Tuning The Properties Of Conjugated Polyions.

Investigating the effect of the placement of different donor groups on a conjugated polyion.

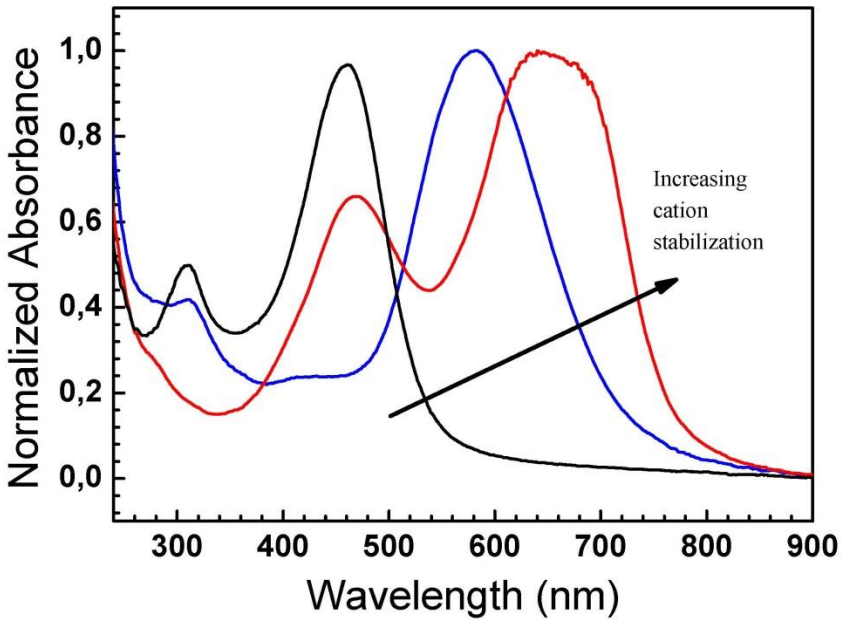

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Table of contents.

Acknowledgements.

This work is part of the research program of the Foundation for Fundamental Research on Matter (FOM), which is part of the Netherlands Organization for Scientific Research (NWO). It would not have been possible without the Molecular Electronics department of the Zernike Institute for Advanced Materials at the University of Groningen.

During the period of this bachelor's project I received a great deal of help from various people. First of all, I would like to thank Thomas Voortman for his intensive daily guidance not only in the lab, but also analyzing the results and finding the information I needed. On conclusion of this project, I was well and truly bitten and switten by the research bug and for that I'm grateful. Next, I would like to thank Prof. Dr. R.C. Chiechi for his supervision during the entire project and for his assistance when Thomas was not around. The discussions, although not many, really helped me get a better understanding of what I was doing.

Thirdly, I would like to thank the Chiechi group for welcoming me to the world of research and making me feel at home within the group. The lively spirit and humor throughout the day made it so much easier to do my work. Finally I would like to thank the Hummelen group for the insight they gave me during group meetings and for making me enthusiastic about doing research.

Summary.

A step in the direction of a durable world is the reduction of the proportion of energy used, which is obtained from fossil fuels or coal. There are green and durable energy sources available like wind and solar power. Alternatively, the production of biofuels can contribute to this goal. The use of plastic solar cells is particular interesting, because once the power conversion efficiency is high enough, they can be mass produced in a R2R process. Yet, as stated by Krebs and coworkers, "a true large-scale production can only be realized by processing from water and more research is needed on how this can be realized." The knowledge acquired from this research is a nanostep in the right direction.

A cross-conjugated polymer poly(fluorene-alt-1,4-phenylenebis-methanone), **PFK**, was prepared in a previous research, to see what the effect of charges in the backbone of a polymer is, on the optical, physical and electronic properties. To do so, **PFK**, containing ketone spacers, was converted to a linear conjugated polymer bearing cations in the backbone, which were stabilized by certain donor groups. As donor group, dimethylaniline was used, creating **PFC**. C stands for cation. As a result, a Donor-Acceptor system is created, the acceptor being the backbone of the polymer.

PFC is a conjugated polyion (CPI): conjugated polymers with closed shell cationic charges in the backbone, which is linear conjugated. The charges are created by a process called "spinless doping", to avoid free radicals ending up in the backbone created by traditional redox doping. The polymer obtained has stable, closed shell cations.

In this research, two analogs of this polymer were synthesized to investigate the tunability of the polymer. Also, **PFC** was synthesized differently, since the conversion of the ketones to the donor groups was insufficient. The three polyions created are **PFC_dMA**, (previously called **PFC**) **PFC_Ph** and **PFC_Me**, containing dimethylaniline, phenyl and methyl as donor group respectively. All polymers contain hexyl pendant groups for increased solubility in organic solvents. Unfortunately, the conversion of **PFK** to the three different polyions was not equal, therefore appropriate comparison could not be performed. The optical band gaps of **PFC_Ph** and **PFC_Me** were compared separately, since the conversion of these two polymers in the polymer analog reaction was about the same.

The optical, physical and electronic properties of the CPIs were compared. Due to the cations in the backbone, the CPIs show pH dependent band-gaps. This dependency is an equilibrium process in which sp^2 methylium carbons are converted to OH-trapped methylene carbons and vice versa.

To obtain the optical ban-edge of the polymers, UV/Vis measurements were performed. The polymers were measured as synthesized, after adding HBF_4 and after the addition of H_2SO_4. HBF_4 is used because it deprotects the donor groups, creating the cations in the polymer backbone. Sulfuric acid has the same effect, but also protonates any unreacted ketone groups still present in the polymer. Now the oxygen atom becomes cationic and will regain its two lone pairs by converting the carbonyl double bond to a single bond. This results in obtaining the polymer in its conjugated form. **PFK** was measured with H_2SO_4 for this exact reason, although the cations created were only transient.

The UV/Vis measurements showed that **PFK** has a band edge at 543 nm, **PFC_Me** at 715 nm while **PFC_Ph** has a band edge at 773 nm. This is expressed in an optical band gap of 2,28 eV, 1,73 eV and 1,60 eV respectively. The red shift between **PFC_Me** and **PFC_Ph** is 58 nm, which means that phenyl is a better donor to stabilize the cation with respect to methyl, as was expected beforehand, since the cation can delocalize in the benzene ring.

1. Introduction.

1.1 A brief history.

The field of organic semiconductors originated in 1948, when Eley et al[1] observed thermally activated conductivity in metal-free and copper phthalocyanines. Subsequently, in 1954 Akamatu et al[2] found that some complexes between polycyclic aromatic compounds and halogens, in the solid state, have fairly good electrical conductivity, i.e., ~10^{-3} S cm^{-1}. Although these materials were unstable and did not maintain that property for long, it did open up a new field of science.

Strangely, this area of science did not receive much attention until some discoveries of vital importance were made. The TTF/TCNQ charge transfer complex in 1973,[3] the first intrinsically conductive polymer i.e., polymeric sulfur nitride in 1975[4] and high electrical conductivity in doped polyacetylene in 1977.[5]

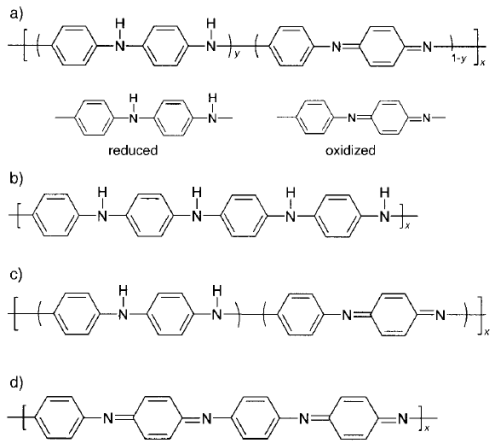
The TTF/TCNQ complex was the first organic compound which behaved like a metal, having a room temperature conductivity of 652 S cm^{-1}. Shirakawa et al[5] found that the semiconducting polymer, polyacetylene, showed dramatic increase in conductivity upon doping with halogens or arsenic pentafluoride. Upon doping they could achieve an overall change in conductivity of eleven orders of magnitude.

These discoveries are historical in the world of organic (semi)conductors. There is however another system that is worth mentioning, i.e., polyaniline. It was first reported in the 19th century, but it was not until the 1980s that it received much attention from the scientific community. In the section below, the system is explained in more detail.

1.2 Conductive Polymers.

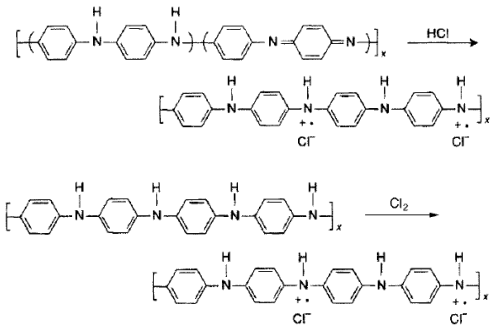
1.2.1 The PANI System.

