechanism

2,6-dibromonaphthalene-1,8,4,5-tetracarboxydianhydride was obtained by a free radical bromination with Dibromoisocyanuric acid(DBI), the reaction mechanism is as in Section 3.1.5.

### Procedure

NDA (1.509 g, 5.63 mmol) was mixed with 50 mL oleum for 2 hours under $N_2$ to give a black/brown suspension. A solution of DBI (1.703 g, 5.94 mmol) in 25 mL oleum under $N_2$ was added dropwise over 2.5 hours, reaction mixture was left at room temperature for 3,5 hours, stopped by being poured onto ice, precipitation was filtered off and washed with diluted HCl, yielding 2.222 g mixed solid with reactant, mono- and dibrominated product.

$^1$H-NMR spectra on page 57.

## 3.1.9. Preparation of 1-iodo-2-octyldodecane

### Reaction mechanism

1-iodo-2-octyldodecane was obtained by halogenation of 2-octyldodecan-1-ol (cf. Figure 21), the lone pair on triphenylphosphine attacks the electrophilic Iodine to form iodotriphenylphosphine (A), iodotriphenylphosphine is then attacked by the lone pair from the oxygen in the alcohol group, while the hydrogen gets attacked by the lone pair from nitrogen in imidazole and iodine function as a leaving group to form iodine ion (B). The iodine ion attacks carbon in a $Sn_2$ reaction and triphenylphosphine oxide is the leaving group (C). [Slagle et al., 1981]

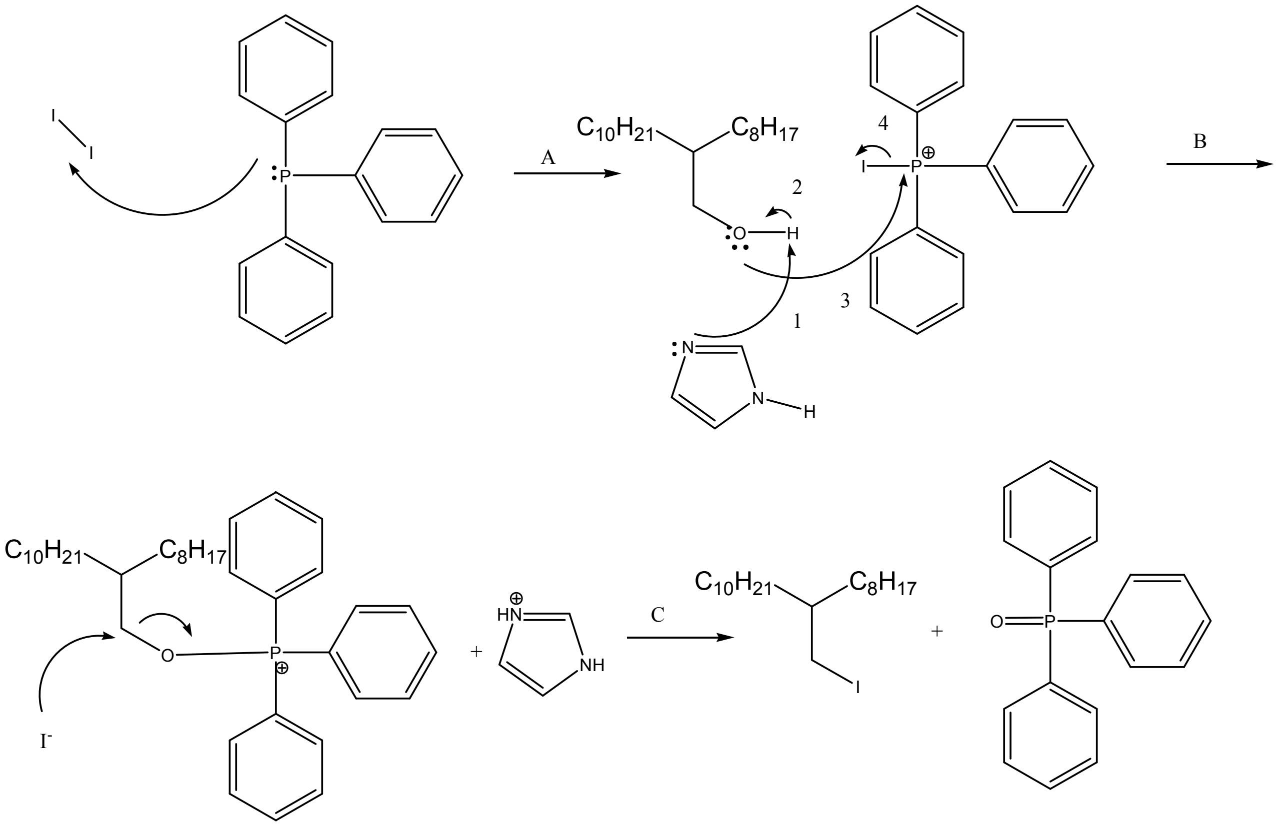

Figure 21: Halogenation of 2-octyldodean-1-ol to 1-iodo-2-octyldodecane.

## Procedure

2-octyldodecyl-1-ol (6.20 g, 0.0208 mol), triphenylphosphine(6.57 g, 0.0250 mol), and imidazole (1.743 g, 0.0256 mol) was added to 40 mL DCM under $N_2$, the temperature was lowered to 0 ˚C and iodine (6.04 g, 0.0238 mol) was added. After 15 minutes, the temperature raised to room temperature over 2 hours, saturated $Na_2SO_{3(aq)}$ was added. The organic layer was separated and concentrated, taken up in pentane and washed 3 times with water and once with brine, passed through a silica plug and dried over $Na_2SO_4$, solvent removed to give 8.06 g (0.0197 mol, 94.9%) of colorless oil.

$^1$H NMR ($CDCl_3$): $\delta$ = 3.27 (d, 2H), 1.28 (m, 33H) 1.13 (m, 1H), 0.88 (t, 6H)

### 3.1.10. 2-octyldodecyl-1-amine

## Reaction mechanism

2-octyldodecyl-1-amine was obtained by Gabriel synthesis from 1-iodo-2-octyldecane (cf. Figure 22: Formation of 2-octyldodecyl-1-amine by Gabriel synthesis.Figure 22)

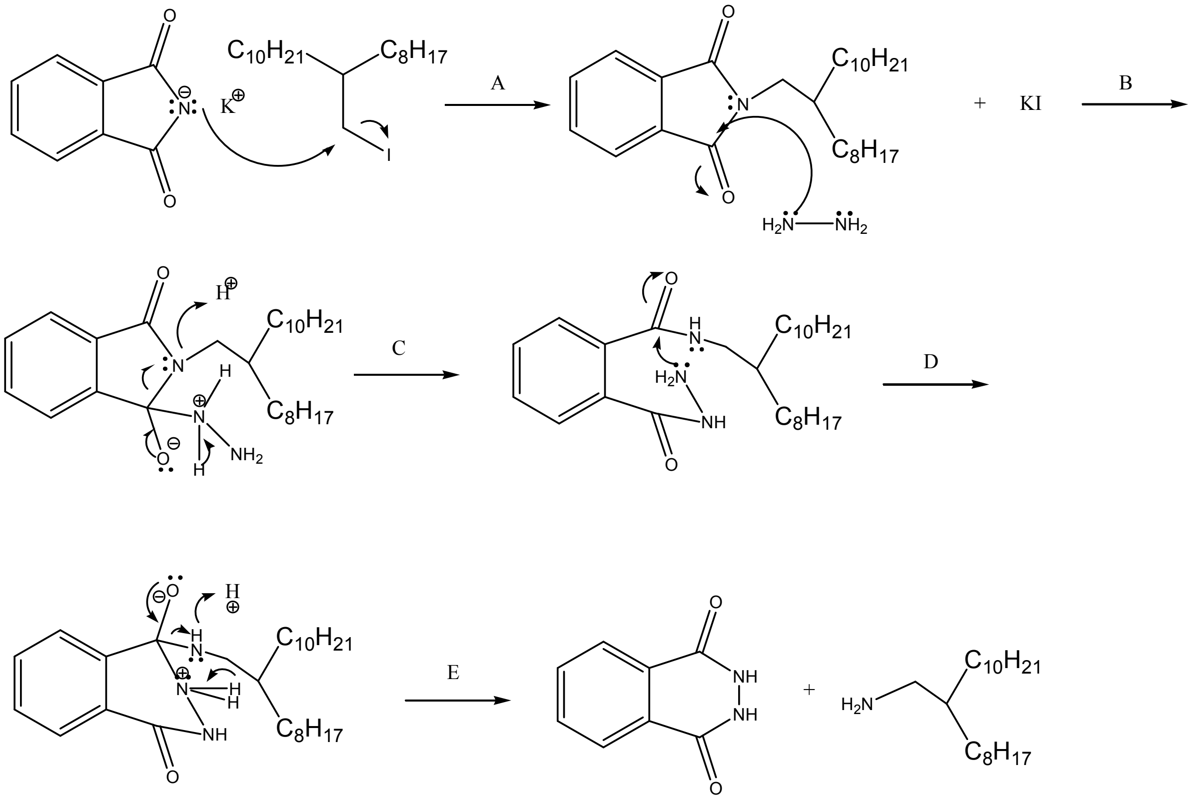

Figure 22: Formation of 2-octyldodecyl-1-amine by Gabriel synthesis.

Firstly, the lone pair on nitrogen attacks halide carbon and a nitrogen-carbon bond is formed, iodine is the leaving group (A). Secondly, the lone pair of nitrogen in the hydrazine hydrate attacks the carbonyl carbon and a bond between the nitrogen and carbon is formed (B). Thirdly, rearrangement within the molecule causing the bond between the carbonyl carbon and nitrogen broken, then protonation of the oxygen and deprotonation of the quaternary nitrogen occurs (C). The lone pair from the second nitrogen in hydrazine hydrate attacks the other carbonyl carbon (D). Rearrangement, protonation, and deprotonation occurs as before (E).

