

# **Characterization of Conjugated Polyions PTFC-Ph**

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## **Abstract**

Conjugated polyions (CPIs) are new type of materials which potentially can be high efficiency light harvesting materials. Via spinless doping from its precursor cross-conjugated polyketone, the influence of spin and charge on optical properties can be dissociated. This charged material can still undergo further redox doping processes. However, although CPIs can be produced scalably with green processes, their special physical properties make it difficult to be characterized and applied to devices. In this thesis, we tried several different strategies to characterize the incompletely converted polyions and reveal some special properties of the CPI PTFC-Ph and propose a precursor solution for CPI film fabrication.

# 1. Introduction

## 1.1 Conjugated polymer

Polymers that have continuous  $sp^2$  hybridized carbon centers in their main chain are called conjugated polymers. In these systems, the difference of energy level between the bonding orbital and anti-bonding orbital of conjugated  $\pi$  electrons is relatively small (around 1.2 to 3 eV), which is also similar to traditional inorganic semiconductors. [1] In 2000, Alan Heeger, Alan MacDiarmid and Hideki Shirakawa are awarded the Nobel Prize in Chemistry for their pioneering work of conductive conjugated polymer in 1977. Oxidized iodine-doped polyacetylene has been reported to have metal-like conductivity. Since then, synthesis and applications of conjugated polymers has become a heated point of research in the following 40 years. [2] Conjugated polymers not only have metal or semi-conductor-like electrical and optical properties but also the advantages of traditional polymer materials, which includes low specific weight, flexibility, easy processing and low cost. From the view of resources, owing to the rapid development of organic synthesis techniques, a variety of building blocks of conjugated polymers are available. Also, by modifying the chemical structure of conjugated polymer, it is feasible to control and improve its physical properties. The utilization of conjugated polymers in turn has become more flexible. [3]

Due to these attractive properties, a variety of device applications have been exploited, including Organic Light Emitting Diodes (OLEDs), Organic Field-effect transistors (OFETs), Organic Solar Cells (OSCs), and Organic sensor. [4]

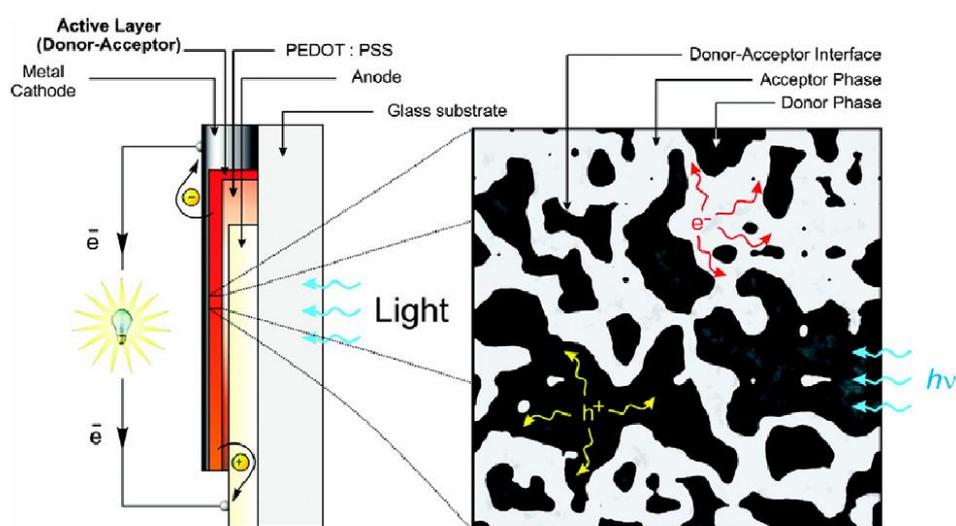
## 1.2 Application of conjugated polymers to organic solar cells

With the exhaustion of fossil fuels, utilization of solar energy has become increasingly urgent.

Despite the fact that almost all commercial solar cells are silicon and other inorganic semiconductors, organic solar cells are still attractive due to the advantages mentioned above.

The efficiency of organic solar cell has also been improved from 1% 15 years ago to over 11% now.

There is still a high potential to obtain higher efficiencies.



**Figure 1** The device structure of polymer solar cell based on bulk heterojunction configuration. [5] The photon to electron conversion process consists of four steps. Excitons are generated when the active layer absorbs photons with certain energies; excitons diffuse to the interface of the acceptor and donor phases; excitons dissociate to electrons and holes at the interface; electrons and holes move to the electrodes through the acceptor and donor, respectively. Finally, the anode and cathode collect electrons and holes and generate photo-current and photo-voltage.

Nowadays, almost all high efficiency organic solar cells use fullerene based materials as acceptors. Regrettably, there are still many problems with fullerene derivatives, including high costs, poor photochemical stability, and limited light absorption ability in the visible-near infrared region. Therefore, it is meaningful to find a new acceptor material with low cost, high photochemical stability and better band structure. [6] However, the majority of existing

conjugated polymer light harvesting materials is p-doped (donor). Only a limited number of n-doped materials have been reported. The reason may be that p-doped conjugated polymers are more stable in our oxidative atmosphere.

Apart from the reasons listed above, typical organic materials have dielectric constant below 4. However, in organic solar cells, increasing the dielectric constant can result in a longer lifetime of an exciton. The short lifetime of an exciton is an important factor affecting the efficiency of organic solar cells. As a result, increasing the dielectric constant of an active layer has become a new concept of efficient organic solar cell fabrication. [7] Koster et al. also predicated a dramatic increase of power conversion efficiency of an optimized device from 13% to over 20% with the increase of the dielectric constant. [8] If it could become realistic, organic solar cells could become also competitive to wafer-based devices in terms of efficiency.

### **1.3 Conjugated polyelectrolytes**

Although conjugated polymers are comparatively more processable than silicon, its solubility and requirement of toxic solvents (chlorobenzene, dichloromethane for example) obstruct its large scale application. [9] In 1987, Wudl et al. reported a water soluble conjugated polymer poly(thiophene) (PT) which is semiconductive. Later on, conjugated systems including poly(phenylenevinylene) (PPV), poly(phenyleneethylene) (PPE) and poly(fluorenebenzene) (PFB), have been deeply looked into and a variety of conjugated polyelectrolytes have been reported. [10] Typical conjugated electrolytes have hydrophilic pendent groups linked to a conjugated backbone. These materials have both advantages of traditional conjugated polymers and are water soluble (or other green solvent soluble). The ionic pendent groups can also interact with

other materials which makes them accessible to inkjet print and layer-by-layer self-assembly methods to fabricate organic photovoltaic devices. Compared to traditional spin coating, these methods are more feasible to large area production with low cost. [11]

In addition, a reversible redox process with acid has been found with conjugated polyelectrolytes. Accompanied with color change, these processes also indicate corresponding changes of conductivity. [12] With the adjustments of counter ion of redox complexes and immobilization methods, the redox behavior can be affected significantly.

The structure of a hydrophobic backbone and hydrophilic pendant groups makes conjugated polyelectrolytes interesting materials for self-assembly. However, it also causes aggregation in solution. Therefore, device fabrication with conjugated polyelectrolytes has become rather difficult. [12]

## **1.4 Spinless doping**

Almost all conjugated polymers are neutral intrinsic semiconductors and can be converted to charged metallic state by adding or removing electrons to or from the  $\pi$  molecular orbital. These redox processes can be in analogy with n-type or p-type doping and create radical anions or cations respectively. The created polarons can serve as charge carriers and impart a dramatic increase of conductivity. As the pioneer work in 1977, iodine vapor oxidized polyacetylene achieved nearly a billion times higher conductivity than normal polyacetylene. On the other hand, through these processes, unpaired spins have also been introduced and mid-gap states have been created. It leads to significant reducing of band gaps and red-shifting of the optical absorption. As a result, instead of shifting band structure by the impact of charge, the redox

process mainly influence optical properties by creation of new states. [13]

In 2005, Chiechi et al. reported an n-dopable conjugated polymer based on cross-conjugated polyketone. [14] When it is reduced, the influence of spin and charge can be dissociated. Although these phenomena are transient and only exist at cathodic potentials in air-free conditions, they indicate the possibility of spinless doping. This polymer could be reduced into a metallic, doped state and a charged, but semiconducting state. The differences between these two states can be distinguished by spectroscopic methods and conductivity measurements.