The first report about PANI, polyaniline, appeared in 1862, but it was not until the 1980s that it became an extensively studied polymer.[6-9] Although PANI can be obtained electrochemically[10], it is often produced via a different pathway. An aqueous solution of $(NH_4)_2S_2O_8$ is added slowly to a solution of aniline dissolved in 1 M HCl at 5 °C. After one hour, the precipitate that formed is removed by filtration, washed several times with 1 M HCl and dried under vacuum for 48 hours. Via this synthetic route, the PANI is obtained as emeraldine base, one of several forms in which PANI can exist.[6] The general states of PANI that can be formed are shown in scheme **1**.



Scheme **1**. a) the general form of PANI, indicating the reduced and oxidized form, b) completely reduced polymer, c) half-oxidized polymer, i.e., the emeraldine base, d) fully oxidized polymer. Taken from [7].

Most conducting polymers, such as polypyrrole, polythiophene and polyfuran, can undergo either p- and/or n-redox doping.[7] PANI can also be redox doped, either p or n. The property which separates polyaniline form other conducting polymers is that its doped, highly conductive form can also be reached by a process called protonic acid doping. Treatment of the emeraldine base with, for instance, 1 M HCl results in complete protonation of the imine nitrogen to render the emeraldine hydrochloride salt completely protonated, i.e., its most conductive form. The same conductive polymer can be obtained by chemical oxidation (p-doping) of the completely reduced form with chloride. The two processes are shown in scheme **2**.



Scheme **2**. The two processes which render polyaniline in the emeraldine salt state. Taken from [7]

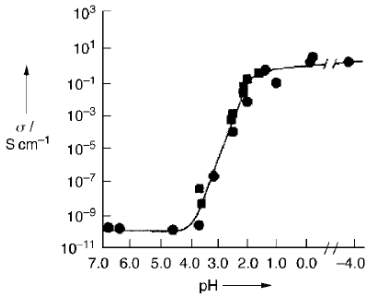


Fig. **1**. Conductivity of the emeraldine base as a function of the pH of the HCl doing solution. Taken from [7].

The fact that polyaniline can be acid doped means that the conductivity is pH dependent. This can be seen in fig **1**. An overall change in conductivity of about 10 orders of magnitude is observed.

Why does polyaniline show such high conductivity in the doped emeraldine base form? It is proposed that the polymer is highly stabilized by resonance as is depicted in fig. **2**.[6]

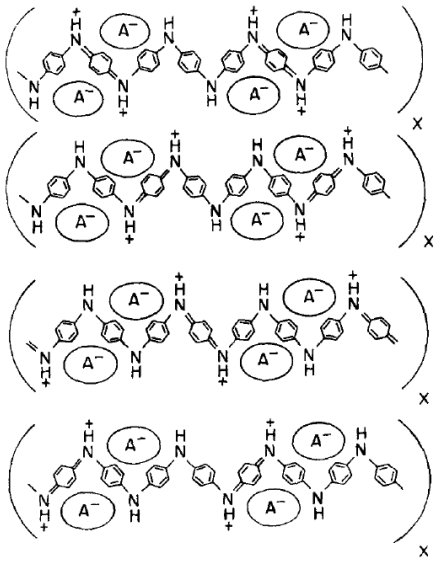


Fig. **2**. Proposed resonance forms of polyaniline in the emeraldine salt state. Taken from [6].

If this is indeed the case, then all N atoms, all C-N bonds and all C_6H_4 rings would electronically be identical. Every nitrogen atom would have a +0.5 charge and would be intermediate between an amine and an imine nitrogen. Similarly, all C-N bonds would possess half single- and half double-bond character. Finally all C_6H_4 rings would be

intermediate between benzenoid and quinoid. As a result, the highly conjugated and delocalized π-system would explain the conductivity observed.

1.2.2 Towards Large-Scale Production.

The discovery of the conducting polymers led to an important theory. In polyacetylene, each carbon atom has sp^2 hybridization, therefore, the π-electrons are free to delocalize into a band. The same is true for the polymeric sulfur nitride. Each NS molecule contains unpaired electrons free to delocalize. This delocalization of electrons forms the basis of a metallic conduction band, as is seen in polyaniline.

All aforementioned discoveries paved the way for new organic based electronic devices such as organic field-effect transistors, organic light emitting diodes and organic solar cells.[11]

An oft cited reason why organic solar cells are particularly interesting, is the idea that R2R solution processing of the solar cell is a viable option.[12] With R2R processing, large areas of thin organic films can be produced. Although this sounds fairly interesting, there are still some problems to address. First, all the preferred processing procedures in the laboratory and those suitable for R2R processing are generally not the same.[13] Second, there is a huge difference between preparing and aligning a small multilayer structure typically on a solid substrate like glass, and the precise coating and/or printing of large areas with the same accuracy on flexible substrates which move with speeds of 1-20 m/min.

A vital feature for any long lasting, large-scale production method, is that it does not harm the environment. As stated by Krebs and coworkers[13] "a true large-scale production can only be realized by processing from water and more research is needed on how this can be realized." However, the rigid, non-polar backbone of conjugated polymers prohibit solvation in renewable, protic and polar solvent like water and methanol. conjugated polyelectrolytes (CPEs) are a class of semiconducting polymers that are water soluble. CPEs are often used as cathode interface layer.[14] These materials are made water soluble by installing anionic pendant groups, typically containing sulfonate anionic end groups.[15,16] Although these CPEs are water soluble, they do form aggregates in polar protic solvents, in which the rigid, nonpolar hydrophobic backbones clutch together, creating a shell of anionic pendant groups minimizing unfavorable solvent interactions.

A first step in the direction of R2R processing of organic solar cells is creating organic, water soluble, conducting materials, capable of harvesting energy from light, while maintaining the tunability of traditional conjugated organic materials.

Chiechi and coworkers[12,17] have addressed this problem by creating ionic water-soluble backbones. Their materials contains sulfonate anionic pendant groups, but in addition to that, also contain cations in the backbone. They achieve this by a process they call "spinless-doping". In this process, a cross conjugated polyketone is converted to a linear conjugated polymer that is a charged, intrinsic semiconductor by the addition of a nucleophile during post-polymerization modification. The cations in the backbone are stabilized by installing certain electron donating side groups. In 2005 they reported an n-dopable conjugated polyketone in which the influence of spin and charge could be separated.[18] The problem however, was that they were transient, existing only while held at cathodic potential under air-free conditions. The newly synthesized polymer, which they named conjugated polyions (CPIs), does not suffer from these problems. CPIs are robust, air-stable and exhibit dynamic band gaps. They separate the influences of the unpaired electrons that result from traditional redox doping from the inclusion of charges and show dramatic physical changes, including solubility, without changing the position of the conduction band with respect to their

cross conjugated precursors.

Due to this design, conjugated polyions have donor acceptor characteristics. The cation in the backbone of the polymer is stabilized by an electron donating group. As a result of this, the polymer backbone acts as electron acceptor. Dimethylaniline was used as electron donating group, creating the configuration depicted in fig. 3.

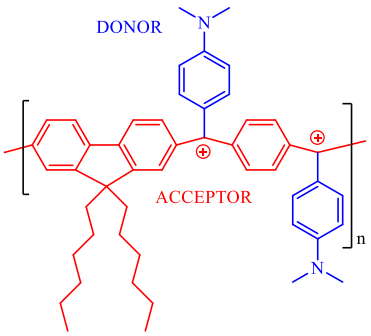


Fig. 3. Donor acceptor configuration of CPIs.

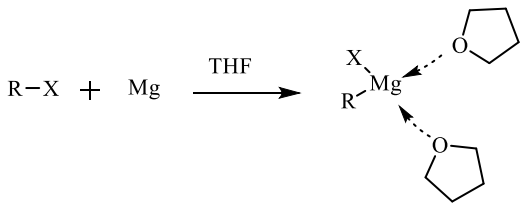
This bachelor research continues on the CPI project. The effect of different donor groups on the optical, electronic and physical properties is investigated, to determine the tunability of conjugated polyions. In the following two sections, the main chemistry involved to reach this goal is explained in a little more detail.

1.3 The Grignard.

In organic synthesis, the most important reactions are those which render new carbon-carbon bonds. For instance, addition to a carbonyl group would give the alcohol and simultaneously form a carbon-carbon bond. To perform such transformations, a carbon based nucleophile is necessary.

Professor F.A.V. Grignard discovered a new class of compounds called organometallic reagents, capable of such transformations.[22] For this he received the Nobel Prize in chemistry in 1912.[19] Most often, organometallic compounds, also called Grignard reagents, of lithium or magnesium are used. To prepare these compounds, direct reaction of the metal with a haloalkane is performed. Therefore, diethyl ether or THF must be used as solvent.

Grignard reagents are often denoted as RLi or RMgX. This is an oversimplified structure of the reagents. As displayed, the metal ions lack electrons. To regain the electron octet, they act as Lewis acids and coordinate to the Lewis basic solvent molecules. Therefore, diethyl ether or THF must be used as solvent. This coordination of solvent molecules is crucial for the formation of Grignard species. The general reaction can be found in scheme 3.



Scheme 3. The general reaction scheme of the Grignard reaction.

The formed Grignard reagent has a strongly polarized metal-carbon bond, creating a nucleophilic carbon to form new carbon-carbon bonds. Grignard reagents react with water, so they must be prepared in air- and water-free conditions. Furthermore, because of their sensitivity to water, they are often directly used in subsequent reactions.