## Procedure

1-iodo-2-octyldodecane (0.996 g, 2.43 mmol) and potassium phthalimide (0.5 g 2.70 mmol) were dissolved in 8 mL DMF and stirred vigorously for 72 hours at 25 ˚C. The reaction mixture was taken up in pentane washed 4 times with water, passed though a silica plug, concentrated to give a colorless oil. The oil was added to 25 mL ethanol, and 0.8 mL (0.826g, 16.5 mmol) hydrazine hydrate was added and refluxed overnight. The mixture was left at -18 ˚C for 8 hours, the resulting precipitation was filtered, dissolved in water. The solution was made alkaline with NaOH(aq), extracted with pentane, washed 4 times with water and once with brine, dried over $Na_2SO_4$, concentrated to a colorless oil. NMR measurement show very little and very impure product, for this reason octylamine was used further on.

# 3.1.11. N,N'-bisoctyl-2,6-dibromonaphthalene-1,8,4,5-bis(dicarboximide)

## Reaction mechanism

N,N'-bisoctyl-2,6-dibromonaphthalene-1,8,4,5-bis(dicarboximide) was obtained by reaction between 2,6-dibromonaphthalene-1,8,4,5-tetracarboxydianhydride and octyl-1-amine (cf. Figure 23).

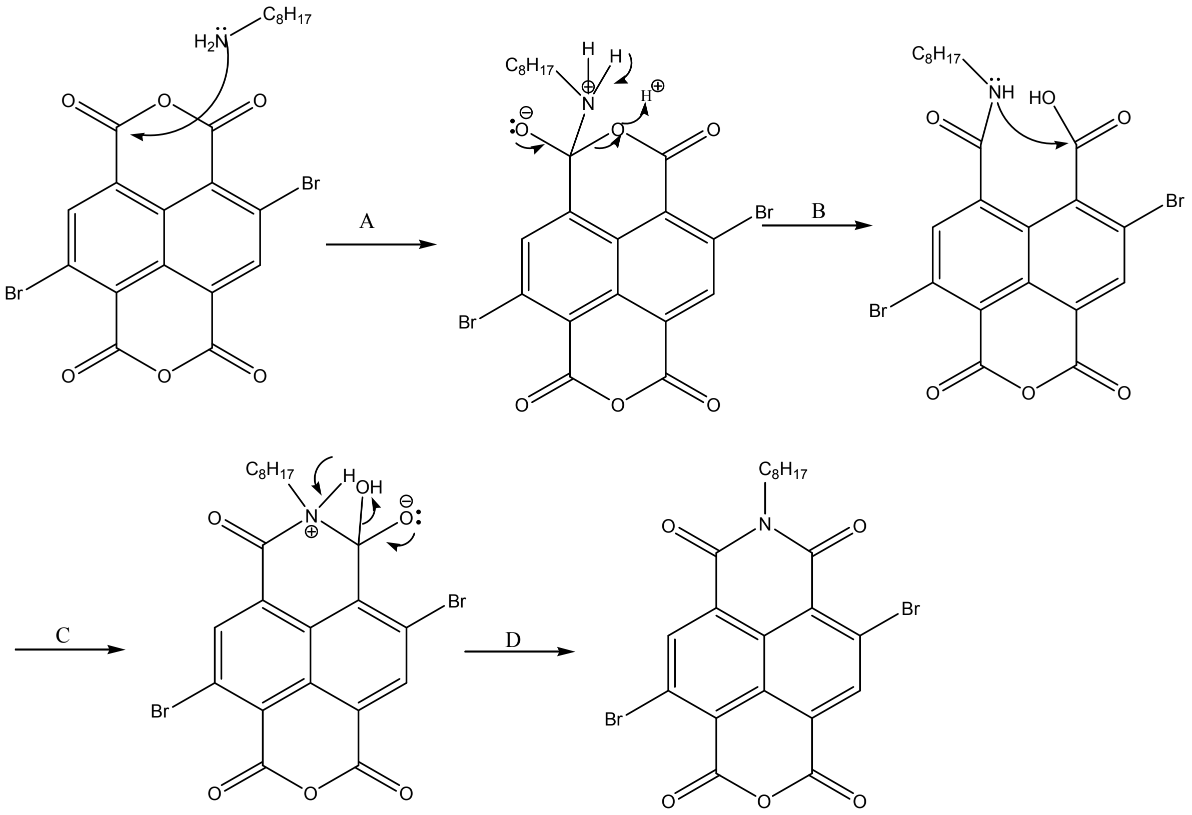

Figure 23: Formation of N,N'-bisoctyl-2,6-dibromonaphthalene-1,4,5,8-bis(dicarboximide).

Initially the lone pair electrons from octylamine attacks one of the carbonyl carbons of 2,6-dibromonaphthalene-1,4,5,8-tetracarboxydianhydride (A), then charge rearrangement occur which finally ends up in the breaking of the carbon-oxygen bond and protonation of the oxygen, and deprotonation of the quaternary nitrogen (B). Then the lone pair electrons attack the other carbonyl carbon (C) leading a charge rearrangement and $H_2O$ is released (D). This combination was then done on the other dianhydride.

## Procedure

1.857 g of the crude product from above was mixed with 100 mL 1-methyl-2-pyrrilidone, and 50 mL of glacial acetic acid under $N_2$. The temperature was raised to 85 ˚C, and 10 mL of 1-octylamine was added, after 6 hours the reaction mixture was cooled to room temperature and poured into 250 mL methanol, left at -18 ˚C overnight, the precipitation was filtered off, purified by silica column with Pentane/DCM (3:2), resulting in 0,143 g (0.221 mmol) of yellow powder.

$^1H$ NMR ($CDCl_3$): $\delta = 8.98$ (s, 2H), 4.17 (d, 4H), 1.72 (m, 4H), 1.41 (m, 4H), 1.35 (m, 4H), 1.27 (m, 16H), 0.86 (t, 7H).

## 3.1.12. Preparation of N,N'-bisoctyl-2,6-dithiophenenaphthalene-1,8,4,5-bis(dicarboximide)

### Reaction mechanism

N,N'-bisoctyl-2,6-dithiophenenaphthalene-1,8,4,5-bis(dicarboximide)(NDI2O-T) was obtained by stille coupling of 2-(tributylstannyl)thiophene and N,N'-bisoctyl-2,6-dibromonaphthalene-1,4,5,8-bis(dicarboximide) Figure 24. First an oxidative addition of N,N'-bisoctyl-2,6-dibromonaphthalene-1,4,5,8-bis(dicarboximide) to the palladium-complex to form a palladium-ligand$_2$-R-Br complex, then it gets transmetalised and being attack by 2-(tributylstannyl)thiophene to give a palladium-ligand$_2$-R-R'-complex and tributyltin bromide, thirdly a rearrangement of the complex occur, and finally a reductive elimination of the complex resulting in the formation of the R-R' product and the regeneration of the catalyst. [Tollis et al., 1998]

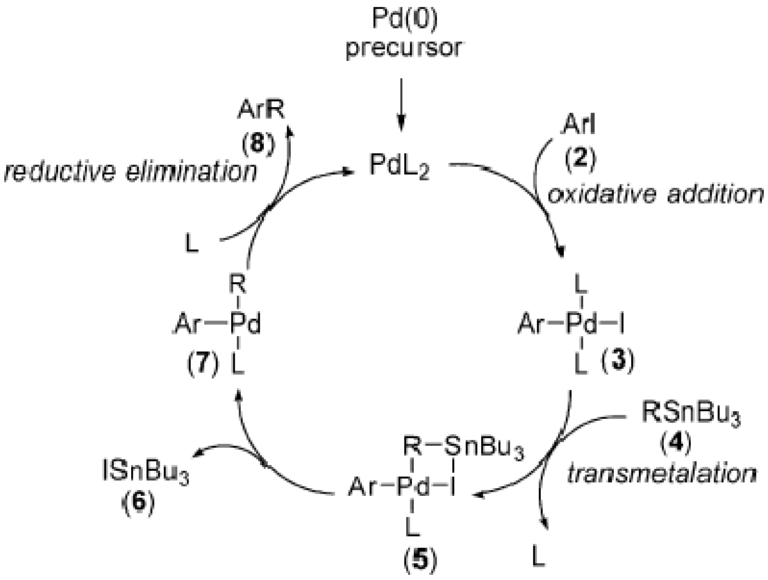

Figure 24: The catalytic circle for Palladium(0) catalyst in a stille coupling.[Santos et al., 2007]

### Procedure

N,N'-bisoctyl-2,6-dibromonaphthalene-1,4,5,8-bis(dicarboximide) (0.137 g, 0.211 mmol), 2-(tributylstannyl)thiophene (1.12 g, 2.99 mmol ), and Tetrakis(triphenylphosphine)palladium(0) (9.1 mg, 0.0078 mmol) was added to 10 mL dry toluene under $N_2$. The temperature was raised to 80 ˚C, the reaction was monitored by TLC, after 22 hours, the reaction mixture was cooled to room temperature, added to DCM, washed with water and dried over $Na_2SO_4$. The solvent was removed, the residue was added to acetone the precipitation was filtered off, and washed with acetone. The residue was purified by preparative TLC with DCM/pentane (1:2) as eluent, resulting in 49 mg (0.0748 mmol, 35.5%) of red solid.

$^1$H NMR ($CDCl_3$): $\delta$ = 8.75 (s, 2H), 7.58 (d, 2H), 7.30 (t, 2H), 7.21 (d, 2H), 4.10 (d, 4H), 1.68 (m, 5H), 1.36 (m, 5H), 1.26 (m, 24H), 0.86 (t, 7H).

## 3.2. *Ultraviolet/visible light spectroscopy*

The optical properties of the synthesized molecule were measured with Ultraviolet/visible light spectroscopy (UV/vis). This was done from chloroform solution with a concentration of 25 µg/mL.

## 3.3. *Solar cell manufacturing/characterization*

Solar cell devices were prepared by Jan Alstrup from National Laboratory for Sustainable Energy, Risø DTU.