Spinless doping is defined as the introduction of charges into the band structure of a conjugated polymer without redox and without the spontaneous formation of unpaired spins. [15] Unlike simple addition of charges, spinless doping refers to the introduction of charges in the conjugated backbone via closed-shell, two-electron processes. Thus, all unpaired electrons in the band structure need to be formed spontaneously. Owing to the dissociation of influence of spin and charge, the absolute positions of the valence and conduction bands would be more strongly determined by the electron-rich groups used to stabilize the charges. In addition, with the absence of spin, no mid-gap states would be created. Consequently, after spinless doping, conjugated polymers can undergo another electrochemical doping process. These unique properties make cross conjugated polymers a potential light-harvesting material.

## **1.5 Conjugated polyions**

In 2014, Voortman et al. have reported another cross conjugated polyketone PFK (Poly fluorene ketone) which can be converted to a linearly conjugated polymer PFC (Poly fluorene

cation) and form conjugated polyion (CPI) by adding nucleophiles. [16] Unlike the previous transient doping where charges are generated in situ, in the spinless doping process, charges are generated by stabilizing trivalent carbocations via addition and then dehydration. These CPIs are robust, air stable and exhibit dynamic band gaps. They separate the influence of unpaired electron from the inclusion of charge and present significant changes of physical properties. PFC has a narrow band gap of 1.6 eV and can be further optimized. With time-dependent density functional theory calculation, they also indicate that like other conjugated polymer, traditional redox doping does lead to a p-doped polymer with a significantly reduced band gap.

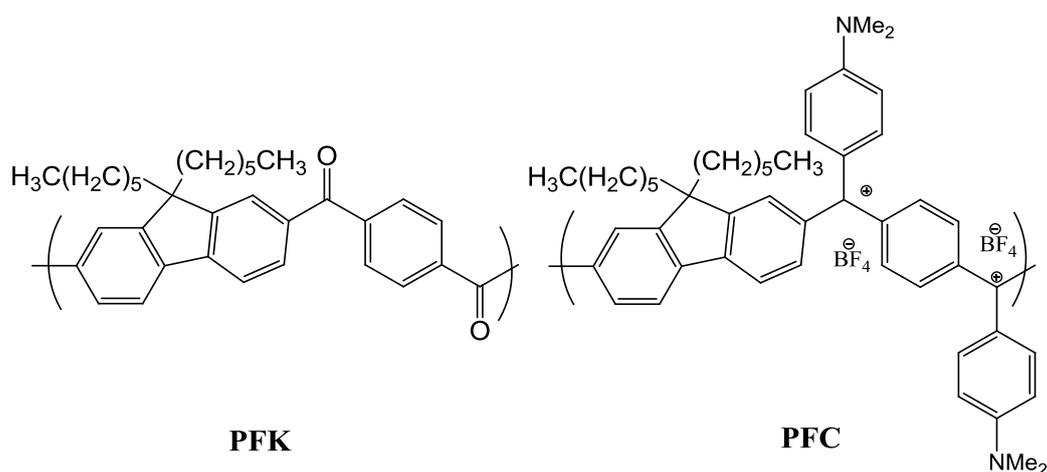
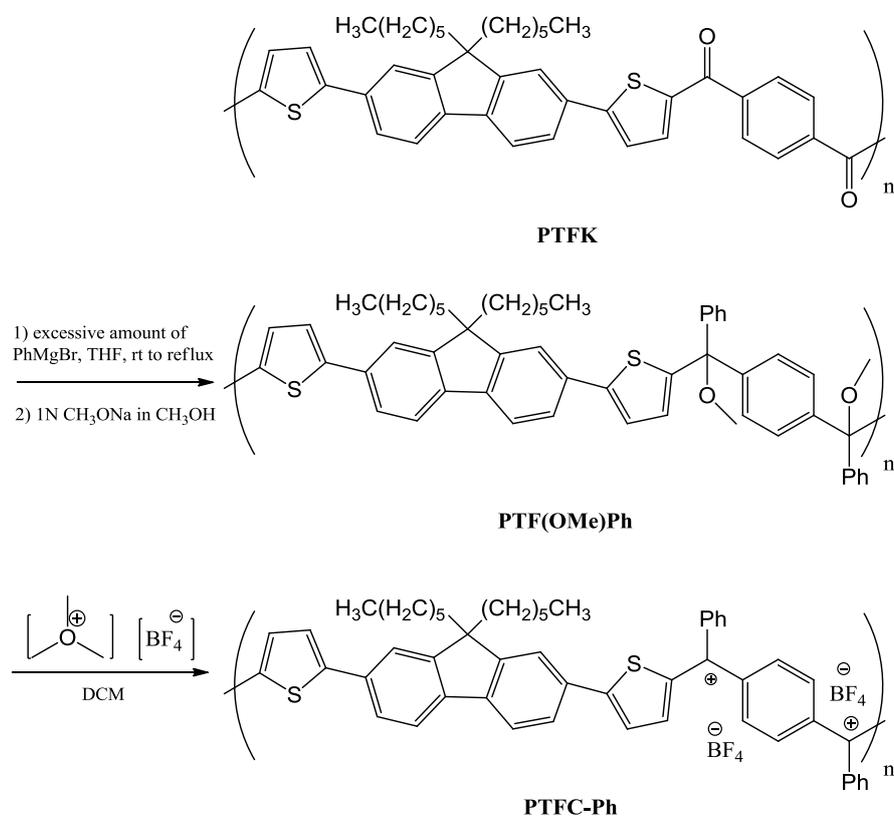


Figure 2 structure of conjugated polyketone PFK and conjugated polyion PFC [16]

In addition, the synthesis steps of CPIs are relying on scalable processes and without toxic Sn or Pb. These above advantages make CPIs a promising light harvest material in organic solar cells.

Later, Voortman et al. reported a modified conjugated polyketone PTFK (poly thiophene fluorene ketone) as a precursor of CPI. [17] By improving the Friedel-Crafts polycondensation method, they further improved the processability and the degree of polymerization. PTFK as a cross-conjugated polymer itself can already be utilized as an active material in an organic device. Although it is still not an option for high efficiency organic solar cells, PTFK is easy to process,

robust and through scalable chemistry. Also, the band gap of converted CPI PTFC-Ph has been optimized to 1.4 eV.



**Figure 3 Scheme of spinless doping process from PTFK to PTFC-Ph [17]**

However, the exciting properties of PTFC-Ph including the band structure, in-situ conductivity, dielectric constant and charge carrier mobility are difficult to be determined. The mismatch of solubility of pendant group and backbone caused aggregation of CPI in solvent once it is produced and the aggregated material is difficult to be processed further.

Consequently, CPIs, as a new concept material and a promising type of light harvesting material, is expected to be developed in depth. However, the difficulties charactering its properties are obvious obstacles for its research and application.

## 1.6 Aim of this thesis

PTFC-Ph has been proved to be a narrow band gap conjugated polyion generated from PTFK via spinless doping. However, the problem of aggregation in solvent makes PTFC-Ph difficult to process and prevents us to take a further look at its properties. We would try to avoid aggregation and fabricate a thin film of PTFC-Ph for characterization.

The properties to be explored may include HOMO and LUMO level, in-situ conductivity, dielectric constant and charge carrier mobility.

## 1.7 Methods that followed

We would finish spinless doping followed Voortman's method as indicates in Figure 3.

Though aggregation in solution seems to be inevitable, there are still several methods that may help us avoid this problem.

Aggregation makes it difficult to fabricate a film for characterization. However, we may be able to fabricate a film of PTF(OMe)Ph first and then convert the methoxy groups on the film to cations.

In addition, the process of aggregation may be slowed down at low concentration of polyion and low temperature. We may also be able to finish fabrication of film or other characterization from dilute solution before the materials starts to aggregates.

## 2. Synthesis and characterization of PTF(OMe)Ph

Following Voortman's pathway, [17] PTFK is reacted with excess amount of Grignard reagent overnight to ensure all the ketone is converted obtaining a deep green solution. The cations were then quenched in sodium methoxide to form PTF(OMe)Ph which is yellow in solution.

We characterize PTF(OMe)Ph by  $^1\text{H-NMR}$  and Infrared spectroscopy. The results are shown in Figure 4 Compared to  $^1\text{H-NMR}$  of PTFK. A peak appeared at 3.02 ppm, corresponding to the hydrogen from the methoxy group of PTF(OMe)Ph, which indicates the conversion of PTFK. However, the  $^1\text{H-NMR}$  result is difficult to be precisely interpreted and we cannot draw any conclusions of how well the PTFK has been converted.