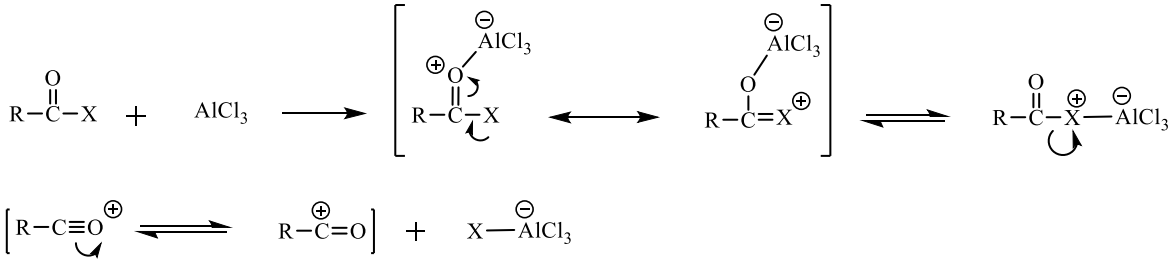
1.4 The Friedel-Crafts Reaction.

The most useful aspect of the Grignard reaction is that it creates a new carbon-carbon bond. There are more reactions capable of doing this and one of them is the Friedel-Crafts reaction. This reaction involves an electrophilic substitution on a benzene ring and was discovered by Friedel and Crafts in 1877.[23] They discovered that in the presence of a Lewis acid, halogenated compounds react with benzene.

In fact, there are two Friedel-Crafts reactions i.e., alkylation and acylation. In this research, the Friedel-Crafts acylation is performed, so the alkylation is not discussed any further.

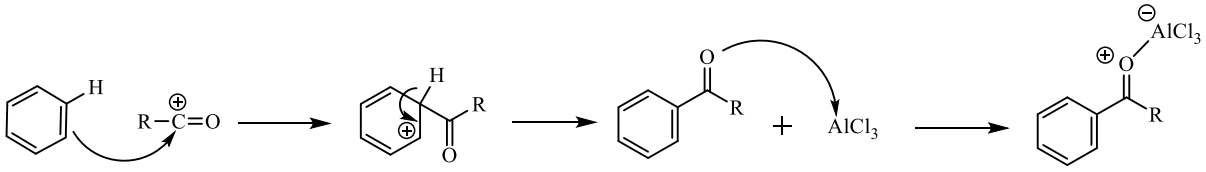
Benzene reacts readily with acyl halides in the presence of aluminum halide to produce phenyl ketones. In this case, fluorene is used in a reaction with terephthaloyl chloride. As Lewis acid, $AlCl_3$ is used in the presence of 10 wt% LiCl. The product of this reaction is **PFK**.

The key reactive intermediates in the acylation reaction are acylium cations.[19] These intermediates are formed in the reaction of acyl halides with aluminum chloride. The first step of the reaction is the coordination of the Lewis acid to the carbonyl oxygen. This complex is in equilibrium with an isomer in which the aluminum chloride is bound to the halogen. Dissociation then renders the acylium cation, which is stabilized by resonance and, opposite to the alkyl cation, is not susceptible to rearrangements (scheme **4**).



Scheme **4**. Formation of the acylium cation species.

The formed acylium cation is sufficiently electrophilic to react with benzene in an electrophilic substitution reaction. Because the acyl group is electron withdrawing, it prevents further substitution. Therefore, polyacylation does not occur, whereas polyalkylation does. This effect is enhanced by the formation of a strong complex between the ketone product and the Lewis acid catalyst (scheme ***5***). Due to this complex, $AlCl_3$ is removed from the reaction mixture and necessitates the use of at least one full equivalent of Lewis acid. The ketone product is obtained by aqueous work up of the complex.



Scheme ***5***. Electrophilic aromatic substitution followed by the formation of the ketone catalyst complex.

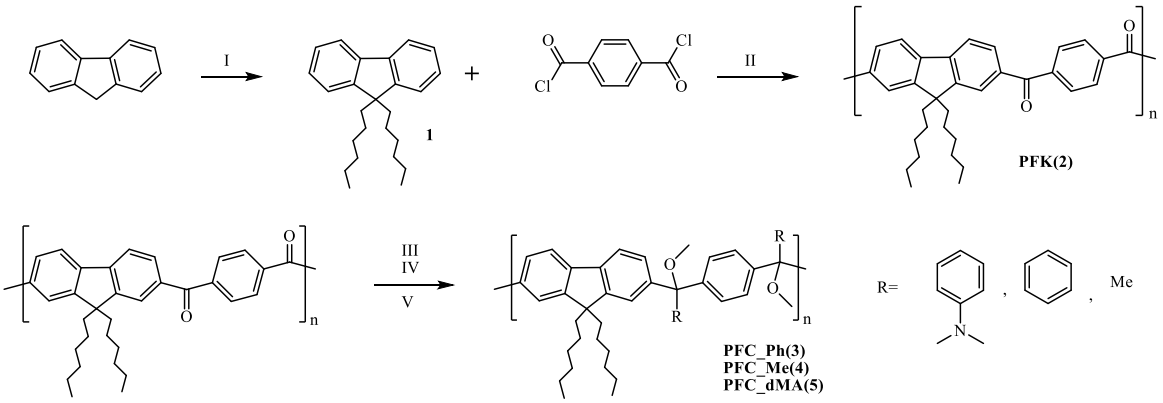
2. Results and Discussion.

2.1 Nomenclature.

In this bachelor report, abbreviations are frequently used. To assist the reader, we denote polyfluorene as "**PF**", Ketone with "**K**" and cation with "**C**". Furthermore, to distinguish CPIs with different donor groups, "**_X**" is used, **X** being the donor group in question. The CPIs are in the methoxy ether form unless stated otherwise. Finally, the CPIs can also be denoted with a number according to scheme **6**.

2.2 The Synthesis.

2.2.1 The general reaction.



Scheme **6.** Reaction scheme of the polymerization and of the polymer analogous reaction. (I) THF, n-BuLi, -78 °C, 1-bromohexane (II) ODCB, $AlCl_3$(3,5 eq.), LiCl 10 wt%, reflux. (III) THF, Phenylmagnesium bromide, rt 2h, reflux, NaOMe. (IV) THF, methylmagnesium chloride, rt 2h, reflux, NaOMe. (V) THF, n-BuLi (10 eq), 4-bromo-N,N-dimethylaniline (11 eq) -78 °C 2h, rt, NaOMe.

To examine the effects of different donor groups on the optical, electronic and physical properties of the CPI, three different polymers were synthesized according to scheme **6.** First, the dihexyl-fluorene monomer was made via **I**. Next, the cross-conjugated polymer, **PFK**, was synthesized in a Friedel-Crafts reaction.[19] In this reaction, anhydrous conditions were of the highest priority. Therefore, anhydrous $AlCl_3$ and anhydrous LiCl were used. Also, the terephthaloyl chloride was freshly recrystallized from hexane before use, since it hydrolyses to the acid when reacting with water from the air.

To synthesize the CPIs with the different donor groups, a polymer analogous reaction was performed, with Grignard reagents. The reaction was quenched on alkaline methanol to obtain the CPI as a methoxy ether, for the ease of handling. The CPI could then be obtained in its cationic state with a strong enough acid, which has a non-nucleophilic conjugate base, such as HBF_4 or H_2SO_4.

Upon adding the Grignard reagent to the cross-conjugated polymer, the change to a dark deep color of the reaction mixture was observed, characteristic of Grignard reactions. To be sure of good conversion, the reaction mixture was stirred overnight. After quenching the reaction with NaOMe, the solvents were removed and the obtained solid was extracted with H_2O and DCM. Water was used to wash out salts formed in the reaction. However, separation of the two layers was not so easy, since almost no difference in color was observed. Upon adding brine this improved some, but good separation was still difficult due to a layer of undissolved flakes. Next, a wash with 1N

HCl was performed, dissolving these flakes and giving a nice and clear separation of the organic and water layer. These undissolved flakes turned out to be polymer product, since the yield of the reaction was higher upon washing with 1N HCl.

The conversion of the polymer analogous reaction was checked with FT-IR. Reduction of the ketone stretches observed with **PFK** indicated a good conversion. For more complete analyzes, ^{1}H NMR spectroscopy was also performed. Furthermore, to determine the optical band-gap of the polymers, UV/Vis spectroscopy was performed, which included three measurements for each polymer. First, just as synthesized. For the second measurement, HBF_4 was added and the third measurement involved the addition of H_2SO_4. Acid deprotects the donor group and protonates all unreacted carbonyl groups. It will be discussed with more detail in the optical properties section.

2.2.2 The Dimethylaniline Polymer.

The polymer **PFC_dMA** was synthesized before by Voortman et al[17] by means of Friedel-Crafts chemistry in the polymer analogous reaction. In order to compare the polymers, the polymer analogous reaction should have the same conversion with each donor group.