They were prepared on a ITO coated glass substrate, which was spin coated with PEDOT:PSS and annealed for one minute at 150 ˚C. The active layer was spin coated on top of the PEDOT:PSS layer from the solutions in Table 2:

| | Donor | Accepter | Solvent |
|---|---|---|---|
| 1 | P3HT (20 mg/mL) | NDI2O-T (20 mg/mL) | 1,2-dichlorobenzene |
| 2 | P3HT (20 mg/mL) | PCBM (20 mg/mL) | 1,2-dichlorobenzene |

**Table 2: The active layers and the solvents, they were spin coated from.**

The spin coating speed was adjusted to get an active layer with a thickness of 80-100 nm. To finish the device aluminum was deposited on top of the active layer.

The photovoltaic device was tested under simulated sun (AM1.5, 1000 w/m2), their response was measured using a Solar Constant 575 from Steuernagel Lichttechnik GmBH, Germany.

# 4.Results and discussion

## 4.1. *Synthesis*

The synthesis of NDA-$Br_2$ was attempted in four different ways and yielding a mixture of compounds with different degree of bromination (cf. Figure 25).

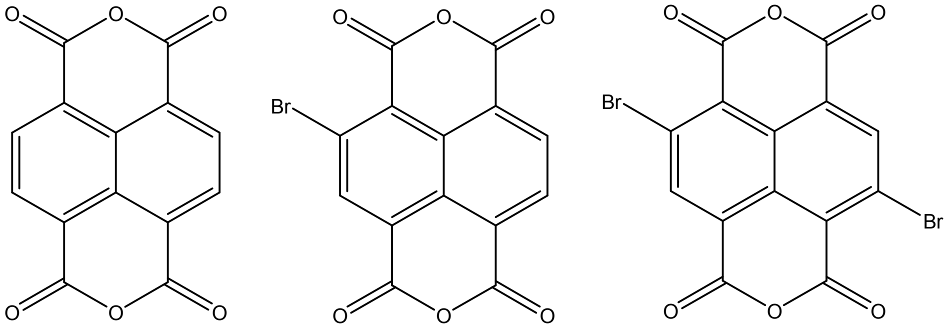

Figure 25: naphthalene-1,8,4,5-tetracarboxydianhydride with different degree of bromination.

Bromination with bromine as descript in 3.1.8 only yielded in very small amount of dibrominated and some monobrominated product but mostly reactant was obtained after reaction (cf. Appendix B). The method of reaction was supposed by [Marks et al., 2009]. It was modified by adding excess bromine and iodine, and by prolonging the reaction time, since they reported mostly monobrominated but also some dibrominated product. NBS was also used as a bromination agent. It was done with both oleum and DMSO as solvent. When DMSO is used as solvent no reaction seems to occur (cf. page 55), whereas some brominated product appears with oleum as solvent (cf. page 56). These suggest the need of oleum to activate the NDA molecule. DBI is the most commonly used compound for bromination of NDA. As bromination with NBS, it is a free radical reaction, but when bromination with NBS only yielded in small amount of dibrominated product. Bromination with DBI led in a reasonable mixture of the three compounds (cf. page 57). The mixture was according to [Kishore et al., 2008] inseparable by silica column, due to poor solubility in most organic solvents.

2-octyldodecyl-1-amine was not obtained in pure form after the Gabriel synthesis. The Gabriel synthesis is as descript in Section 3.1.10 a two step reaction. From the NMR spectra page 54 there seems to be problems in the first step of the reaction due to occurrence of the protons with a chemical shift 3.6 ppm. These represent according to [Semmelhack et al., 2006] the protons on the carbon next to iodine. Whereas the protons for the first carbon in 2-octyldodecyl-1-amine have a chemical shift of 2.6 ppm [Letizia et al., 2008]. Therefore some product has been formed, but not in extensive amount. A problem might also have occurred in the second step of the reaction due to the occurrence f aromatic protons with a chemical shift 7.7-7.9 ppm.  A structural similar molecule can be formed by reduction of nitrile groups to form amine groups [Carey, 2004]. The formation of nitrile groups can be done by reaction between alkylhalide and a metalcyanide (cf. Figure 26) [Smith & March, 2007]. The product from this method would be 2-octyltridecyl-1-amine.

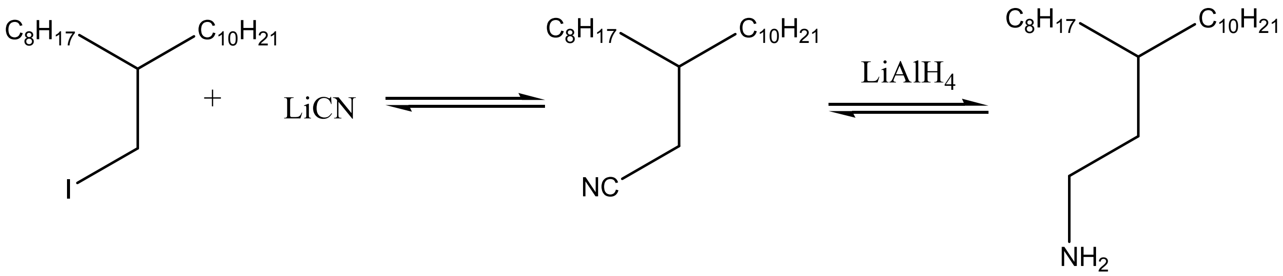

Figure 26: Formation of primary amine by reduction of a nitrile group formed by reaction between lithiumcyanide and alkylhalide.

3,3´-dinitro-2,2´-dithiophene-5-tributyl stannyl chloride was not obtained most likely due to difficulties in the halogen-lithium exchange. This might have been caused by the low temperature. However the temperature needs to be below -90 ˚C to secure nitro groups, innitration at ortho positions, against reduction by the lithium ions [Johnson & Covington, 1982]. This temperature does not seem low enough to ensure nitro groups in meta position from being reduced. [Buck & Köbrich, 1970] reports formation of 30% phenol group from nitro groups in meta position even at -110 ˚C, when substituting bromine to carboxyl acid via halogen-lithium exchange. Halogen-lithium exchange with nitro groups in ortho position have been reported with good yield, this is due to the formation of stabilizing resonance structure (cf. Figure 27).

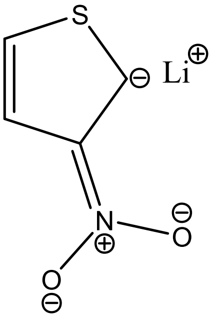

Figure 27: Stabile resonance structure for halogen-lithium exchange with a nitro group in ortho position.

This is not possible to form with the nitro groups in meta position. To overcome this problem another method of coupling could be considered. Suzuki coupling will however not be a favorable choice, [sixto et al., 2007] reports a cross coupling with 2-nitrothien-3-ylboronic acid pinacol ester as one of the reagents, but only got a yield of 15%. They believe the low yield is due to deborylation caused by instability prompted by the strong electron withdraws of the nitro group. Kumada coupling would also have been a coupling method. According to [Sapountzis, 2004] it is however not possible to make Grignard reagent with a nitro group in meta position without a group in ortho position to stabilize it. Another approach could be to obtain the tributyltin reagent on the NDI2O-$Br_2$ instead of the nitrothiophenes. Due to the possibility stabilized resonance structures within the carboximides structures (cf. Figure 28).

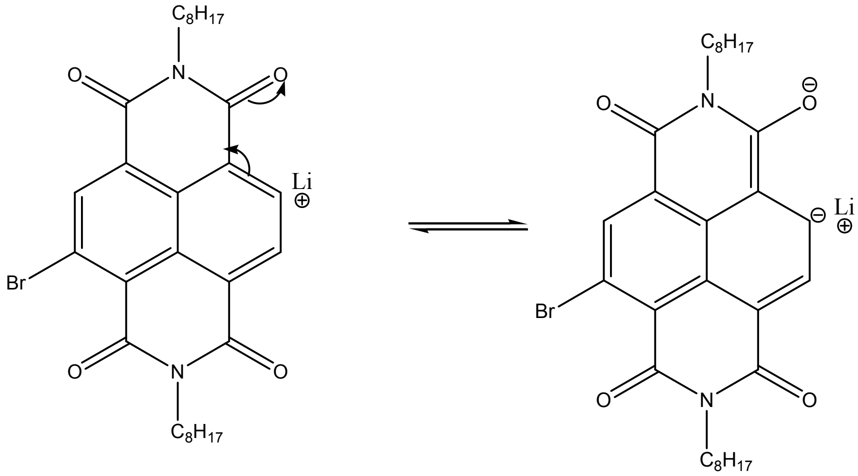

**Figure 28: Possible stable resonance structure after halogen-lithium exchange for N,N'-bisoctyl-2,6-dibromonaphthalene-1,4,5,8-bis(dicarboximide).**

This reaction might also have the advantage for being suitable for higher temperature making the halogen-lithium exchange easier.

NDI2OD-T-3-$NO_2$ was not obtain due to the before mentioned problems instead NDI2O-T was synthesized.

## 4.2. Ultraviolet/visible light spectroscopy

The absorption spectrum of the solution is plotted in Figure 29.