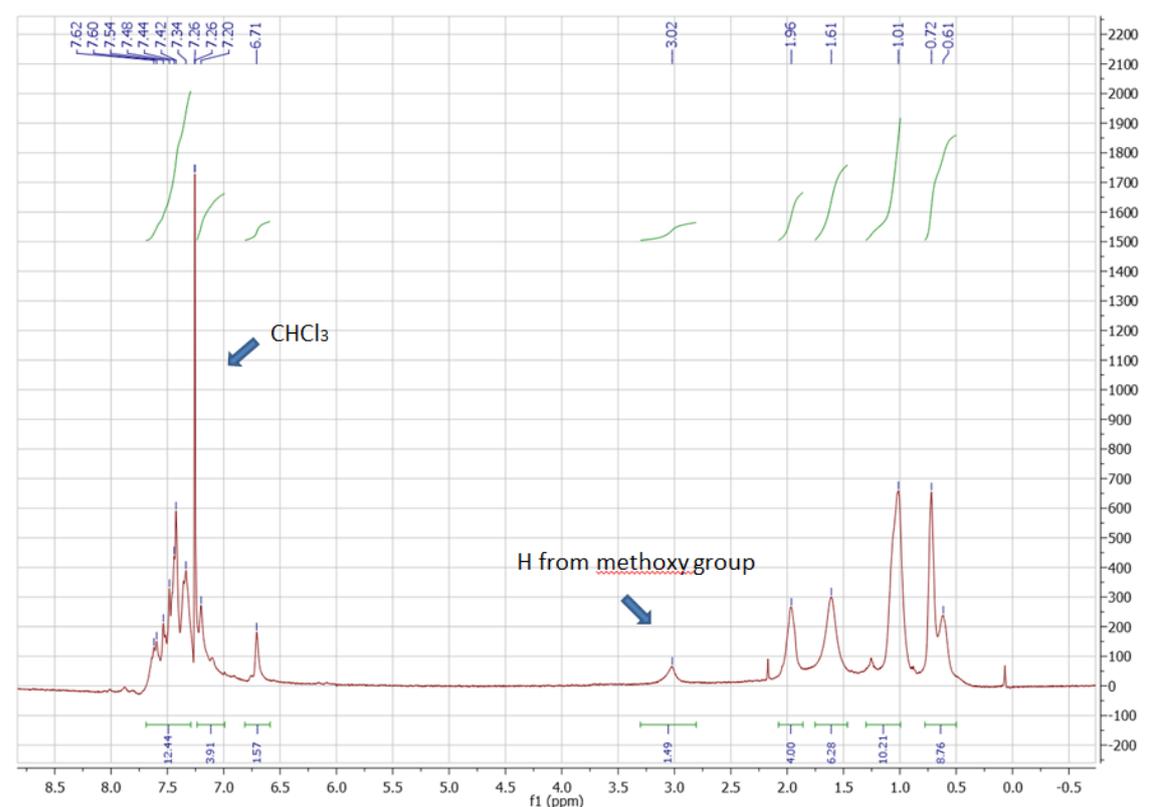
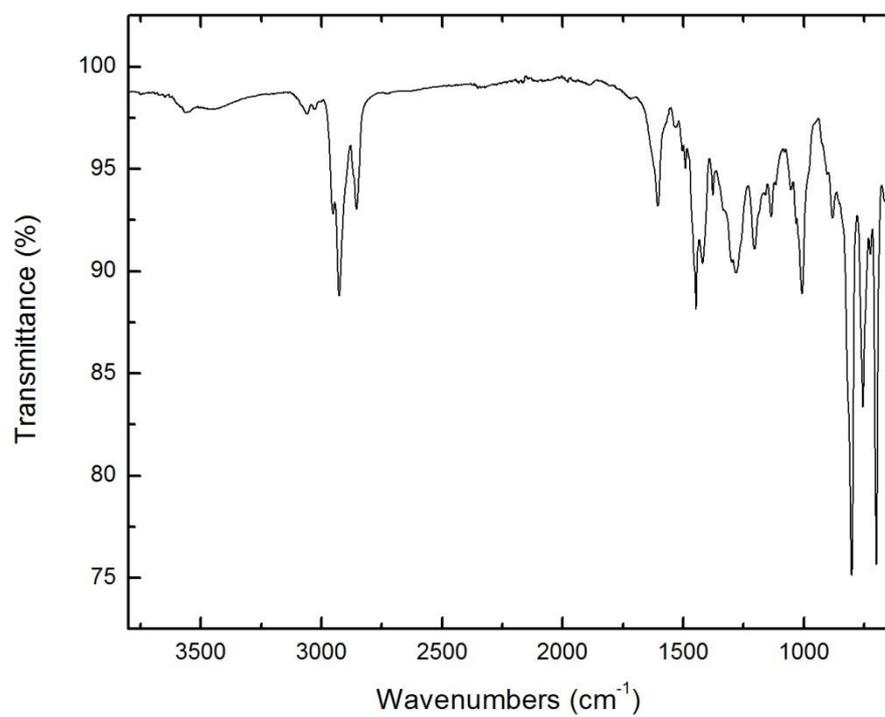


Figure 4  $^1\text{H-NMR}$  results of PTF(OMe)Ph

In Infrared spectra of PTFK, two strong peaks at  $1628\text{ cm}^{-1}$  and  $1279\text{ cm}^{-1}$  are present, which correspond to stretching and bending modes of carbonyl group, respectively. [17] In the Infrared

spectrum of PTF(OMe)Ph, these peaks do not exist, which indicates that most ketones have been converted to a methoxy group.



**Figure 5 Infrared spectrum of PTF(OMe)Ph**

### **3. PTFC-Ph characterization**

To characterize the electronic and optical performance of the permanent CPI PTFC-Ph, we need to prepare a stable film of PTFC-Ph. There might be three pathways towards a stable film of PTFC-Ph from PTF(OMe)Ph.

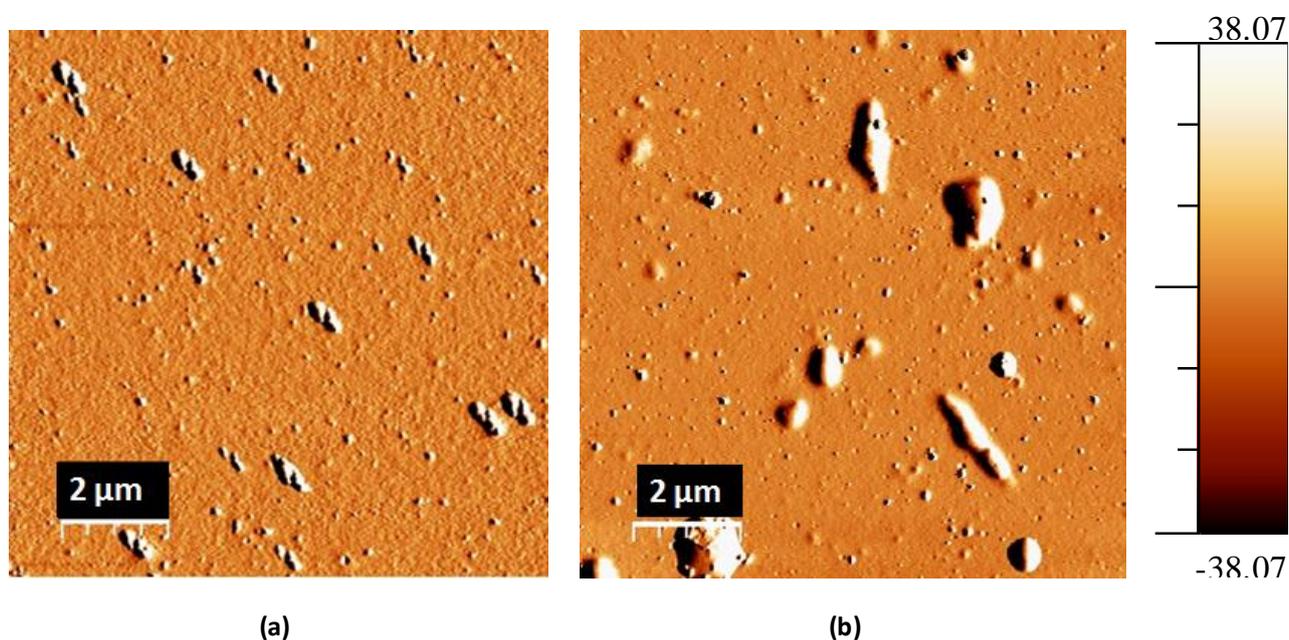
- (1) To form a stable film of PTF(OMe)Ph and then convert PTF(OMe)Ph to PTFC-Ph.
- (2) To convert PTF(OMe)Ph to PTFC-Ph, then form a film by spin coating.
- (3) To prepare a precursor solution containing PTF(OMe)Ph and alkylating agent.