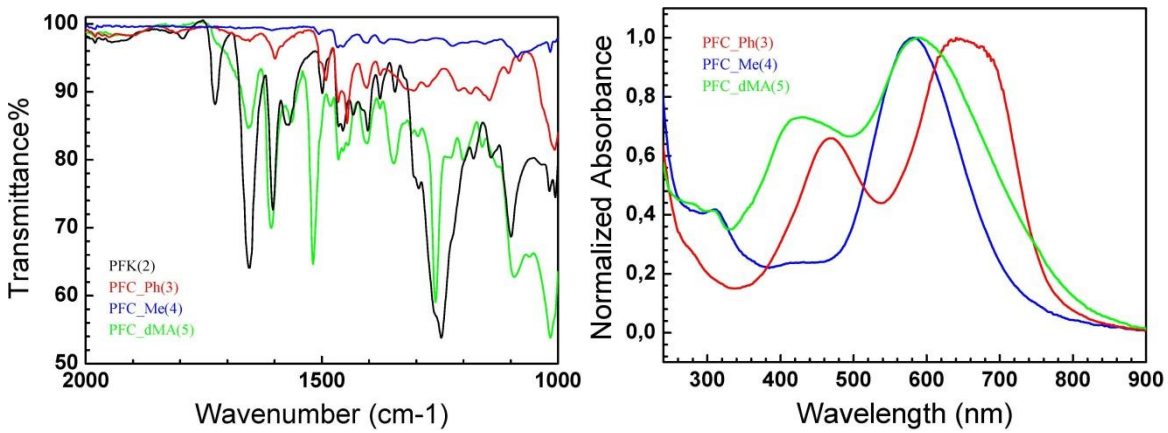


Fig **4**. IR-spectra of PFK and the three analogous polymers **3**, **4** and ***5*** (left) and the acidified absorption spectra of the three different polymers (right).

The conversion of each of the polymers, analyzed by FT-IR, and the absorption spectra are compared in fig **4**. It is clear that the conversion of ***5*** is not equal to **3** and **4**, since the characteristic ketone peaks at 1600 and 1250 cm^{-1} are still clearly visible, resulting in a $\lambda_{max, abs}$ close to 600 nm for ***5***, which is in between the values observed for **3** and **4**.

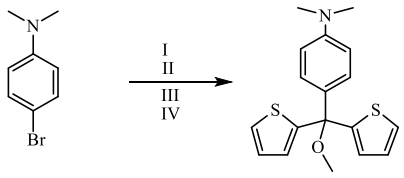
Dimethylaniline has a higher electron density then phenyl, enhancing the ability to stabilize the cation. Also, the structure with the nitrogen atom bearing the cation is a large contributor to the resonance structures. Therefore, it is expected that the band-edge of ***5*** to be most red shifted. This is not the case probably due to the low conversion of ***5*** in the polymer analogous reaction. Since the polymer analogous reaction using Grignard reagents was such a success, a lot of effort was put into synthesizing ***5*** with the use of a Grignard.

The synthesis of **3** and **4** caused no problems what so ever, probably because the Grignard reagents were commercially available, but the Grignard of Dimethylaniline first needed to be synthesized what proved to be somewhat problematic. Different ways of synthesizing the Grignard were tried and all of them involved a reaction

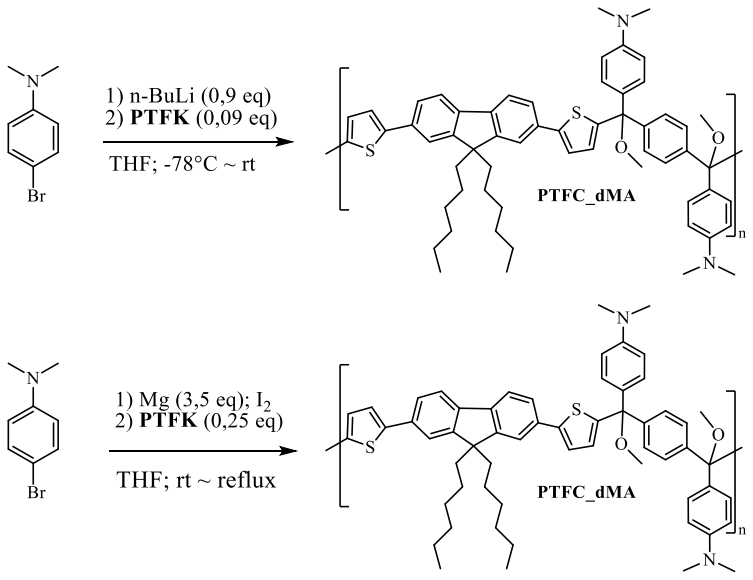
with 4-bromo-N,N-dimethylaniline, which upon reacting with magnesium or lithium, should give the organometallic reagent.

For the reaction with magnesium to start, the oxide layer covering the magnesium should be removed. First, this was tried mechanically, using small pieces of glass. Second, the oxide layer was removed using I_2.[20] A third way involved the use of iPrMgCl, the so called turbo Grignard.[21] Finally, a reaction of 4-bromo-N,N-dimethylaniline with n-BuLi was performed to produce the lithium reagent.

In order to see what worked best, a test reaction was performed. The organometallic reagent was subjected to dithiophene ketone (**DTK**) with the same reaction conditions as in the polymer analogous reactions which showed a good conversion. The conversion was checked with TLC and, although it was far from complete, the lithium reagent seemed to have the best conversion. All the test reactions and the polymer analogous reactions with dimethylaniline can be found in scheme **7** and **8** below. With method I and III, the magnesium did not react, so the second step was not performed, which was the addition of dithiopheneketone.



Scheme **7**. The test reactions of the dimethylaniline donor group. I) Mg(0,75 eq), mechanical cleaning, **DTK** (0,25 eq), THF, rt → reflux. II) Mg(0,75 eq), I_2, **DTK** (0,25 eq), THF, rt → reflux. III) i-PrMgCl, **DTK** (0,25 eq), THF, rt → reflux. IV) n-BuLi(1,8 eq), **DTK** (0,25 eq), THF, rt → reflux.



Scheme **8**. The polymer analogous reactions involving the dimethylaniline donor group.

Because the conversion was incomplete, the stoichiometry was changed. Instead of 3,5 equivalent of the organometallic donor reagent, a 10 fold excess was used. It was performed on a different polymer, i.e., poly(thiophene fluorene ketone) (**PTFK**). Not only changing the donor group alters the properties of CPIs, but also different polymer backbones will change these properties. However, this is not within the scope of this research. It was performed to see the conversion with the lithium reagent.

The conversion was checked with IR and can be found in fig. *5*. For comparison, also the spectrum of **PTFC_Ph** is included in the graph. The main region to focus on here is between 2000 and 1000 cm^{-1}, since the typical ketone peaks are in this region. Significant reduction of these peaks means that the conversion was sufficient, as can be seen with **PTFC_Ph**. Opposite to **PTFC_Ph**, **PTFC_dMA** does not show this reduction. The peaks are reduced only by a small amount. This indicates that the conversion was insufficient and therefore the reaction was unsuccessful. The polymer analogous reaction with dimethylaniline was not further pursued and not attempted of **PFK**.

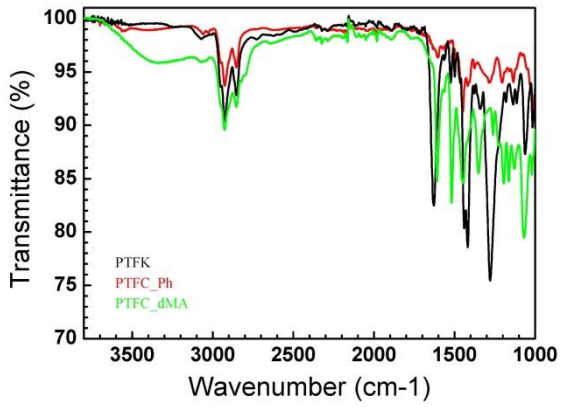


Fig. *5*. The IR spectra of **PTFC_dMA** compared to **PTFK** and **PTFC_Ph**.

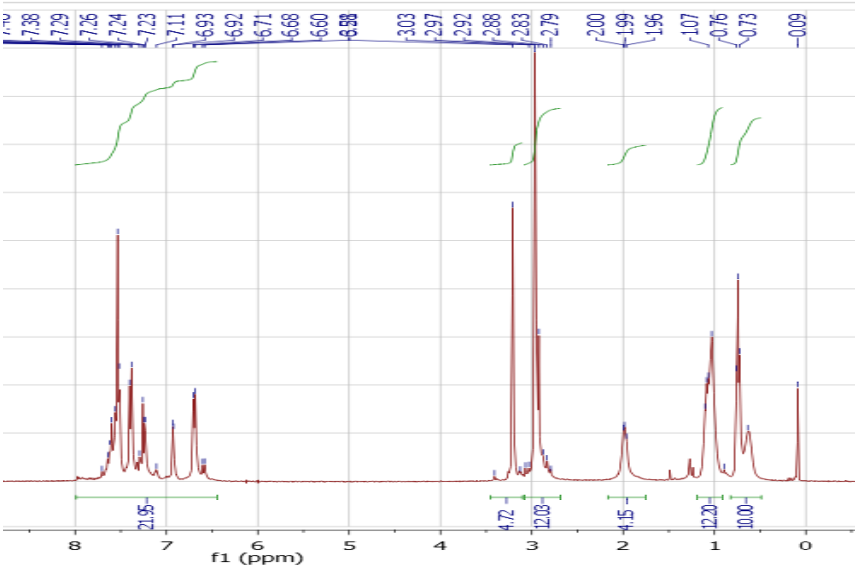


Fig. 6. NMR spectrum of PTFC_dMA.