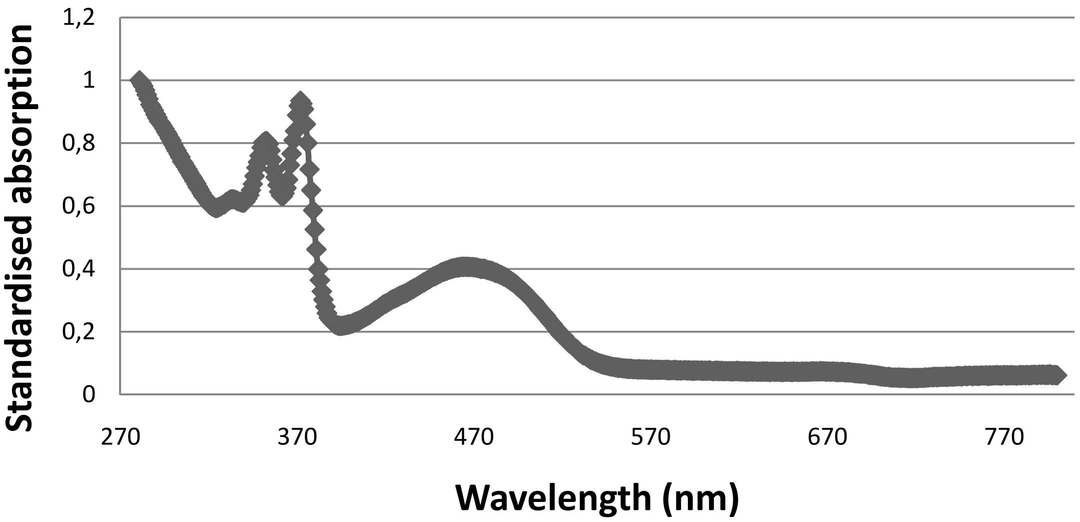

**Figure 29: Absorption spectra from N,N'-bisoctyl-2,6-dithiophenenaphthalene-1,4,5,8-bis(dicarboximide) in chloroform.**

The spectrum for NDI2O-T show absorption in two different areas, one at 330-400 nm and one at 405-540 nm. This leads to an optical band gap of 2.27 eV determined by the edge method. This is a very large band gap for an electron accepter to be used in OPV. This is however expected when compared with the band gap development for PDI. As descript in Section 2.1 a bandgap below 2 eV will be highly unlikely for 2,6-dithiophenenaphthalene-1,4,5,8-tetracarboxydianhydride.

## 4.3. *Solar cell characterization*

The manufactured solar cells were characterized with a current-voltage curve. From the curves the open circuit voltages, short circuit current, and the fill factor were determined. These parameters are together with the intensity of the light source used to calculate the power conversion efficiency. The results from the different blend with P3HT are plotted in Figure 30.

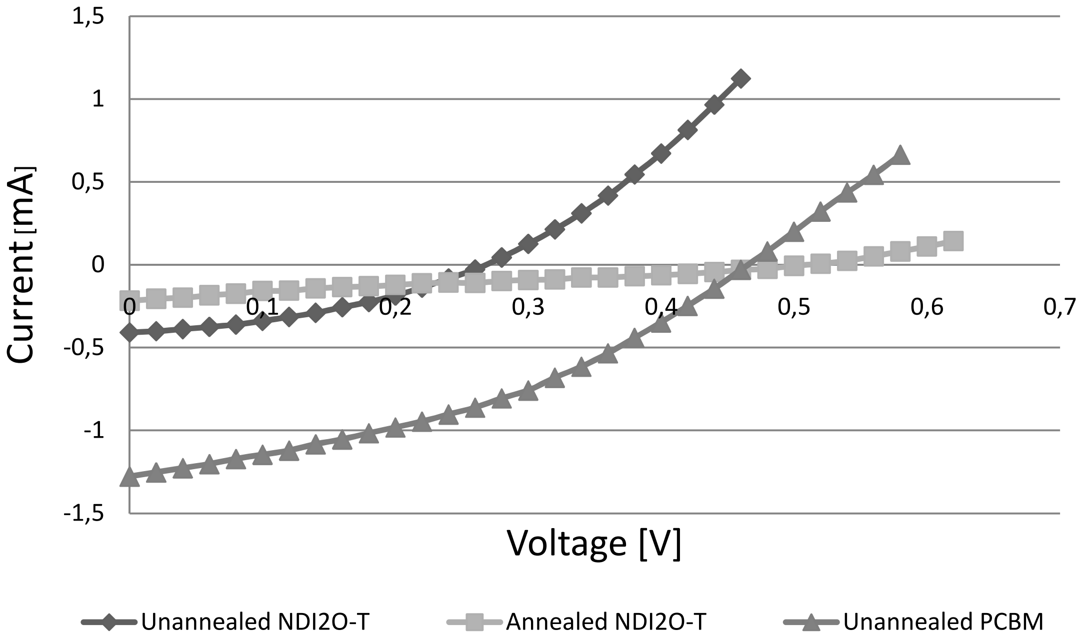

**Figure 30: I-V curves for the three fabricated solar cells, all of them a BHJ with P3HT as electron donor.**

The data withdrawn from these I-V curves are presented in Table 3.

| Active layer | PCE (%) | $V_{OC}$ (V) | $I_{SC}$ (mA) | FF (%) | MaxPow (mW) |
|---|---|---|---|---|---|
| Unan NDI2O-T/P3HT 1:1 | 0.0840 | 0.270 | -0.411 | 37.81 | 0.0420 |
| An NDI2O-T/P3HT 1:1 | 0.0549 | 0.508 | -0.218 | 24.87 | 0.0275 |
| Unan PCBM /P3HT 1:1 | 0,483 | 0.476 | -1.28 | 39.67 | 0.241 |

**Table 3: Data obtained from the I-V curves.**

The solar cells manufactured from NDI2O-T/P3HT yielded low efficiencies in comparison with the PCBM/P3HT cell. This is most likely due to lower electron transport and less favorable exciton dissociation.

Annealing the active layer improves the $V_{OC}$, but decreases the $I_{SC}$ and the FF. An overall improvement of the NDI2O-T/P3HT cell was not obtained. The PCE decreases from 0.0840% to 0.0549%. This is not uncommon to observe different ways to improve morphology for one cell cannot always be transferred to a different type of cell [Yano et al., 2 009]. One reason for the low

PCE could be impurities, this could also be an explanation for the higher PCE for the PCBM/P3HT photovoltaic cell.

# 5.Conclusion

The novel electron accepter N,N’-bisoctyl-2,6-dithiophenenaphthalene-1,4,5,8-bis(dicarboximide) was synthesized by Stille coupling of 2-(tributylstannyl)thiophene with N,N’-bisoctyl-2,6-dibromonaphthalene-1,4,5,8-bis(dicarboximide). The optical band gap was 2.3 eV. It was tested in four organic photovoltaic cell with poly(3-hexylthiophene) as the electron donor, with an average power conversion efficiency of 0.0840%. Annealing the active layer at 150 ˚C for 2 minutes decreased the overall PCE to 0.0549%, although the open circuit voltages improved, but a decrease in both short circuit current and fill factor.

The synthesis of monomers for the electron accepter was successful except for two steps. The formation of 2-octyldodecyl-1-amine by Gabriel synthesis from 1-iodo-2-octyldodecane failed. Also the formation of the 3,3´-dinitro-2,2´-dithiophene-5-tributyl stannyl chloride failed due to problems with the halogen-lithium exchange.

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# Appendix A

| | | |
|---|---|---|
| 2-Bromothiophene 95 %, | Aldrich, | Lot.: 85183-479 |
| Sulfonyl chloride 97% | Sigma-Aldrich | Lot.: 74090 |
| Nitric acid 68-70% | ACS, Acros Organics, | Lot.: A0235818 |
| Sulfuric acid 95-97%, | Fluka, | Lot.: 70580 |
| Copper | Merck, | Lot.: 104831 |
| N-bromosuccinimide 99%, | Sigma-Aldrich, | Lot.: S67255-488 |
| Potassium bromate, | Acros Organics, | Lot.: A013558801 |
| Dibromoisocyanuric acid, | TCI, | Lot.: UP2EJ-11 |
| Oleum (Sulfuric acid fuming (20 % SO3)), | Sigma-Aldrich, | Lot.: 82070 |
| 1,4,5,8-Naphthalenetetracarboxylic dianhydride | Fluka, | Lot.: 70300 |
| Tert-butyllithium 2.5 M, | Acros Organics, | Lot.: A0189279 |
| Tributyltin chloride 96%, | Aldrich, | Lot.: S43879-118 |
| Tetrakis(triphenylphosphine)palladium(0), | Aldrich, | Lot.: 12596TK |
| 2-octyldodecyl-1-ol, | Aldrich, | Lot.: 464481 |
| Dimethylformamide, | Sigma Aldrich, | Lot.: 91380 |
| Triphenylphosphine, | Acros Organics, | Lot.: A018040401 |
| Dichloromethane, | Sigma Aldrich, | Lot.: 1407470 |
| Ethanol 99.9%, | Kemetyl A/S, | Batch: 0607061128 |
| Hydrazine hydrate | Fluka, | Lot.: 53850 |
| Potassium phthalimide | Acros Organics, | Lot.: A01560241 |
| Iodine, | AppliChem, | Lot.: 4L000974 |
| Bromine >99.8%, | Acros Organics, | Lot.: A014746001 |
| Sodium sulfate, | Acros Organics, | Lot.: A018018301 |
| Sodium Sulfite | Sigma Aldrich | Lot.: 85030 |
| Tolune, | Sigma Aldrich, | Lot.: SZBA030M |
| Palladiumacetate, | Aldrich, | Lot.: S89662-299 |
| Potassium carbonate >99 %, | Aldrich, | Lot.: 013K0073. |
| Polyethylene grycol 4000 MW | Fluka, | Lot.: 49320 |
| Sodium, | Riedel-de häen, | Lot.: 71140 |
| Acetone, | VWR, | Batch: 10C23935 |
| Dimethyl sulfoxide, | VWR, | Batch: 09J20010 |
| Hydrochloric acid 36%, | Sigma aldrich, | Lot.: 91980 |
| Sodium hydroxide 50%, | J. T. Baker, | Lot.: M09050 |
| Bromobenzene, | Fluka, | Lot.: 1333487 |
| Imidazole, | Fluka, | Lot.: 1377754 |
| Sodium bicarbonate, | J. T. Baker, | Lot.: 0425110016 |
| Acetic acid 100 %, | Prolabo, | Lot.: J222 |
| Xylene, | Merck, | Lot.: 108681 |
| Tetrahydrofuran, | Sigma Aldrich, | Lot.: S2E9287M |