#### **3.1 To form film of PTF(OMe)Ph before converting it to PTFC-Ph**

PTF(OMe)Ph can be dissolved in dichloromethane (DCM), chloroform (CF), tetrahydrofuran (THF), chlorobenzene (CB) and other solvents. DCM and CF is not a good option because they can dissolve the polymer only in low concentration (less than 15 mg/mL). Also, DCM dried too fast during spin coating and we are not able to form stable and homogeneous film with these solvents even with a low spin speed of 250 rpm. THF can dissolve PTF(OMe)Ph better and the high concentration solution (over 20 mg/mL) of PTF(OMe)Ph in THF can result in free-standing films. However, the formed film is not homogeneous. Using Chlorobenzene as a solvent can solve the problems mentioned above and result in a yellow and homogeneous film. Nevertheless, Chlorobenzene evaporates so slow that we can hardly make a film thicker than 50 nm.

To convert PTF(OMe)Ph to PTFC-Ph, we place the PTF(OMe)Ph film in a vacuum chamber and pump out the air. Then we close the vacuum pump and introduce acid vapor into the vacuum

chamber by the difference of pressure. An acidic vapor environment is established and PTF(OMe)Ph film was kept in the vacuum chamber for 5 minutes to allow the reaction to take place. In this way, we can both avoid PTF(OMe)Ph quenched with the water in air and prevent acid vapor from going to the vacuum pump. To generate acid vapor, we tried hydrochloric acid, acetic acid and tetrafluoroboric acid. Acetic acid is not strong enough to deprotect the methoxy group. The volatility of tetrafluoroboric acid is not strong enough to produce efficient amount of vapor to deprotect PTF(OMe)Ph. Hydrochloric acid can deprotect PTF(OMe)Ph and achieve a color change of the film associated with the conversion to free cations. The yellow film of PTF(OMe)Ph turned bright green with acid treatment and after introducing ammonia to the green film, it could turned back to yellow. These processes can be repeated on the same film, reversibly.



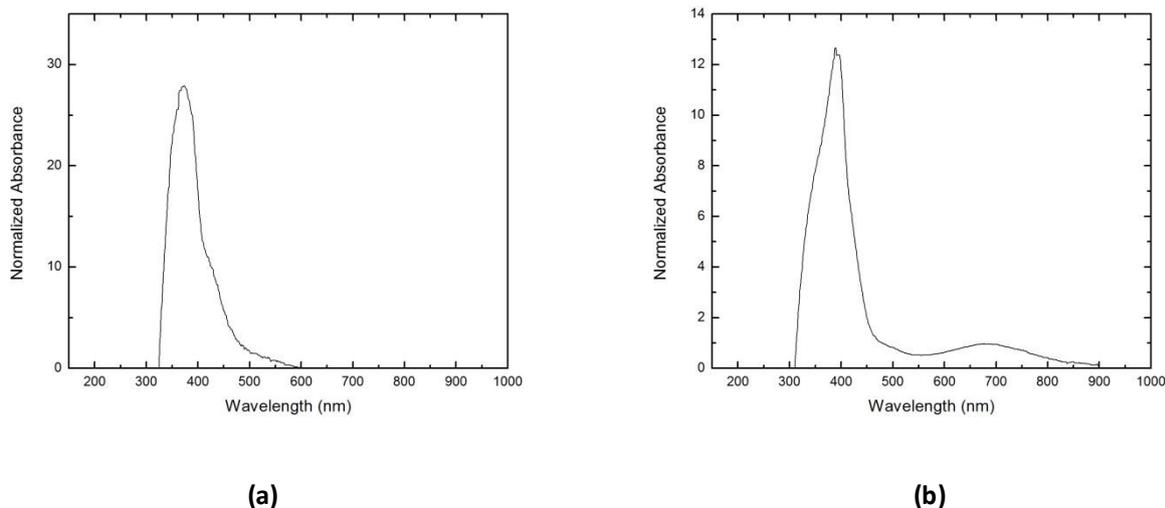
**Figure 6 (a) AFM image of PTF(OMe)Ph film made by spin coating, (b)AFM image of PTF(OMe)Ph film after acid vapor treatment.** The periodically appeared protuberances may be the contamination of AFM tip or dust.

**Table 1 AFM data of PTF(OMe)Ph film and acid treated film[18]**

	RMS Roughness (nm)	Roughness Average (nm)
PTF(OMe)Ph film	9.6	6.4
Acid processed film	30.0	15.2

Also, we compared the surface of the film before and after acid vapor treatment. Acid processing has significantly changed the morphology of film, as indicated in Figure 6. Compared to the thickness of the film (50 nm), the increase in RMS roughness of the acid processed film seems to be a potential problem for further characterization.

To characterize the result of deprotection, we used Ultraviolet-visible spectroscopy (UV-vis) to investigate optical properties of these films. Unfortunately, although the phenomenon of color changing with a low pH atmosphere could indicate the reaction on the surface, UV-vis results do not show significant difference before and after acid vapor introduced. The reasons may be that cations are quenched during the measurement. Also, it could be that the acid vapor cannot penetrate the film deep enough. That is, most part of the film is still unconverted PTF(OMe)Ph while only a small part has been converted and showed a really strong color effect. It can still be that the film is too thin to give a significant result. We have tried to keep the film in acid vapor atmosphere for 20 minutes for a longer processing time. However, the result remains the same.



**Figure 7 Normalized UV-vis spectroscopy of PTF(OMe)Ph film (a) and acid treated film (b).**

Black line represents PTF(OMe)Ph. Red line represents the film after acid vapor treatment.

We have also tried to use cyclic voltammetry (CV) and *In situ* conductivity measurement to characterize the properties of film made by this method. However we are not able to acquire meaningful data. Corresponding to the extremely small difference appeared in UV-vis, almost no signal can be detected by cyclic voltammetry. With the noisy CV result, we were also not able to acquire *In situ* conductivity measurement results.

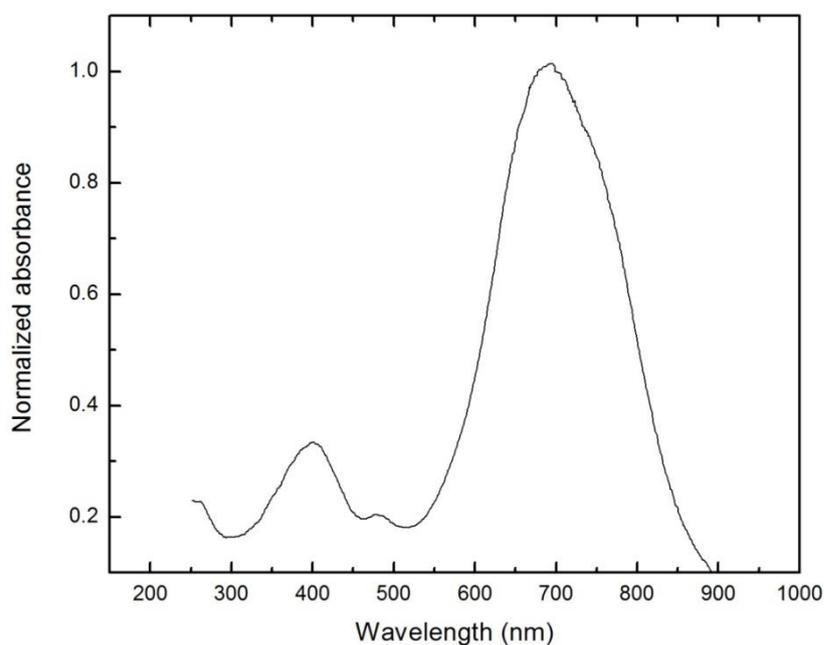
As a conclusion of the data we collected above, we are able to fabricate PTF(OMe)Ph film with reasonable roughness. However, the method we use to convert PTF(OMe)Ph to PTFC-Ph is not effective enough. Thus, avoiding aggregation by this method cannot help us look further into this CPI.