Looking at the NMR of **PTFC_dMA** in fig. 6, one can come to a completely different conclusion. Upon setting the integrals of the hexyl chains to the right amount of protons, the NMR indicates a good conversion. There should be 22 aromatic protons, which is almost exactly what the NMR shows. However, this is including the chloroform solvent peak, so the integral should be lowered by 1. Furthermore, the peak of the amine methyl groups should be around 3, having an integral of 12. This can also be seen in the NMR, apart from an adjacent peak, which could be from the methyl ether group. the integral of this peak is almost 5, which could indicate that a large part of the polymer is in the methoxy ether form. An integral of 6 would mean complete conversion to the methoxy ether instead of the alcohol.

Although the NMR looks convincing, the IR clearly shows an incomplete reduction of the ketone peaks and therefore the polymer analogous reaction was unsuccessful. As to why the polymer analogous reaction with dimethylaniline shows such a low conversion remains unclear. The dimethylamine group activates the benzene ring, increasing the electron density. As a result of this, the Grignard might be too stable, making it unreactive

2.3 What product do we actually obtain, polyether or polyol?

The last step of the reaction, quenching the reaction on alkaline methanol, was performed to obtain the product as methoxy ether in order to make the cationic state of the polymer easily accessible. Treatment of the polymer in solution with HBF_4 protonates the methoxy group, creating a methanol leaving group, rendering the polymer cationic. The conjugate base, BF_4^-, is non-nucleophilic, so it only acts as counter ion.

In the early stage of the synthesis, the methanol used in quenching the reaction was not dry methanol. The NMR of PFC_Ph$^+$ (fig. 7) shows the appearance of a new peak in the aromatic region. It is known that the presence of cations lowers the chemical shift of neighboring protons.[24] Yet, apart from the fact that a full conversion cannot be achieved, the initial peak has not fully disappeared indicating that not all cations are trapped as methoxy ether. Some could have been converted into alcohol groups for which HBF_4 is not acidic enough to create water as leaving group, rendering the cations in the backbone of the polymer.

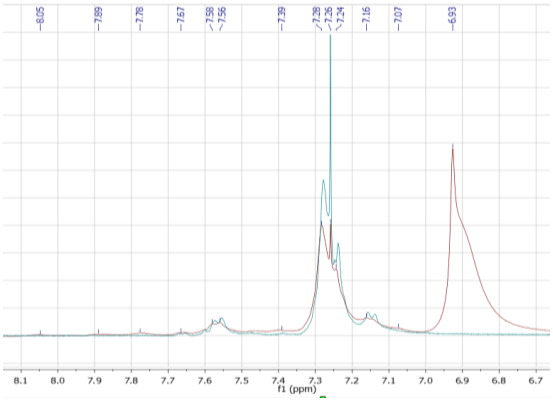


Fig. 7. PFC_Ph (blue) superimposed on PFC_Ph$^+$ (red).

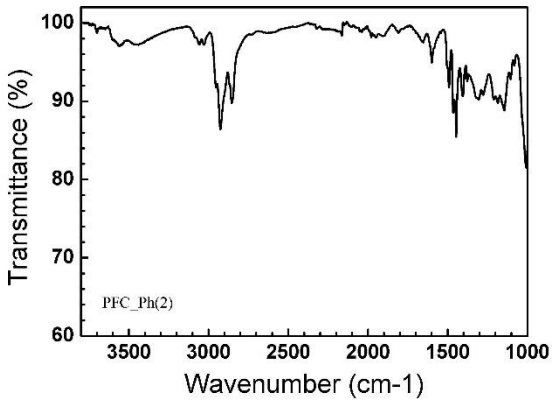


Fig 8. IR-spectrum of PFC_Ph showing the broad peak at 3500 cm^{-1}, probably from OH.

In fig. 8 the IR spectrum of PFC_Ph is displayed. Whether we have the polyol or polyether cannot be concluded from just this spectrum. Despite the broad peak at 3500 cm^{-1}. Alcohols show strong and broad hydrogen-bonded stretching bands centered at around 3400 and 3300 cm^{-1}, however the O-H stretch from water, if present, is also in this region.[26] To exclude water from the polymers entirely, they were dried in vacuum at 55 °C for a week. With both polymers, the broad peak at 3500 cm^{-1} did not diminish, so it can be concluded that at least part of the polymers is in the polyol form.

The lack of a strong absorption peak at 1200-1100 cm^{-1} in the modified polymers seems questionable for two reasons. First of all, alcohols show a C-O stretch around 1260-1000 cm^{-1}. This band can be used to assign a primary, secondary or tertiary structure to an alcohol. In this case, if the product is in fact a polyol, the C-O stretch should be at 1150, +/- 30 cm^{-1}, since it can only be a tertiary alcohol. The second reason is that the asymmetric C-O-C stretching vibration of ethers also occur in this region, i.e., at about 1120 cm^{-1}.

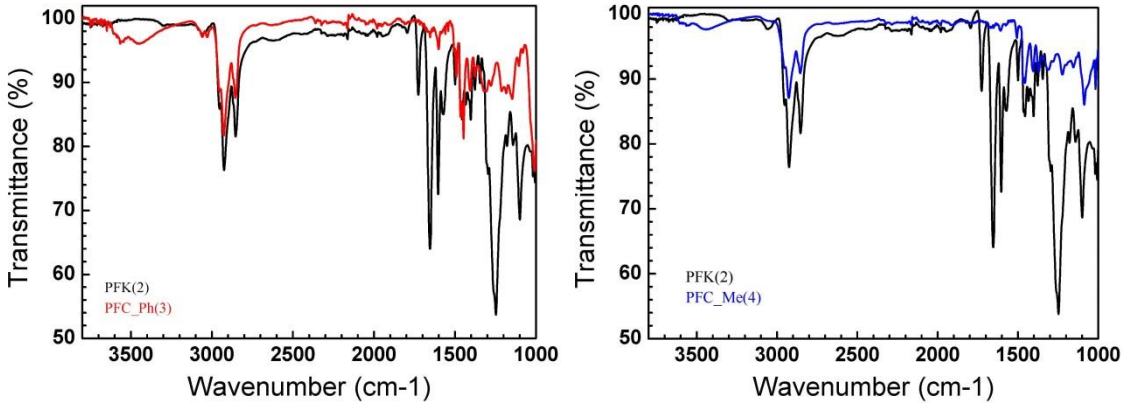


Fig. 9. IR-spectra of PFK (black) and PFC_Ph (red) on the left. On the right, PFK (again black) and PFC_Me (blue).

In fig. 9, the IR spectra of the cross conjugated polymer and the CPIs with phenyl or methyl as donor group is shown. Here, the disappearance of the C=O stretch at 1600-1700 cm^{-1} and the C(CO)C bending vibration at 1250 cm^{-1} clearly indicates that the polymer analogous reaction using Grignard reagents was indeed a success.[26] Conjugation effects the IR spectra, making it difficult to identify the C-O stretch, either from the alcohol or the methoxy group.

2.4 Optical Properties.

As can be seen in fig. 3, CPIs have a donor acceptor configuration which is known to decrease optical band gaps.[27] The optical band-gap of the CPIs and PFK was determined with UV/Vis spectroscopy, using DCM as solvent. In order to create the free cations in the polymer, HBF_4 50 wt% in water was added. As described before, the acid protonates the methoxy group, creating a methanol leaving group. Subsequently, to perform the measurement, only the DCM was collected. To completely deprotect the polymer and protonate all unreacted ketone groups, a third measurement was performed with sulfuric acid. H_2SO_4 was added to the polymer dissolved in DCM and the absorbance was directly measured, before the polymer precipitated completely.