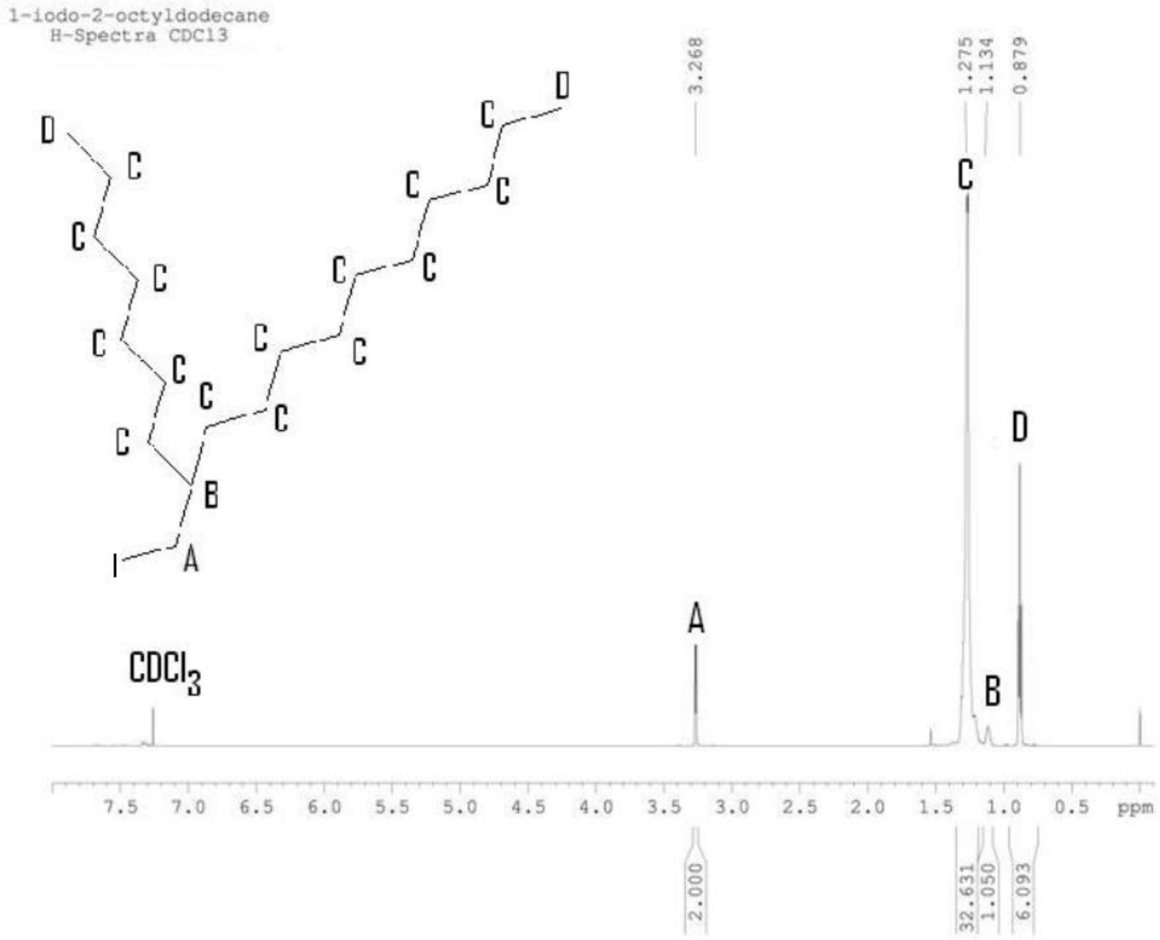
# Appendix B

NMR spectra were calibrated using TMS, Solvent protons peaks and signals caused by residual water are also listed in Table 4

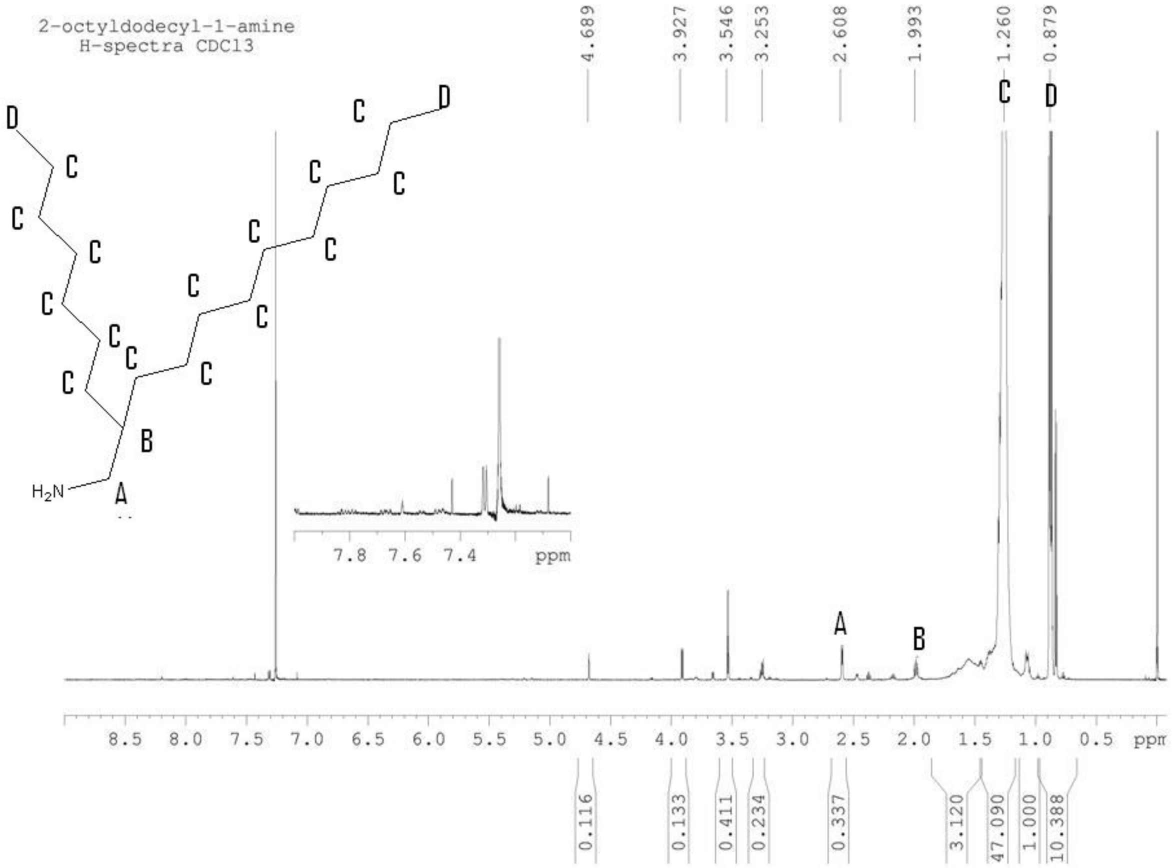
| Solvent | $^1$H signal [ppm] | Water signal [ppm] |
|---|---|---|
| $CDCl_3$ | 7.26 | 1.56 |
| DMSO-$d_6$ | 2.54 | 3.33 |

Table 4: NMR signals from solvents and water.