### **3.2 To convert PTF(OMe)Ph to PTFC-Ph before film fabrication**

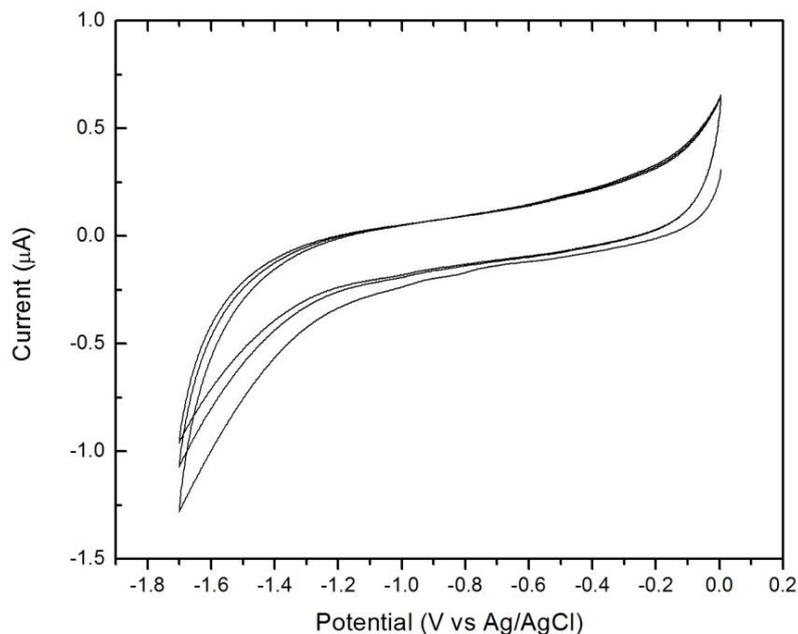
Due to the difficulties of effectively deprotecting PTF(OMe)Ph, we may have to take one step

back. We find that extracting an extremely dilute solution of PTF(OMe)Ph (0.04mg/mL) with fluoroboric acid or Trimethyloxonium tetrafluoroborate can form a temporary stable solution of PTFC-Ph. The concentration is high enough to show a result for UV-vis spectroscopy. However, extreme dilute solution cannot be used for spin coating to form continuous films.

Due to the film of PTFC-Ph being unavailable, we use cyclic voltammetry to characterize properties of PTF(OMe)Ph and PTFC-Ph in solution. Unlike results for UV-vis spectroscopy, the CV results for PTF(OMe)Ph could be obtained but we still could not acquire useful data for PTFC-Ph. The low concentration of solution may have caused signal not to be strong enough to be detected.



**Figure 8 Normalized UV-vis spectroscopy of PTFC-Ph solution (0.04 mg/mL in DCM).** The cut-off absorption is at 860 nm. The band-gap is 1.4 eV, as previous report.[11]



**Figure 9 Cyclic Voltammetry of PTF(OMe)Ph solution.** A smooth curve without any peaks is obtained. It is reasonable because there is no redox reaction that can occur easily on PTF(OMe)Ph.

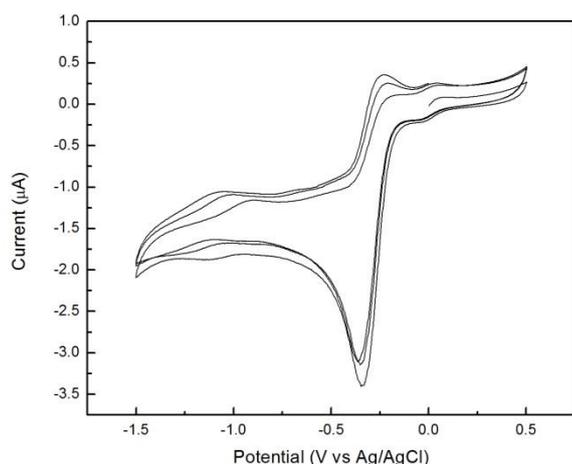
We find that extracting concentrated PTF(OMe)Ph solution (4mg/mL) with insufficient acid (0.6 equivalents, 30 % of PTF(OMe)Ph converted) can result in a solution that do not aggregate for quite a long time. Additionally, the graph of cyclic voltammetry of PTF(OMe)Ph do not have any significant peaks. If the incomplete conversion of PTFC-Ph can show significant peak in cyclic voltammetry, we may also be able to acquire meaningful data revealing the properties of CPI PTFC-Ph.

We extract a PTF(OMe)Ph solution (4mg/mL in a mix solution of DCM and ODCB with 1:1 ratio) with 0.1 mol Tetramethyl hexafluorophosphate as electrolyte. We use 3mL of fluoroboric acid to form CPI and then use sufficient amount of sodium sulfate to remove water in the system. Tetraethylammonium hexafluorophosphate should be a better choice. Compared to fluoroboric acid, it does not introduce water into the solution and since no water is formed as a byproducts.

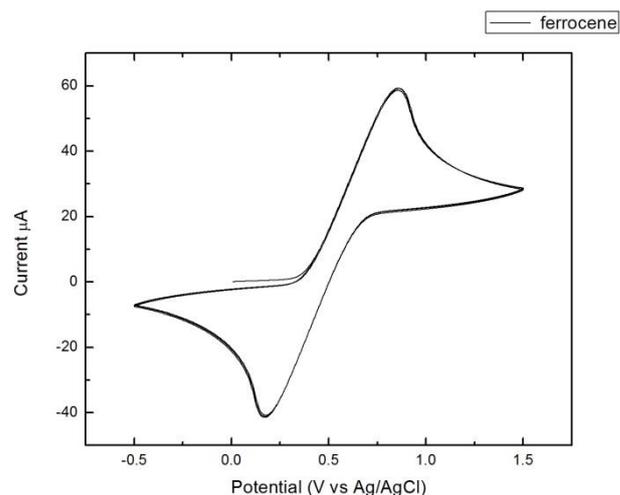
The formed cations are less likely to be quenched. However, this alkylating agent does not dissolve easily into DCM or ODCB. Instead of dissolving, Tetramethyl hexafluorophosphate precipitated with aggregated polymers. As a result, we are not able to obtain homogeneous solution by this method.

We acquire cyclic voltammetry of this solution and the results are shown in figure 10. The signal is weak because at most only 30% of polymers have been converted, that is, most of the material are still insulator. Also, sodium sulfate may have removed a lot of the materials. For the CV voltammetry result of fully converted PTFC-Ph, two oxidative peaks are expected because two cations should exist per repeat unit. Because less than half sufficient amount of acid has been added, the second peak is not obvious. Furthermore, this graph is not very reproducible. In addition to the weak signal, we are not able to acquire data using Fc/Fc<sup>+</sup> couple as internal reference. (Peaks of PTFC-Ph cannot be observed with Fc/Fc<sup>+</sup> couple exists). Consequently, we measure Fc/Fc<sup>+</sup> couple in mixed solution of DCM and ODCB (1:1) as external reference (0.51V). According to cyclic voltammetry result, the onset of reductive peak is at -0.24 eV. We can calculate the LUMO level of this mixed system is at -4.86 eV with equation 1.

$$E_{(LUMO)}(eV) = E_{reductive}(eV) + 5.1(eV) \quad (\text{Equation 1})$$



(a)



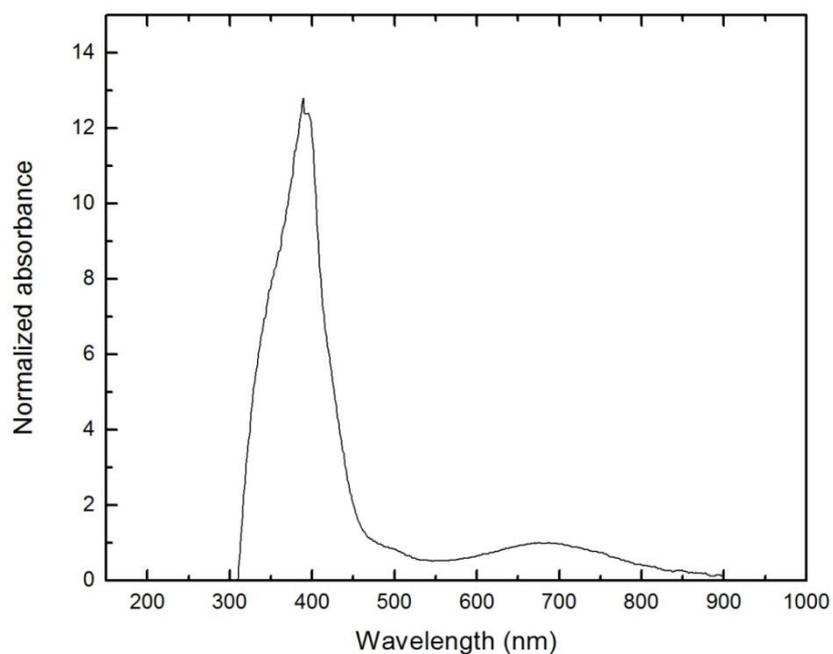
(b)