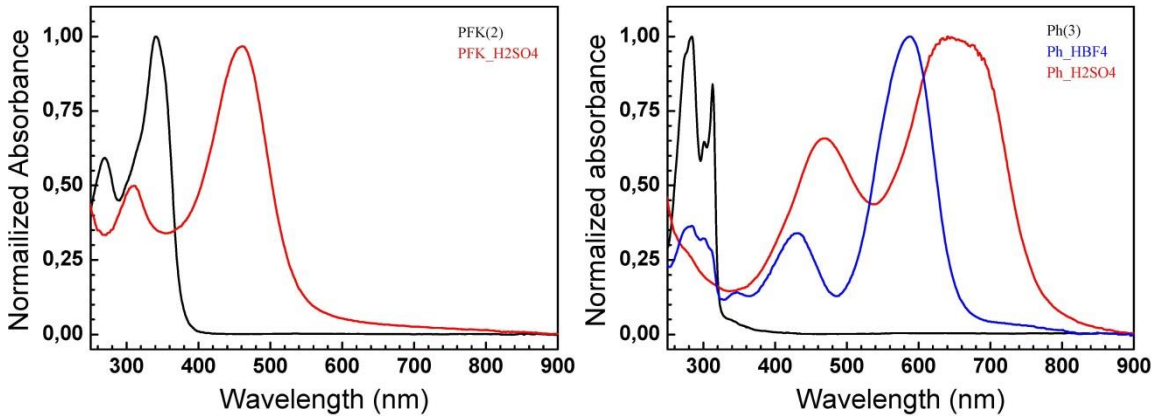


Fig. 10a. The UV/Vis spectra of 2 (left) 3 (right),

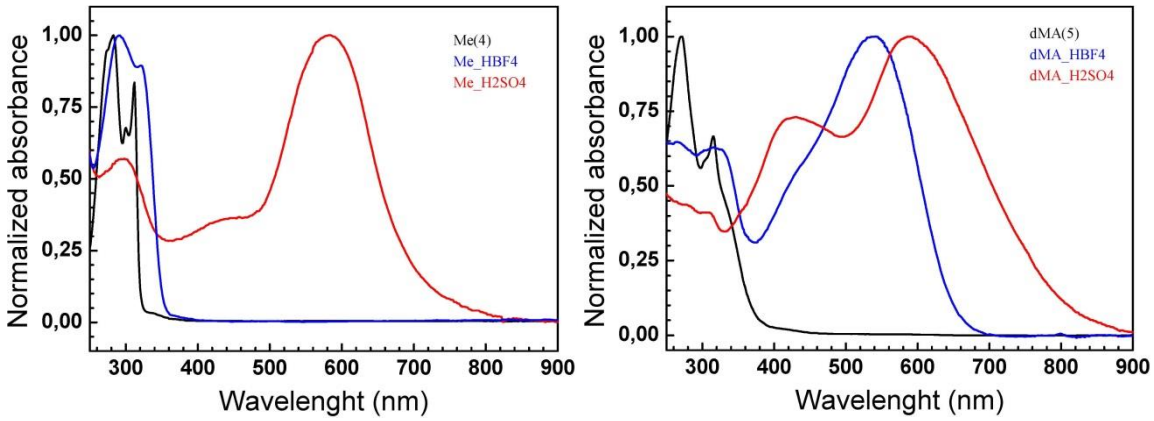


Fig. **10b**. The UV/Vis spectra of **4** (left) and **5** (right, taken from [17]). The samples were measured as synthesized (black), after the addition of HBF_4 (blue) and after adding H_2SO_4 (red).

As synthesized, the polymers absorb at 250-300 nm (fig. **10a** & **10b**). With **4** there is no shift in absorption upon adding HBF_4 to the sample. This might be because the stabilizing ability of methyl is insufficient. This means that HBF_4 is not a strong enough acid to create the cations in the backbone. Opposite to methyl, phenyl and dimethylaniline do possess this stabilizing ability, since the cation can diffuse in the donor group.

PFK is only measured as synthesized and with the addition of H_2SO_4. This is because HBF_4 is not acidic enough to protonate the ketone groups. Upon protonation, the oxygen atom becomes cationic. To regain the two lone electron pairs, the double bond is converted to a single bond, creating cations in the backbone of **PFK**. However, the cations are only transient. Since the CPIs in the methoxy ether form are non-conjugated, there is a blue shift observed compared to **PFK**, especially with **3** and **4**.

The effect of creating cations in the backbone of the CPIs is that the extent of conjugation increases. In fact, a non-conjugated polymer is transformed into a linear conjugated polymer, because the cation can delocalize in the backbone. There are two peaks observed in the UV/Vis. It is often cited that, within a d-a polymer, the peak at lower wavelength is from a $\pi \rightarrow \pi^*$ transition of the donor and the peak at higher wavelength is from internal charge transfer between the donor and acceptor.[28,29] Yet, there is a different explanation as to why the first absorption peak is observed. The first absorption peak, instead of a $\pi \rightarrow \pi^*$ transition, can be from protonated ketone groups which were not converted in the polymer analogous reaction. This peak has lower intensity in the HBF_4 measurement, because it is a weaker acid then H_2SO_4.

In the presence of conjugated double bonds, the electronic levels of a chromophore move closer together.[19] As a result, the energy to realize a transition from an occupied electronic level to an unoccupied electronic level decreases, resulting in an increase in the wavelength absorbed. Conjugation not only results in a bathochromic shift but also increases the intensity of the absorption, known as the hyperchromic effect.

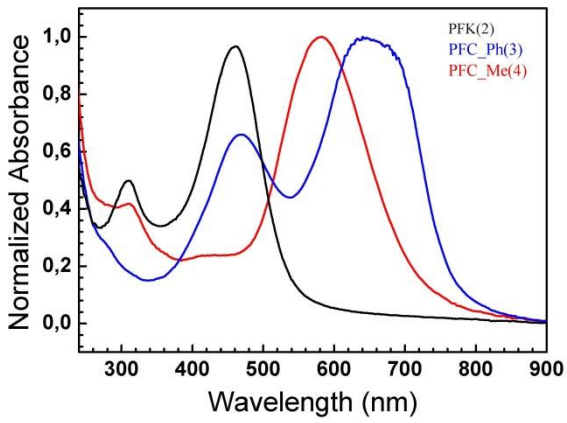


Fig. 11. UV/Vis spectra of the CPIs with different donor groups and the cross-conjugated polymer **PFK**. The samples are acidified using conc. H_2SO_4 to measure the polymers in their cationic state.

The UV/Vis spectra of the CPIs in the cationic state are compared to **PFK** in fig. 11. The first peak in the spectra of **PFC_Ph** and **PFK** is probably due to protonated ketone groups. With PFC_Me, this peak is nearly invisible, which might indicate a better conversion. From the UV/Vis can be concluded that **2** has a band edge at 543 nm, **4** at 715 nm while **3** has a band edge at 773 nm. This is expressed in an optical band gap of 2,28 eV, 1,73 eV and 1,60 eV respectively. The bathochromic shift between **3** and **4** is 58 nm, which means that phenyl is a better donor to stabilize the cation with respect to methyl, as was expected beforehand, since the cation can delocalize in the benzene ring. Comparing **PFK** with **PFC_Me**, the band-edge is 170 nm red shifted. This means that even a small methyl group, which only stabilizes through induction, is already a great improvement in stabilizing the cation, compared to **PFK**.

2.5 Thermal and Physical Properties.

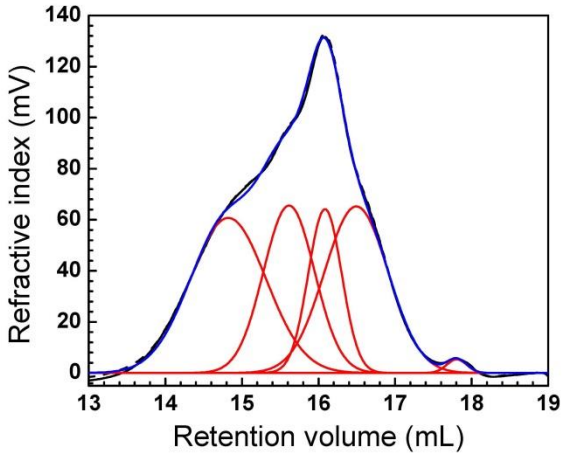


Fig. 12. GPC of **PFK**. The different Gaussians of which the plot consists are shown in red.

In order to ascertain the molecular weight of **PFK** a GPC (Gel Permeation Chromatography) was acquired. The molecular weight was determined using an internal polystyrene standard. The result is shown in fig. 12. This polymerization is a so called step growth polymerization. With this type of polymerization, first dimers are formed, then trimers and oligomers and eventually long chain polymers. Due to the polymerization mechanism, long reaction

time is needed to achieve high molecular weight polymers. The molecular weight values of **PFK** can be found in table **1**.

Sample	Mn	Mw	Mp	Mw/Mn
PFK_1	2,149	4,628	2,186	2,153
PFK_2	2,196	4,707	2,254	2,143

Table **1**. Molecular weights of **PFK** determined with GPC, measured in duplo.

The molecular weight of the polymer is not so high as one would wish. Due to the mechanism of polymerization, this can be improved with longer reaction time. The simulated Gaussians demonstrate the multimodal curve. The weight of the repeating unit in **PFK** is about 460 g mol^{-1}. Looking at the Mn, it can be concluded that the polymer is actually an oligomer, containing about 5 or 6 repeat units. For this reason, a previous batch of **PFK** was used with a Mp of about 7,000. This is still not a long chains polymer, but that does not have to be problematic, because the band structure saturates at a particular chain length.

PFK was also characterized with Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) as well as the CPIs. TGA measures the changes in physical and chemical properties as a function of increasing temperature. Typical data acquired from TGA is the temperature at which 10% weight loss occurs, i.e., Td. Td indicates the thermal stability of the polymers. Until this temperature, the polymer remains stable and degradation occurs at temperatures above Td. Furthermore, TGA can show a stepwise degradation of the polymer, which means that certain parts of the polymer are discarded. For instance, in the case of CPIs, it can show at which temperature the donor group is being discarded.