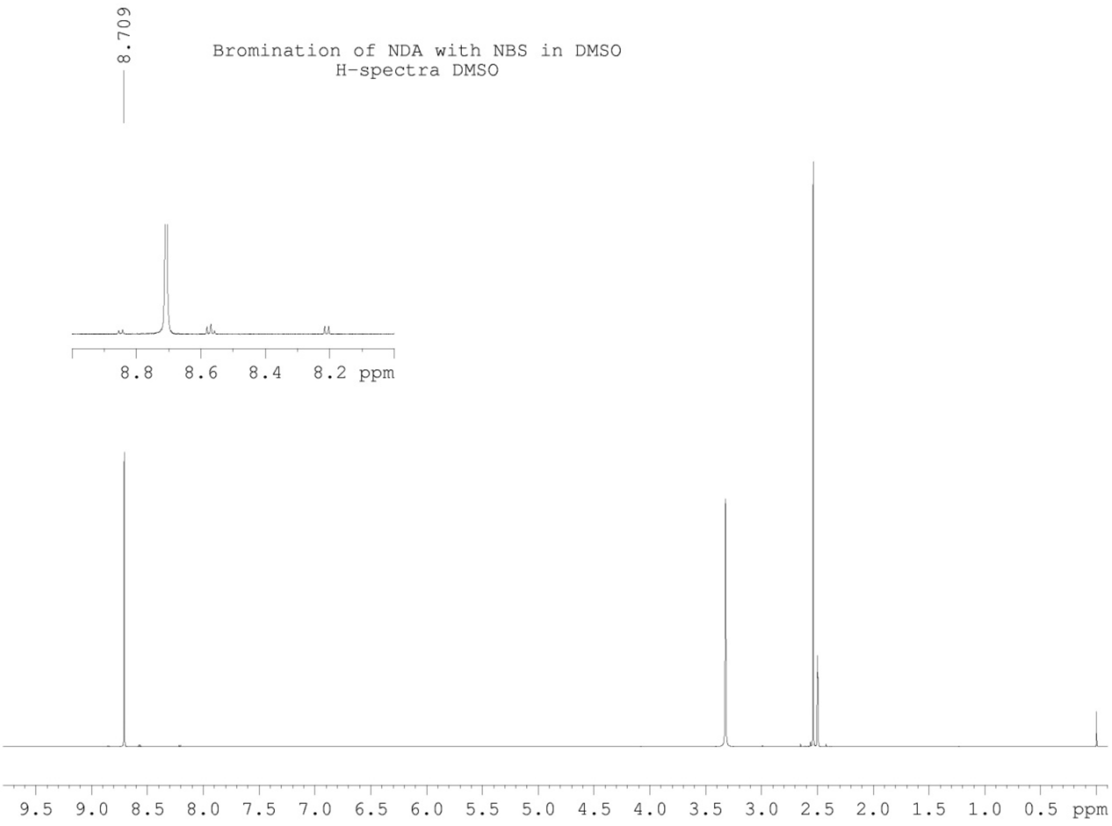
## 1-iodo-2-octyldodecane



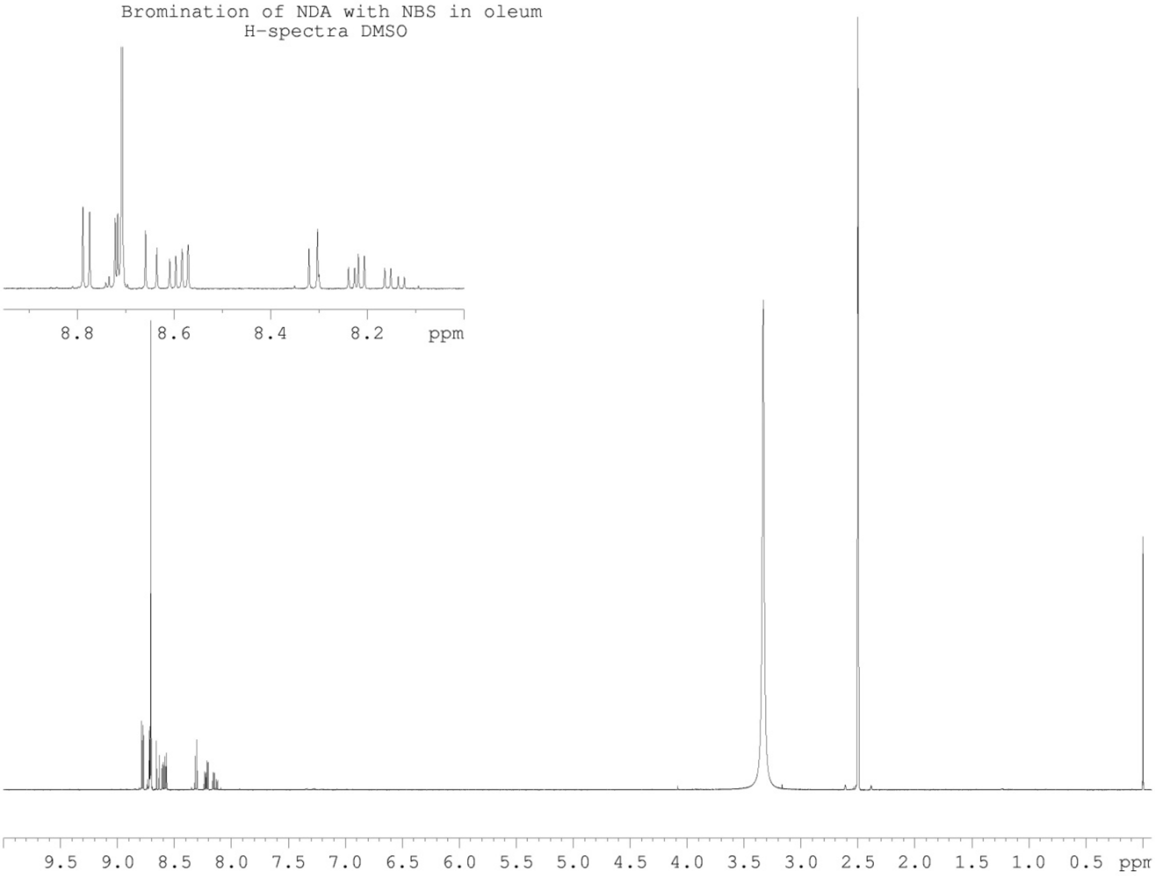
# 2-octyldodecyl-1-amine



## Bromination of NDA with NBS in DMSO

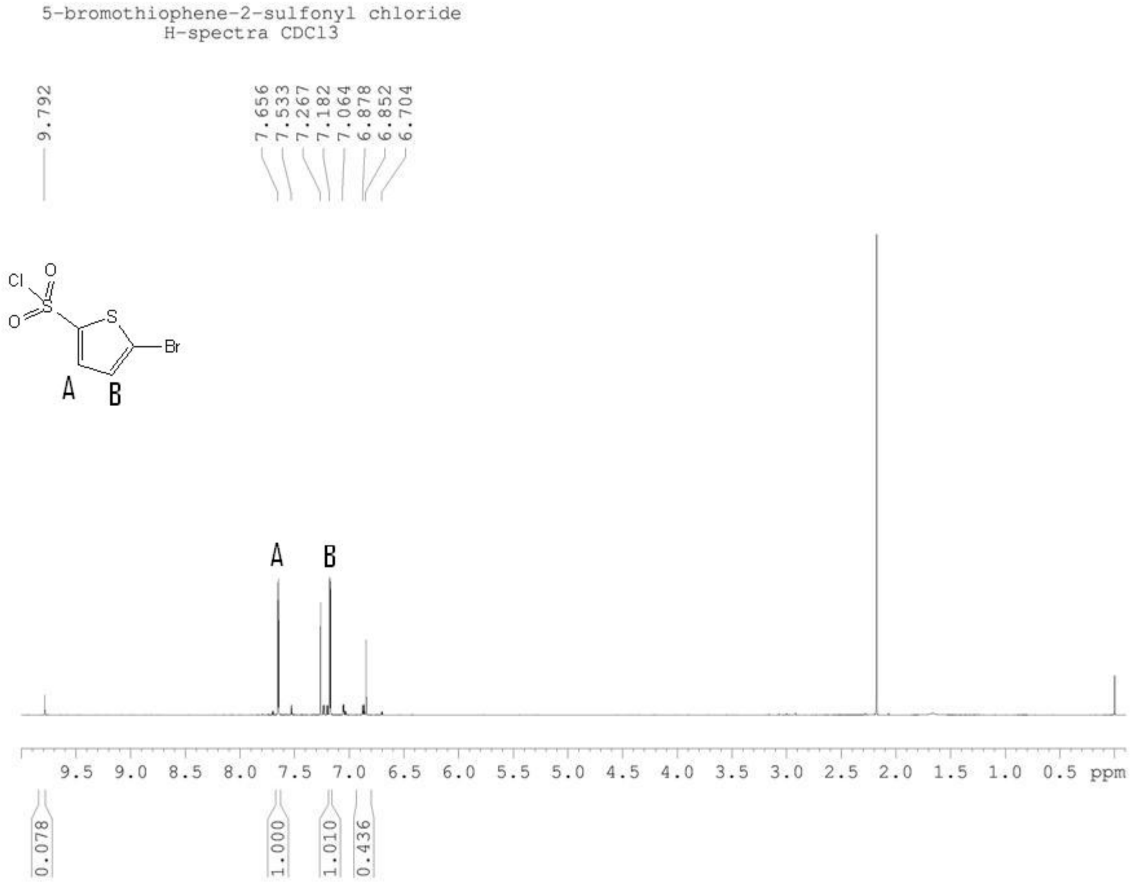