**Figure 10 (a) Cyclic voltammetry of incompletely converted PTFC-Ph solution.**

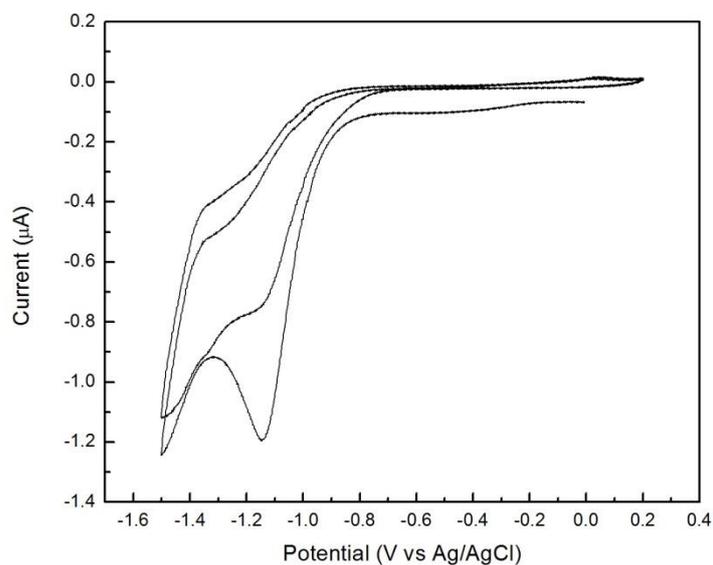
**(b) Fc/Fc<sup>+</sup> couple as internal reference (0.51V).**

We reproduce this solution but without electrolyte and apply it for spin coating and obtained a green film. However, the normalized UV-vis result is almost the same with result we recorded before, indicating poor conversion of PTF(OMe)Ph.

We have also tried to measure the cyclic voltammetry of films drop cast from this solution and hoped to get a similar result as cyclic voltammetry. But as showed in figure 12 we cannot record any meaningful results. There is no paired oxidative and reductive peak. Also, the peak appeared in the first cycle of scan cannot be repeated in the second cycle of scan. The drop cast film is green before cyclic voltammetry measurement, however, the green film turned to yellow after measurement. We suppose that generated cation has been quenched during the measurement and which caused the unrepeatable result. We tried to dry the electrolyte solution and keep all measurement steps as dry as possible. However, these steps did not help to obtain a reproducible cyclic voltammetry curve.



**Figure 12 Normalized UV-vis spectroscopy of PTFC-Ph film** fabricated by spincoating from the insufficient converted solution.



**Figure 13 cyclic voltammetry measurement of insufficiently converted PTFC-Ph film**

As a summary, though it is possible to obtain a temporarily stable solution, solutions with

low concentration cannot be used to fabricate a film. We can acquire the HOMO level of this incompletely converted CPI. We are able to fabricate a film of this incompletely converted CPI but we are still unable to take a further look because the UV-vis cyclic voltammetry results of these film indicate ineffective conversion of CPI.

### **3.3 To prepare a precursor solution containing PTF(OMe)Ph and alkylating agent**

#### **3.3.1 preparation of precursor solution and fabrication of thin film**

Converting PTF(OMe)Ph to a CPI with fluoroboric acid water solution is a bad idea because formed cations could be quenched in water. To improve this situation, a fluoroboric acid solution in organic solvent is a possible alternative. In spite of good solubility of fluoroboric acid in diethyl ether, pure fluoroboric acid would decompose to boron trifluoride and Hydrogen fluoride immediately. Furthermore, we cannot dry fluoroboric acid first and then dissolve it into diethyl ether. Therefore, we mix a fluoroboric acid water solution with a large amount of diethyl ether. This mixture is dried with drying agent (sodium sulfate, calcium sulfate or molecular sieves) three times. The dried acid solution is then concentrated by blowing dry nitrogen through (to around 0.003mol/L).

When we add this acid solution to PTF(OMe)Ph (8mg/mL PTF(OMe)Ph in 1mL mixed solution of DCM and ODCB (1:1)) dropwise, the yellow solution would turn green first and then turn back to yellow again. Reversing the process is not feasible because of the insolubility of the

polymer in diethyl ether. We use this yellow solution for spin coating and obtained a green film. The reason why we choose a mixed solution of DCM and ODCB instead of ODCB only is that we found that PTFC-Ph aggregates more slowly in DCM than in ODCB. Also, by the adjusting the ratio of DCM to ODCB, we can control the thickness of the film. This adjustment is much more efficient than changing spin coating condition.

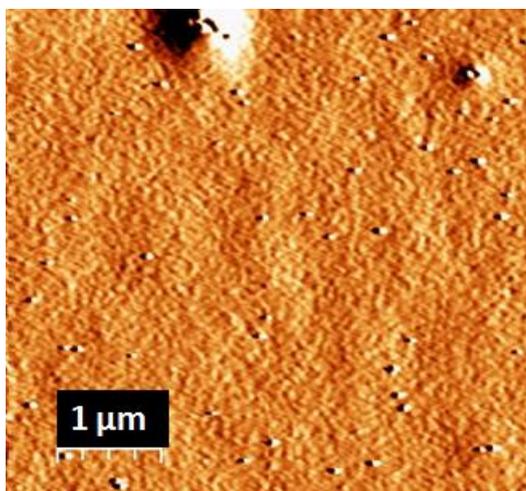
Compared to diethyl ether, PTF(OMe)Ph prefer to stay in the solvent of DCM and ODCB while fluoroboric acid prefers to stay in diethyl ether. In the mixed solution, two components could not react with each other. However, diethyl ether is much easier to evaporate than ODCB. Thus, during spin coating, acid could gradually react with PTF(OMe)Ph.



**Figure 14 precursor solution and film fabricate from this solution. A green film is obtained from the yellow solution. Once this precursor solution is prepared, the bottleneck has start to turn green because of the volatilizable solution left and PTF(OMe)Ph could react with acid.**

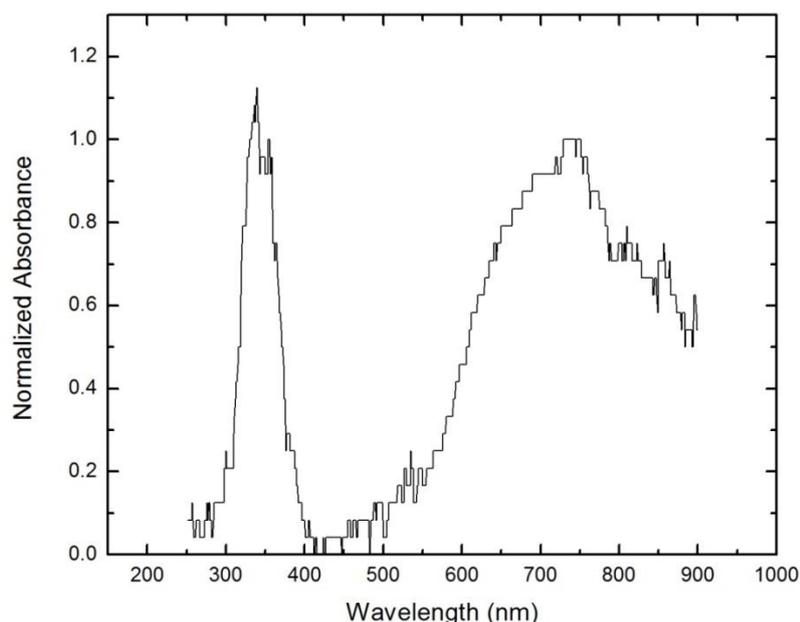
It may explain why the solution turns green first then turn back to yellow when the components are mixed dropwise. Diethyl ether is not sufficient enough at first to prevent acid

reacting with PTF(OMe)Ph. It results in a green solution. With the accumulation of diethyl ether, acid would gradually be moved from DCM/ODCB to diethyl ether, the equilibrium would also be far from CPI generating. As a consequence, the green solution turned back to yellow.



**Figure 15 AFM image of film made from this precursor solution. The RMS roughness is 10.6 nm, the roughness average is 2.7 nm. This film is not as smooth as previous PTF(OMe)Ph film while it is still reasonably flat.**

We used UV-vis to characterize the properties of PTFC-Ph film made by this precursor solution. We find a big difference in the range of blue, which may indicate efficient conversion of PTF(OMe)Ph. However, the spectrum is noisy because the signal is rather weak. In comparison of the UV-vis spectrum of PTFC-Ph in solution, the peak in the range of yellow is still too strong. It is caused by insufficient amount of acid added to the system.