DSC is a technique in which the difference in heat flow between a sample and a reference required to increase the temperature is measured as a function of temperature. It is used to determine if the polymer has a glass-transition temperature, Tg. Above Tg, the polymer can overcome a kinetic trap, thus it can order itself in a thermally more favorable orientation. Tg is particular important for conjugated polymers because it is the temperature at which annealing is performed in device fabrication. The degree of crystallinity has a great effect on the Tg. Different donor groups will mean different packing of the polymer chains and therefore different Tg.

Due to the failed synthesis of **PFC_dMA**, the values for this polymer are taken from **PFC_dMA** synthesized by Voortman et al.[17] It must be noted that due to the lower conversion in the polymer analogous reaction of this polymer, the values might not be comparable.

Polymer	Tg (°C)	Td (°C)
PFK	97	439
PFC_Ph	136	294
PFC_Me	89	343
PFC_dMA	175	402

Table **2**. TGA and DSC results of the cross-conjugated polymer and the CPI analogs.

Looking for a trend in the Tg of the polymers, one can argue that higher monomer weight polymers have a higher Tg, although **PFC_Me** deviates from this trend. Taking only the CPIs into account, then the polymer having the larger donor group also has the higher Tg. The Td of the polymers follows a different trend. The cross-conjugated polymer **PFK** has the highest temperature at which 10% weight loss occurs. The CPIs don't display any trend in this physical property.

3. Conclusion.

The goal of this research was to identify the effect of different donor groups on the optical, electronic and physical properties of a cross-conjugated polymer, i.e., **PFK**. To achieve this goal, three different polymer analogs were synthesized, being **PFC_Ph**, **PFC_Me** and **PFC_dMA** , by means of organometallic chemistry. Unfortunately, the conversion of **PFC_dMA** was insufficient for comparison with the other two polymer analogs. Different synthetic pathways were tried, but none of them achieved an appropriate conversion. Therefore, the optical band gap of the three remaining polymers were compared separately. The UV/Vis results showed that **PFK** has a band edge at 543 nm, **PFC_Me** at 715 nm while **PFC_Ph** has a band edge at 773 nm. As a result of this, the optical band gap is 2,28 eV, 1,73 eV and 1,60 eV respectively. The bathochromic shift between **PFC_Me** and **PFC_Ph** is 58 nm, which means that phenyl is a better donor to stabilize the cation with respect to methyl, as was expected beforehand, since the cation can delocalize in the benzene ring. **PFC_dMA** with good conversion will probably have an even more red shifted band edge, since it is more electron rich then phenyl and it contains a large contributor to the resonance structures in which the nitrogen atom bears the cation.

All in all, this shows that the optical band gap of the polymer can be tuned between 2,28 and 1,60 eV by introducing a different donor group. To get a better understanding of the polymers, CV measurements should be performed to determine the band gap electrochemically.

Future research will include the use of different donor groups in the polymer analogous reaction. Donor groups containing para-substituted phenyl side groups, such as cyanide or triethyleneglycol are interesting. Cyanide because it can be converted to an acid group upon treatment with acidic water. As a result of this, the counterion of the carbocation resides in the polymer. Triethyleneglycol because it enhances water solubility. Another possibility is the use of electron withdrawing groups to see if this will blue shift the bad-edge with respect to **PFC_Me**. Also, **PFC_dMA** should be synthesized differently to be able to compare it with the other polymers made. Subsequently, different acceptors should be investigated, i.e., different polymer backbones, which has already commenced with the synthesis of **PTFK**. Finally, thin films of these materials should be made with spin coating in order to measure the mobility and to see what the device performances of these materials are.

4. References.

[1]D. D. Eley, *Nature*, **1948**, 162, 819.

[2]H. Akamatu, H. Inokuchi and Y. Matsunaga, *Nature*, 1954, 173, 168.

[3]J. Ferraris, D. O. Cowan, V. Walatka and J.H. Perlstein, *J. Am. Chem. Soc.***1973**, 95, 948.

[4]C.M. Mikulsiki, P.J. Russo, M.S. Saran, A.G. MacDiarmid, A.F. Garito and A.J. Heeger. *J. Am. Chem. Soc.* **1975**, 97, 6358.

[5]H. Shirakawa, E. J. Louis, A.G. MacDiarmid, C.K. Chiang and A.J. Heeger, *Phys. Rev. Let.* **1977**, 39, 1098.

[6]J.C. Chang and A.G. Macdiarmid, *Synth Met*, **1986**, 13, 193.

[7]A.G. Macdiarmid, *Angew. Chem. Int. Ed.* **2001**, 40, 2581.

[8]F.L. Lu, F. Wudl, M. Nowak and A.J. Heeger. *J. Am. Chem. Soc.* **1986**, 108, 8311.

[9]Y. Sun, A.G. Macdiarmid and A.J. Epstein, *J. Chem. Soc. Chem. Comm.* **1990**, 529.

[10]B.M. Sheikh and G.E. Wnek, *Chemistry of Advanced Materials: An Overview*, p.73.

[11]Y. Yang and F. Wudl, *Adv, Mater*, **2009**, 21, 1401.

[12]T.P. Voortman and R.C. Chiechi, **2014**, unpublished.

[13]R.R. Sondergaard, M. Hösel and F.C. Krebs, *J. Pol. Sci.* **2013**, 51, 16.

[14]T. Yuan, D. Yang, X. Zhu, L. Zhou, J. Zhang, G. Tu and C. Li, *Roy. Soc. Chem.* **2014**, 4, 50988.

[15]A.O. Pantil, Y. Ikenoue, F. Wudl and A.J. Heeger, *J. Am, Chem, Soc.* **1987**, 109, 1858.

[16]Y. Ikenoue, J. Chiang, A.O. Pantil, F. Wudl and A.J. Heeger, *J. Am. Chem. Soc.* **1988**, 110, 2983.

[17]T.P. Voortman, H.D. de Gier, R.W.A Havenith and R.C. Chiechi, *J. Mat. Chem.* **2014**, 2, 3407.

[18]R.C Chiechi, G. Sonnez and F. Wudl, *Adv. Funct. Mater.* **2005**, 15, 427.

[19]Vollhardt & Schore , *Organic Chemistry Structure and Function*, 6th edition.

[20]D.F. Taber, R.P. Meagley and D. Supplee, *J. Chem. Educ.* **1996**, 73, 259.

[21]W. Lin, L. Chen and P. Knochel, *Tetrahedron*, **2007**, 63, 2787.

[22]F.A.V. Grignard, *Compt. Rend*, **1900,** 130**,** 1322.

[23]C. Friedel, J.M. Crafts, *Compt. Rend*, **1877**, 84, 1392.

[24]G. Fraenkel and R.E. Carter, A. Mclachlan and J.H. Richards, *J. Am. Chem. Soc.* **1960**, 82, 5846.

[26]Lampman, Pavia, Kriz and Vyvyan, *Spectroscopy*, 4th edition.

[27]F. Huang, K.-S. Chen, H.-L. Yip, S.K. Hau,O. Acton, Y. Zhang, J. Luo and A.K.Y. Jen, *J. Am. Chem. Soc.* **2009**, *131*, 13886–13887.

[28]T.L. Wang, Y.T. Shieh, C.H. Yang, Y.Y. Chen, T.H. Ho and C.H.Chen, *J. Polym, Res.* **2013**, 20, 213.

[29]M.S. Sunitha, K.A. Vishnumurthy and A.V. adhikari, *J. Chem. Sci.* **2013**, 125, 29.

5. Experimental.

5.1 General info.

Chemicals were purchased from commercial sources and used without further purification unless stated otherwise. The THF used in the reactions was dry THF obtained from a solvent purification system. Column chromatography was performed using Merck silica gel 60 (230-400 mesh). NMR spectra were obtained with a Varian AMX400 operating at 400 MHz. Chemical shifts are reported in δ = units (ppm) relative to residual protonated solvent $CDCl_3$ (^{1}H NMR: δ = 7.26 ppm). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d= doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. FT-IR spectra were obtained from a Nicolet Nexus FT-IR fitted with a Thermo Scientific Smart iTR sampler. GPC measurements were done on a Spectra Physics AS 1000 series machine equipped with a Viskotek H-502 viscometer and a Shodex RI-71 refractive index detector.

5.2 Materials.

9,9-dihexyl-9H-flourene(1). In a flame dried 3-necked flask fluorene (1,7247 g; 10,4 mmol) was dissolved in 30 mL dry THF rendering a colorless solution. The system was purged with nitrogen and cooled to -78 °C. 13,1 mL n-BuLi (1.6 M in hexane) was added dropwise turning the solution orange. The solution was stirred at -78 °C for 1h. next, 4,2 mL (4,95 g; 30,0 mmol) 1-bromohexane was added dropwise turning the solution red, and after 30 s the solution became light pink/brown. The mixture was allowed to warm up to rt and was stirred overnight, rendering a colorless solution. The reaction mixture was quenched on ice and extracted twice with ether (150 mL). the combined organic layers were washed with $NaHCO_3$ and brine and dried over Na_2SO_4. Finally, the solvent was removed, giving a colorless oily liquid, **1**. The product was purified with column chromatography and further dried under vacuum at room temperature. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.9 Hz, 2H), 7.37 – 7.26 (m, 6H), 1.99 – 1.91 (m, 4H), 1.16 – 0.96 (m, 16H), 0.75 (t, *J* = 7.1 Hz, 6H).