## Bromination of NDA with NBS in oleum

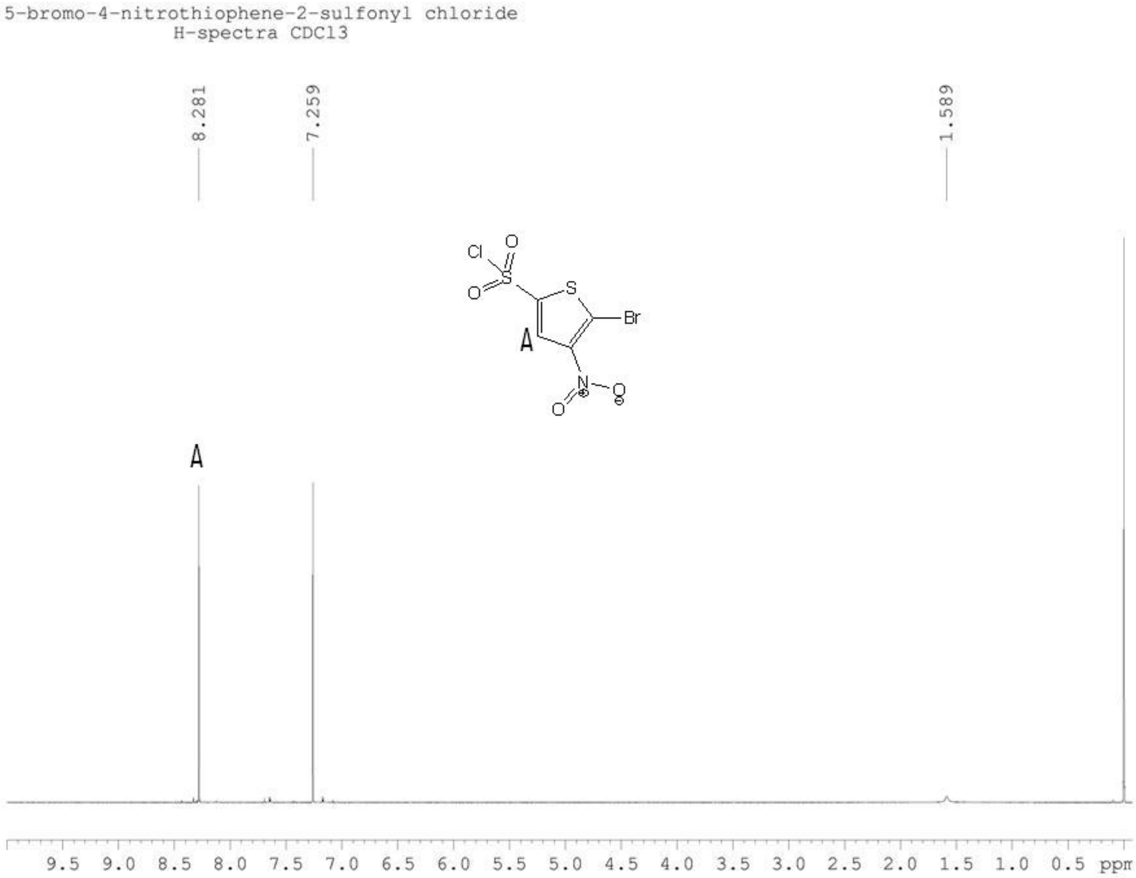


## Bromination of NDA with DBI

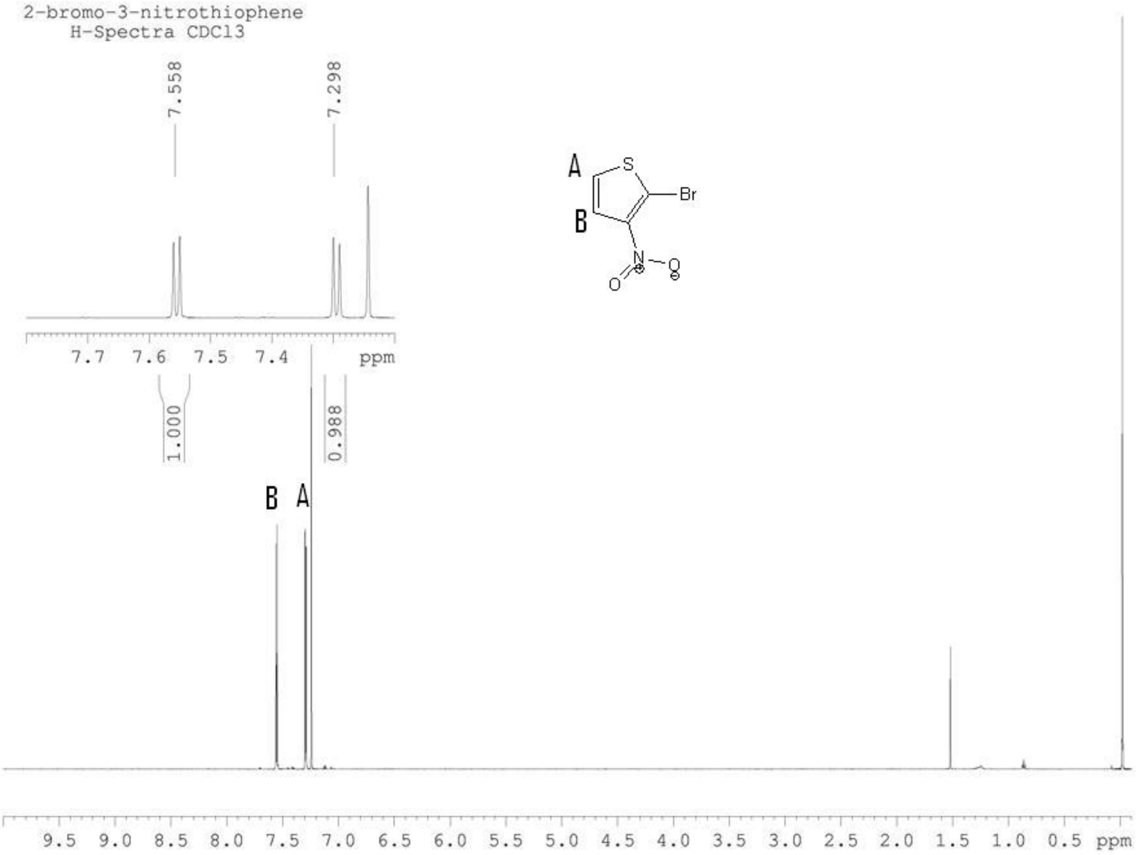
## 5-bromothiophene-2-sulfonyl chloride



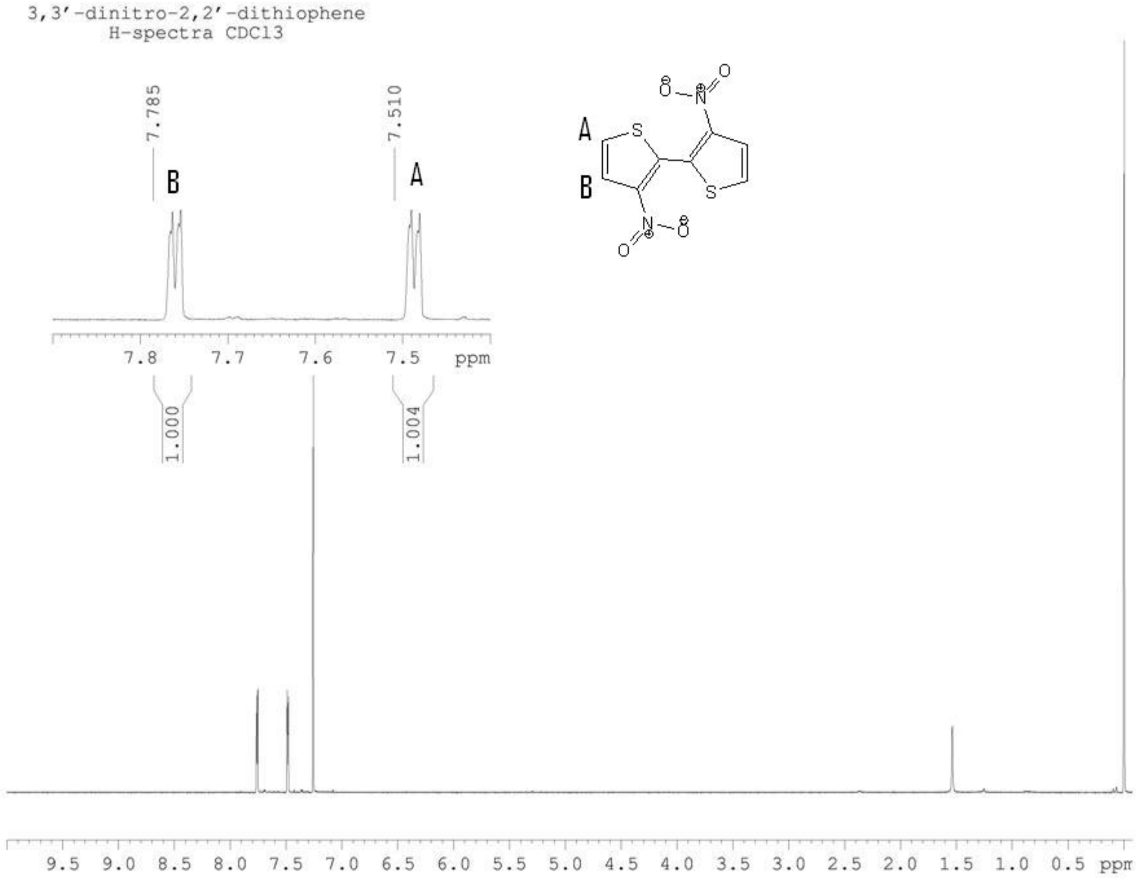
## 5-bromo-4-nitrothiophene-2-sulfonyl chloride