**Figure 16 Normalized UV-vis spectroscopy of film fabricate from this precursor solution.**

To solve this problem of insufficient amount of acid that we can introduce, there are several factors we have tried to control.

### **1. The amount of acid solution**

This is apparently the most direct way to add more acid. However, polymer PTF(OMe)Ph does not dissolve in diethyl ether, 6 mL acid in diethyl ether is the maximum amount we can add to 1 mL PTF(OMe)Ph solution (DCM:ODCB=1:1) because otherwise the polymer would precipitate. If the ratio of DCM:ODCB goes to 3:1, the allowed amount of added solution would decrease to 4 mL. That is, even less amount of ketones can be converted.

### **2. The concentration of acid solution**

As mentioned above, a high concentration of acid would cause severe aggregation. To avoid aggregation and keep the acid solution stable, 0.003 mol/L is the maximum concentration. However, the real concentration can be even lower because we have not taken the loss of acid on

filter, drying agent and container into consideration.

We also tried to use commercially available fluoroboric acid diethyl ether complex to solve the problem of uncertainty of concentration and stability of acid. However, fluoroboric acid diethyl complex did not dissolve in diethyl ether. Consequently, we are not able to dilute fluoroboric acid and use it during solution preparation.

### **3. The concentration of PTF(OMe)Ph**

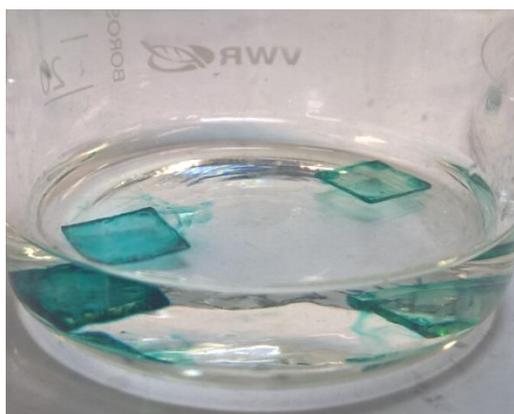
Decreasing the concentration of polymer can reduce the amount of acid required. However, due to large amount of diethyl ether required, the concentration of solution would be extremely low because of the dilute acid. To obtain a thick enough film (around 100 nm), we extract 8mg into a 1mL of mix solution of DCM/ODCB (1:1) and then add 6 mL acid.

Thus, we cannot make a completely converted CPI film for characterization. However, we may still be able to characterize some properties with incompletely converted CPI film.

### **3.3.2 Band structure measurement**

First, we try to use cyclic voltammetry and in situ conductivity measurement to gain in sight in the (semi) conducting properties of the film. However, we find that PTFC-Ph dissolves in the electrolyte solution (0.1 mol/L Tetraethylammonium hexafluorophosphate in Propylene carbonate). We have tried several other solvents. However, we were not able to find a solution that can dissolve Tetraethylammonium hexafluorophosphate while leaving PTFC-Ph unaffected. Even ionic liquids seem to dissolve PTFC-Ph. The cations in the backbones of CPIs may have

caused this problem. It can also explain the unsuccessful cyclic voltammetry measurement in previous work. With previous film cyclic voltammetry measurement, the phenomenon is not obvious because only a small amount of PTFC-Ph is present. Also, a layer of PTF(OMe)Ph remains leaving us the impression that the film has not been destroyed while the cations has been quenched after the measurement.



(a)

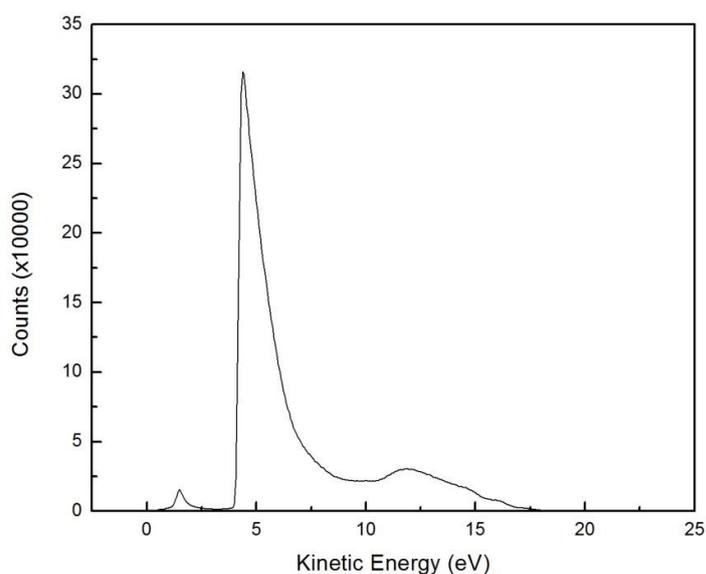


(b)

**Figure 17 (a) The dissolving of PTFC-Ph in polycarbonate.**

**(b) On the left is the film of incompletely converted PTFC-Ph, in the middle is the “PTFC-Ph” film after immersed in polycarbonate for 5 minutes, on the right is the film after exposed to air for 3 days.**

Since we cannot obtain information of the band structure of CPIs from cyclic voltammetry, other characterization methods need to be applied. We use Ultraviolet Photoelectron Spectroscopy (UPS) to identify the HOMO level of PTFC-Ph. As shown in figure 18, although the peak used for determining the HOMO state cut off is very weak, this result is reproducible. So we believe the HOMO level calculated from this UPS plot (figure 18) is convincing.



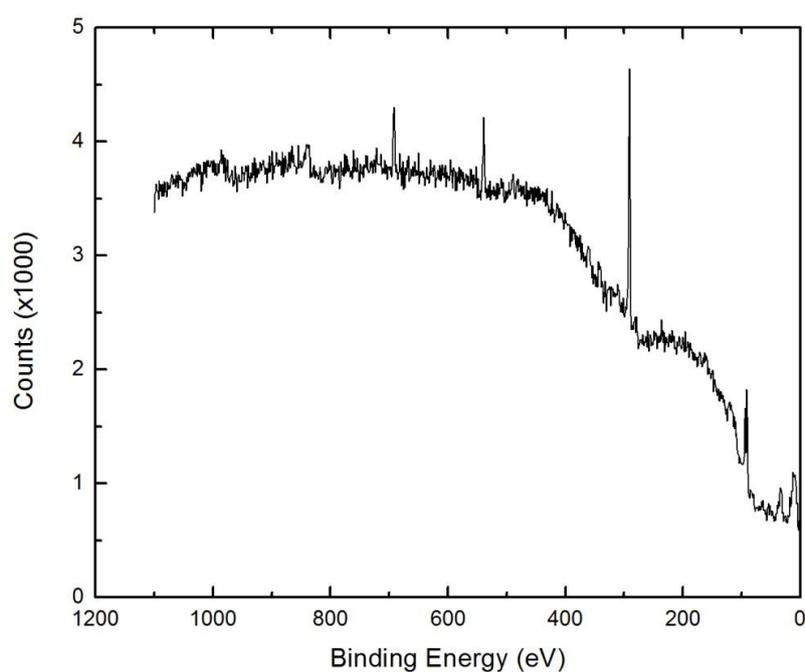
**Figure 18. UPS result of incompletely converted PTFC-Ph film.** The energy cut off is 4.0 eV, the HOMO state cut off is 19.01 eV, the energy of photoelectron is 21.22 eV, and the HOMO level is at 6.20 eV.

According to UPS result, we can calculate the LUMO level of this incompletely converted CPI film is 6.2 eV. The peak we use to calculate the absorption cut off is rather weak. However, this result agree with the previous cyclic voltammetry (in solution) data and UV-vis data. With a band gap of 1.4 eV, the LUMO level equals to 4.9 eV, and HOMO level equals to 6.189 eV. On the other hand, it may indicate the similar percentage of PTF(OMe)Ph have been converted on the film to the previous solution of cyclic voltammetry measurement.

We have also done the X-ray Photoelectron Spectroscopy (XPS) measurement to determine the elemental compositions of film.

We expect to find peaks represents carbon, oxygen, sulfur, boron, fluorine with a ratio of C:O:S:B:F=5.5:0.14:0.2:0.067:0.267. However, we can only recognize peaks from XPS spectrum represents C, O, F and Au with a ratio of: C:O:F:Au=5.59:1:0.22:0.16. Boron and sulfur have not been detected. It may be caused by their relatively low concentration. The ratio of carbon and fluorine agrees with what we expected

and may also indicate the real amount of acid we add to precursor solution is 0.6 equivalent to polymer. We cannot conclude that around 30% methoxy groups have been converted because the in-ignorable amount of cations may have been quenched. The oxygen contained in the film is unexpectedly high. It does not seem to be reasonable to interpret it to be the remaining of diethyl ether though we have kept the sample in high vacuum for 1 hour in load lock chamber to remove organic solvent.