PFK(2). In a flame dried 3-necked flask, **1** (2,006 g; 5,99 mmol) and freshly recrystallized terephthaloyl chloride (1,2175; 5,99 mmol) were issolved in 20 mL freshly distilled ODCB, giving a pale green clear solution. To a second flame dried flask, anhydrous $AlCl_3$ (2,8273g; 21,2 mmol) and 10 wt% anhydrous LiCl were added and this was dissolved in 60 mL freshly distilled ODCB, rendering a pale green suspension. The system was flushed with N_2/vacuum to insure inert conditions. The suspension was cooled to 0 °C using an ice bath. To the stirring cooled suspension, the clear monomer solution was added dropwise over the course of 25 min, turning the suspension deep red. This was stirred for 1h at 0 °C. Next, the suspension was stirred at 55 °C overnight. The reaction mixture was allowed to cool to rt and quenched on 1N HCl/ice, turning it slowly yellow. The organic layer was extracted with ODCB and concentrated. The concentrate was dissolved in minimal amount of hot THF. Subsequently, the product was precipitated in ice cooled MeOH and collected by centrifuge. The product was fractionated by soxhlet extraction: MeOH, Hexane, Acetone, $CHCl_3$. ^{1}H NMR (400 MHz, cdcl$_3$) δ 8.41 – 7.32 (m, 10H), 2.19 – 1.94 (m, 4H), 1.10 (m, *J* = 15.4, 8.7 Hz, 12H), 0.81 – 0.44 (m, 10H). FT-IR (ATR) 2925, 2854, 1656, 1604, 1575, 1496, 1457, 1400, 1240, 1096, 947, 830, 778, 740, 636.

PFC_Ph(3). 2 (401,0 mg; 0,86 mmol; $CHCl_3$ fraction) was dissolved in 40 mL dry THF. The system was purged with N_2. Phenylmagnesium bromide (2,1 mL; 1,6M; 3,36 mmol) was added dropwise, turning the solution deep purple. The reaction mixture was refluxed overnight and a deep purple solid formed inside the flask. The mixture was allowed to cool to rt and was poured into 50 mL alkaline methanol, rendering a cloudy yellow solution. The solvents were removed. The obtained solid was dissolved in DCM and washed with water. The DCM was removed using the rotor vap, obtaining the product as a foam. This was dissolved in minimal amount of DCM and precipitated in 300 mL ice cooled hexane. The product was collected by centrifuge and dried in vacuum at 55 °C overnight ^{1}H NMR (400 MHz, cdcl$_3$) δ 7.63 – 7.49 (m, 2H), 7.37 – 7.00 (m, 18H), 2.94 – 2.76 (m, 0H), 2.00 – 1.68 (m, 4H), 1.15 – 0.85 (m, 12H), 0.68 (dd, J = 40.1, 34.8 Hz, 10H). FT-IR (ATR) 3558, 3448, 3053, 2925, 2854, 1455, 1300, 1140, 1009, 886, 822, 755, 699.

PFC_Me(4). 2 (401,0 mg; 0,86 mmol; $CHCl_3$ fraction) was dissolved in 40 mL dry THF. The system was purged with N_2. Phenylmagnesium bromide (2,1 mL; 1,6M; 3,36 mmol) was added dropwise, turning the solution deep purple. The reaction mixture was refluxed overnight and a deep purple solid formed inside the flask. The mixture was allowed to cool to rt and poured into 50 mL alkaline methanol, rendering a cloudy light yellow solution. The solvents were removed. The obtained solid was dissolved in DCM and washed with water, subsequently, the water was washed with DCM. The combined DCM solution was washed with brine and the layers were separated. Undissolved salts were filtered out of the DCM. The DCM was removed using the rotor vap, obtaining the product as a cloudy yellow oil. This was dissolved in minimal amount of DCM and precipitated in 300 mL ice cooled hexane. The product was collected by centrifuge and dried in vacuum at 55 °C overnight. ^{1}H NMR (400 MHz, cdcl$_3$) δ 7.79 – 7.15 (m, 10H), 2.22 (s, 0H), 1.94 (d, J = 22.9 Hz, 10H), 1.04 (d, J = 29.6 Hz, 12H), 0.71 (dd, J = 38.3, 31.5 Hz, 10H). FT-IR (ATR) 3432, 2925, 2854, 1464, 1219, 1088, 1015, 916, 822, 741.

PFC_dMA. Magnesium (14,9 mg; 0,60 mmol) was added to a flame dried 20 mL 3-necked flask equipped with N_2 inlet and some I_2 was added to activate the magnesium. The flask was gently warmed until purple vapors appeared and disappeared. This was done twice. Next, 4-bromo-N,N-dimethylaniline (152,2 mg; 0,75 mmol) was added under an outflow of N_2. Subsequently, 8 mL of dry THF was added rendering a dark green solution. The solution was refluxed for 2h changing the color to light yellow. By this time, all magnesium was consumed. In a different flame dried 3-necked flask equipped with N_2 inlet, 80,5 mg **2** was dissolved in 6 mL dry THF. The formed dimethylmagnesium bromide was added using a syringe turning the solution green. The mixture was refluxed overnight. 20 mL 1M NaOMe was added to quench the reaction turning the mixture dark grey. The mixture was allowed to cool to rt. The solvents were removed and the obtained solid was extracted with DCM and H_2O. the layers were separated and the organic layer was washed once with H_2O and 4 times with 1N HCl, rendering a swamp green solution. The DCM was removed and the obtained dark yellow oil was precipitated in 300 mL ice-cooled n-hexane. The product, ***5***, was collected by centrifuge. ^{1}H NMR (400 MHz, cdcl$_3$) δ 8.39 – 7.32 (m, 8H), 2.07 (s, 4H), 1.10 (m, 12H), 0.73 (m, 10H). FT-IR (ATR) 2925, 2854, 1655, 1602, 1457, 1401, 1297, 1243, 1098, 968, 830, 740.

PTFC_dMA. Magnesium (14,0 mg; 0,56 mmol) was added to a flame dried 3-necked flask equipped with N_2 inlet and some resublimed I_2 was added to activate the magnesium. 4 mL of dry THF was added giving a orange/brown

solution. In a second flame dried 3-necked flask equipped with N_2 inlet, dry 4-bromo-N,N-dimethylaniline (140 mg; 0,70 mmol) was added and dissolved in 6 mL dry THF rendering a colorless solution. This was added to the Mg solution using a syringe rendering a dark orange/brown solution. The mixture was refluxed until all Mg was consumed, rendering a grey solution. In a third flame dried 3-necked flask equipped with N_2 inlet **PTFK (**100,0 mg; 0,1585 mmol) was dissolved in 12 mL dry THF. This was slowly added to the Grignard solution rendering a deep dark green solution. The mixture was refluxed overnight. 20 mL 1M NaOMe was added to quench the reaction giving a brown suspension. The solvents were removed obtaining a yellow solid. This was extracted with DCM and H_2O. The layers were separated and the organic layer was washed with 1N HCl turning the suspension completely dark green. The organic layer was collected and the water layer was filtered. The residue was dissolved in THF. The combined organic layers were collected and the solvents were removed. The obtained solid was dissolved in hot THF and precipitated in 300 mL ice-cooled n-hexane. The product was collected by centrifugation ^{1}H NMR (400 MHz, cdcl$_3$) δ 8.25 – 6.93 (m, 19H), 3.12 (t, J = 30.1 Hz, 4H), 2.05 (s, 5H), 1.43 (s, 2H), 1.24 (s, 6H), 1.07 (s, 13H), 0.73 (d, J = 21.6 Hz, 10H). FT-IR (ATR) 3337, 2925, 2854, 1627, 1417, 1280, 1132, 1060, 1016, 807, 717.

PTFC_dMA_1. Dry 4-bromo-N,N-dimethylaniline (284,8 mg; 1,40 mmol) was dissolved in 20 mL dry THF. This was cooled to -78 °C with an acetone/liquid N_2 bath. 0,85 mL 1,6 M n-BuLi was added and the mixture was stirred at -78°C for 90 min. rendering a clear solution. 70 mg **PTFK** dissolved in dry THF was added at -78 °C turning the solution dark yellow. The mixture was stirred overnight at rt rendering a green/yellow turbid solution. 20 mL 0,5 M NaOMe in methanol was added to quench the reaction giving a clear solution. The solvents were removed and the obtained solid was extracted with DCM and H_2O. The organic layer was washed with brine twice and once more with water, but the separation was insufficient. Therefore, the combined layers were washed with 1N HCl turning the solution completely dark blue. The organic layer was collected and the solvent was removed giving a dark blue solid. The obtained solid was dissolved in hot methanol and precipitated in basic methanol. Finally, the product was obtained by centrifugation. ^{1}H NMR (400 MHz, cdcl$_3$) δ 7.99 – 6.51 (m, 22H), 3.35 – 3.09 (m, 0H), 3.08 – 2.69 (m, 12H), 1.99 (s, 4H), 1.07 (m, 12H), 0.71 (m, 10H). FT-IR (ATR) 3347, 2925, 2854, 1608, 1518, 1444, 1350, 1192, 1066, 947, 800.