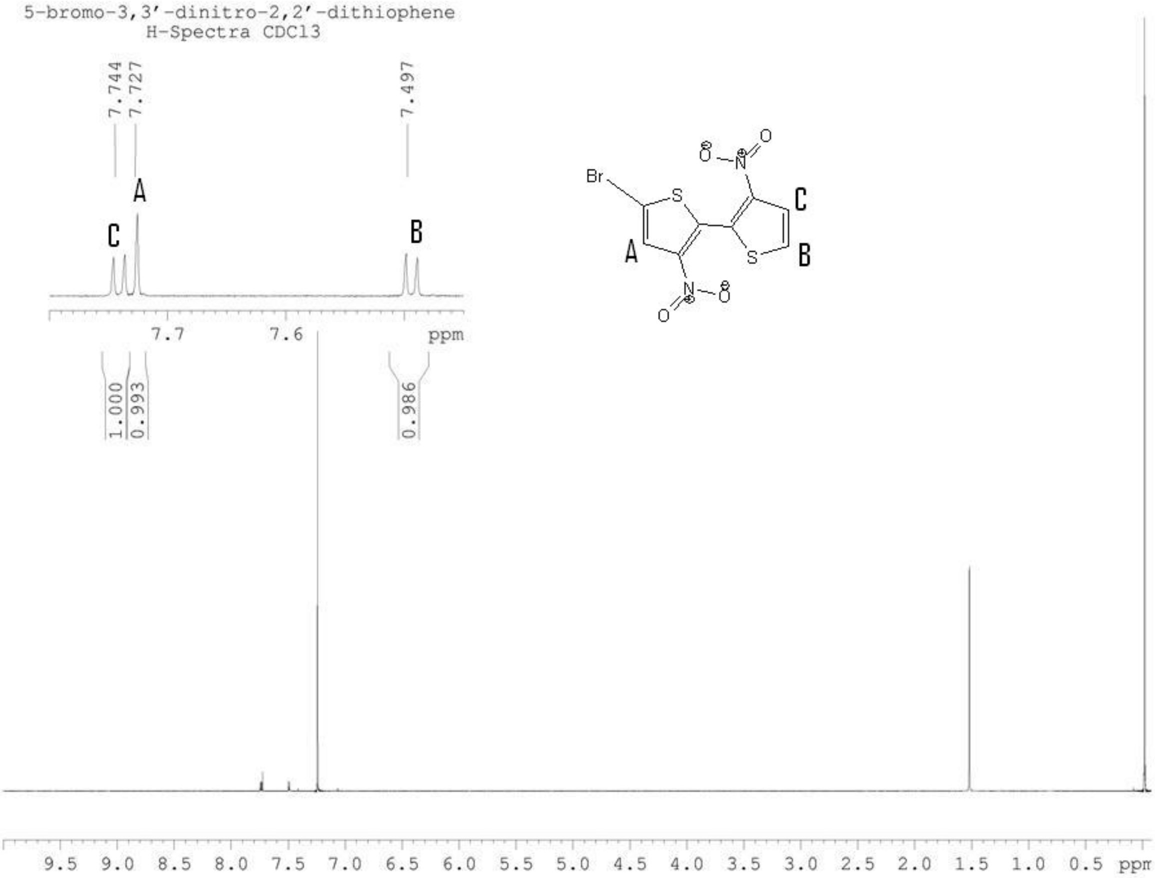
## 2-bromo-3-nitrothiophene



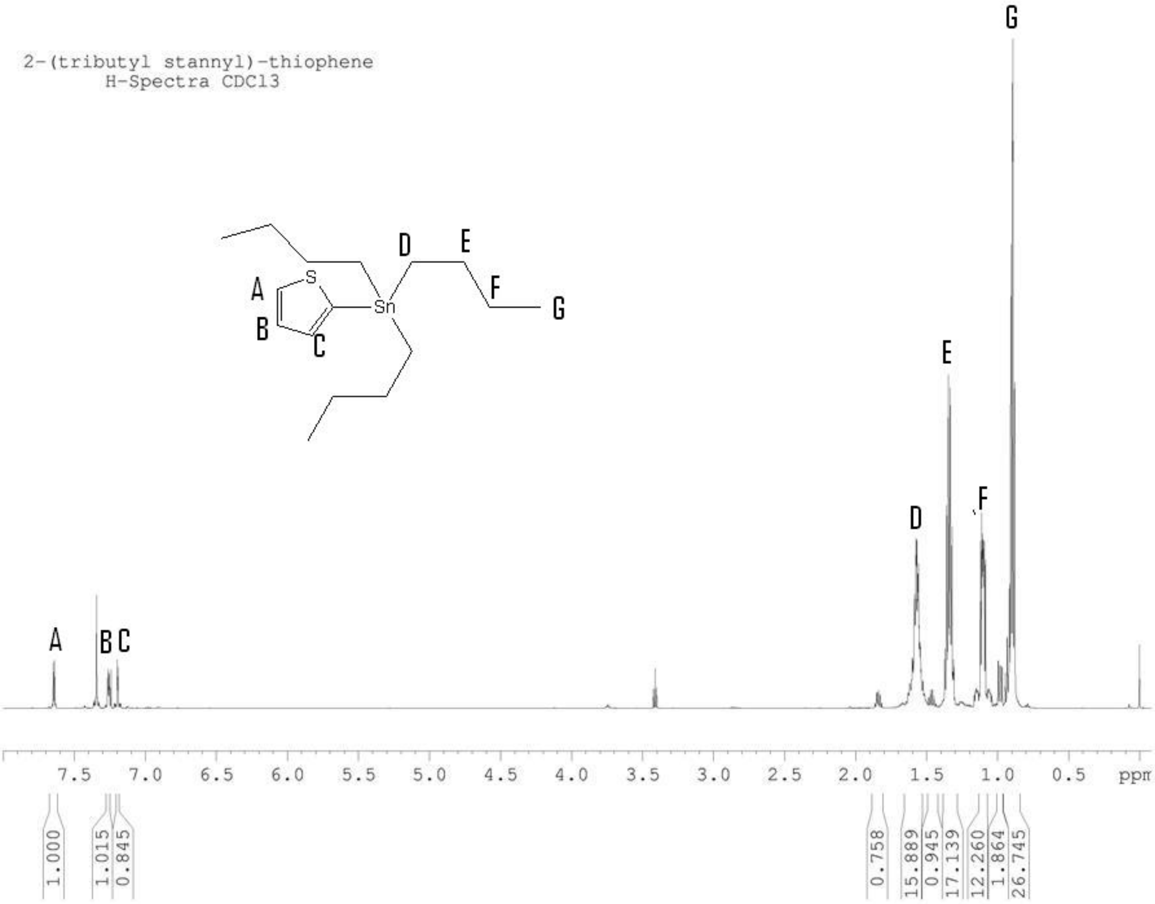
# 3,3’-dinitro-2,2’-dithiophene



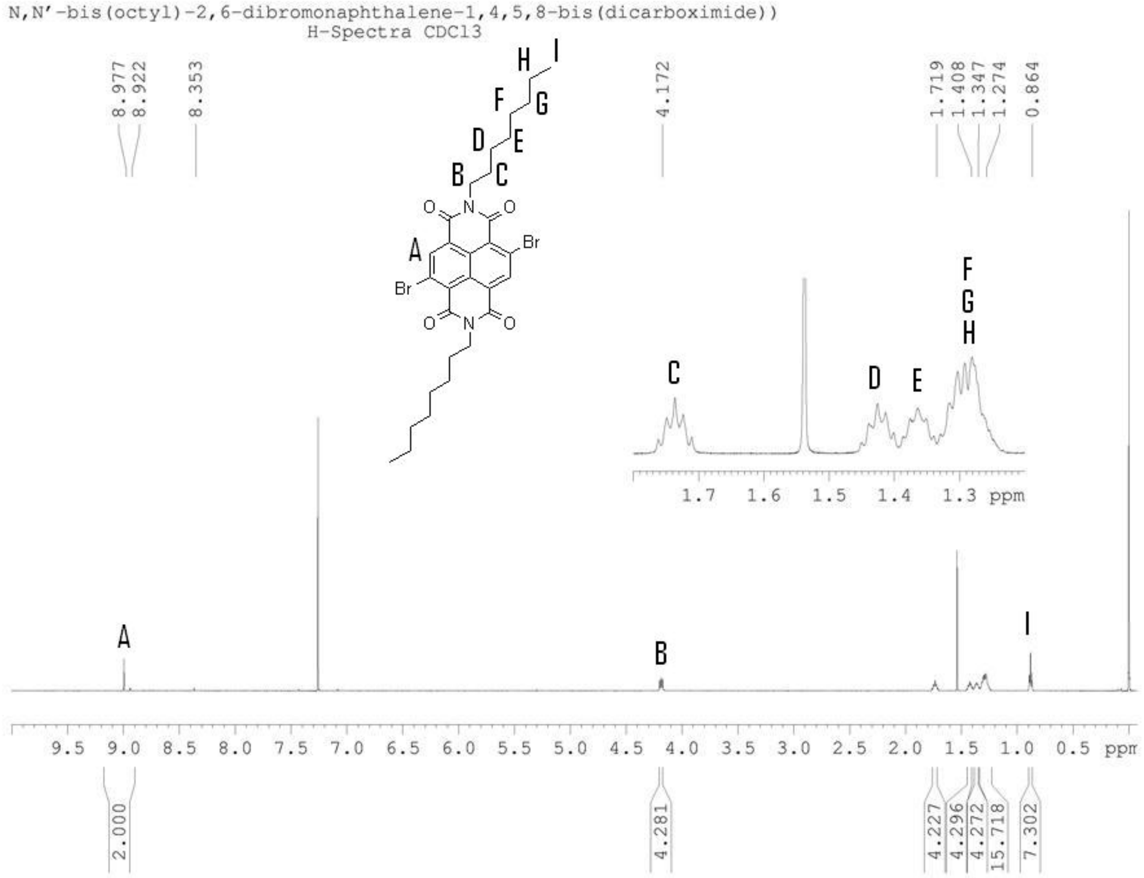
## 5-bromo-3,3’-dinitro-2,2’-dithiophene



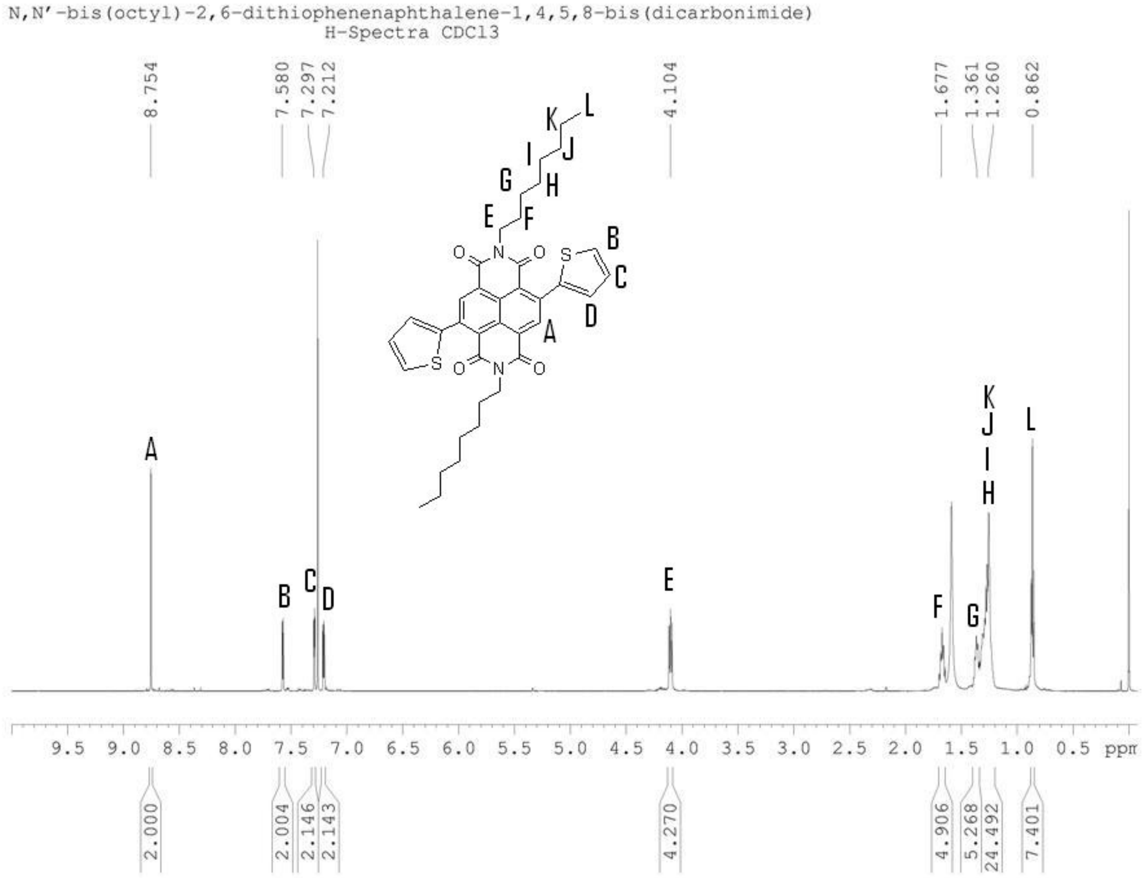
## 2-(tributylstannyl)-thiophene



## N,N’-bisoctyl-2,6-dibromonaphthalene-1,4,5,8-bis(dicarboximide)



## N,N’-bisoctyl-2,6-dithiophenenaphthalene-1,4,5,8-bis(dicarboximide)



# Appendix C

## Activating of copper

2 g of copper was treated with 20 mL 2% iodine in acetone solution by stirring for 10 min., the suspension was filtered the filtrate was added to a solution of HCl/acetone 1:1 filtered again and dried under vacuum.[A. Vogel, 1989]