**Figure 19 Overview of XPS result of incompletely converted PTFC-Ph**

### **3.3.3 Device performance**

According to the data of HOMO and LUMO level we acquired previously, we try to fabricate an electron only device of PTFC-Ph with indium tin oxide (ITO) and aluminum as electrode to form a sandwich structure of ITO/PTFC/Al. By measuring the current density vs voltage diagram,

we can characterize the transport of charge in PTFC-Ph. We expect that this sandwich structure can suppress the injection of holes in the valence band of PTFC-Ph. The current flowing through this device is space-charge limited so it depends on the mobility of charges, the applied voltage, and the thickness of the polymer layer. The mobility of electrons can be fitted in the equation below.

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu_{0n(p)} \exp\left(0.891 \gamma_{n(p)} \sqrt{\frac{V}{L}}\right) \frac{V^2}{L^3}, \quad (\text{Equation 2})$$

J is the current density,

$\epsilon_0$  is the permittivity of a vacuum,

$\epsilon_r$  is the relative dielectric constant of the polymer,

$\mu_{0n(p)}$  is the zero-field electron mobility,

$\gamma_{n(p)}$  is the field activation factor,

L is the thickness of the polymer layer

V is effective voltage

To fabricate an electron-only device, zinc oxide should be a better choice than PEDOT:PSS because of its band structure. However, It is difficult to deposit a PTFC-Ph film on zinc oxide. So the device still uses PEDOT:PSS.

Before we extract electron mobility by fitting experimental J-V curve to equation 2, we have to obtain the dielectric constant of PTFC-Ph. It is extracted by calculating experimental impedance spectroscopy with the following equation:

$$C = \epsilon_r \epsilon_0 \frac{A}{d} \quad (\text{Equation 3})$$

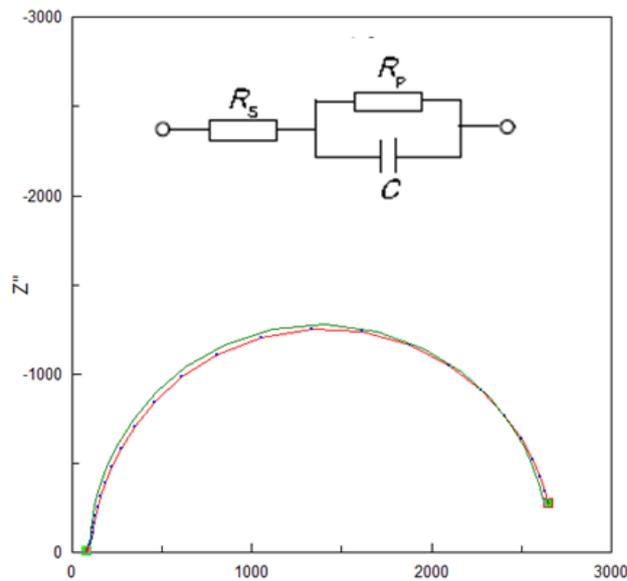
C is the capacitance,

A is the area of overlap of two electrodes,

$\epsilon_r$  is the dielectric constant of material between electrodes,

$\epsilon_0$  is the electric constant ( $\epsilon_0 \approx 8.854 \times 10^{-12} \text{ F}\cdot\text{m}^{-1}$ ),

d is the thickness of film



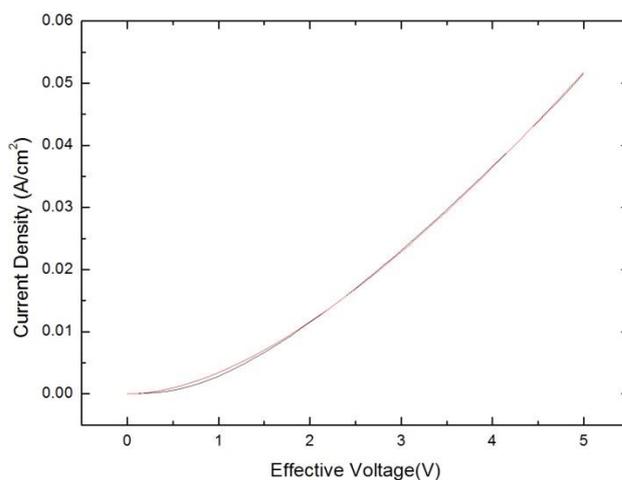
**Figure 20 Impedance spectrum of PTFC-Ph OLED device.** With  $R_s=100$  ohm,

$R_p=2560$  ohm and  $C=6.025 \times 10^{-8}$  F

We expect a higher dielectric constant of PTFC-Ph than PTFK because the polarizability of cations stabilized in the polymer backbone should be higher than ketones. From impedance spectroscopy, the capacitance is  $6.025 \times 10^{-8}$  F. With the thickness of film are 67.50 nm and an area of  $0.95 \text{ cm}^{-1}$ . The dielectric constant is 4.59. It is higher than dielectric constant of PTFK (3.8) and also higher than most of polymers. [17] Considering the limited amount of free cations we have on the film, we can expect an even higher dielectric constant if we could make film with all methoxy groups have been converted to cations.

Unfortunately, although the results of J-V measurements indicate an Ohmic contact has been formed, it does not give us analyzable data to calculate electron mobility. Also, the signal of

emitted light is weak and cannot be detected by emission spectroscopy. We could not observe light emission with our eyes. We kept the device in glove box for 2 days, after which the device failed, which probably means the formed cations have been quenched or the materials have been degraded.



**Figure 21 J-V curve of PTFC-Ph OLED device**

The reason why we cannot acquire desirable data may be that PTF(OMe)Ph are only partially converted. The polymers are still insulator because of the localized cations. However, the polarity has been changed even if the film is partially converted so the dielectric constant increased.

Consequently, what we achieved may be described as a limited amount of cations that have been formed which are distributed on an insulator thin film. An improvement of dielectric constant can be observed but the charge carrier mobility remains unknown.

### **3.3.4 Film thickness optimization**

Because of the high boiling point solvent used for spin coating (ODCB and CB), the thickness of the film is not easy to control and it is difficult to obtain a thick film. By changing the spin

coating conditions, the thickness of the film does not significantly increase. Also, with the same spin coating conditions, the film on a 1 cm x 1 cm substrate is much thicker than on a 3 cm x 3 cm substrate. For a 3 cm x 3 cm substrate, there is a significant difference of thickness of film in the middle and on the edge. However, thickness is an important cofactor of characterization and device fabrication. It can significantly affect the results of dielectric constant and charge mobility.

**Table 2 thickness of film corresponding to different spin coat condition**

	Speed (rpm)	Acceleration (rpm/s)	Time (s)	Thickness (nm)
PTF(OMe)Ph, 15 mg/mL In chlorobenzene	800	400	60	51.42
	1000	400	60	49.87
	1200	400	60	49.34

A film should be flat and thick enough for OLED device. We can conclude from the equation of capacitance that the thickness of the film does not change the properties of dielectric constant significantly. However, such a film cannot reveal the properties of the polymer. Before thickness optimization, the dielectric constant turned out to be only 1.8 with a film thickness of around 30 nm and no information could be distilled from J-V curve. Furthermore, On the other hand, an extremely thin film is also easily to be penetrated by the spikes of ITO causing shorts. Also, when we are calculating the dielectric constant, the error of thickness could directly affect the result of dielectric constant. So we need to measure the thickness of film on or near the area covered with electrode.

With the ineffective control of thickness via spin coating conditions, we use different proportion of chlorinate solvents to control the thickness of film. Because the solution with ODCB:DCM=1:3 is not stable enough to contain enough amount of acid (DCM cannot solubilize PTF(OMe)Ph as well as ODCB, precipitation starts with low amounts of acid.), we fabricated the device with the solution containing ODCB:DCM=1:1. Also, the thickness data we use to calculate

dielectric constant are collected from a scratch near the area covered with the electrode.

**Table 3 thickness of PTFC-Ph film with same spin coat condition but different proportion of solution and substrate (4 mg polymer in 0.5 mL chlorinate solvent, another 3mL HBF<sub>4</sub> diethyl ether solution is added)**

	ODCB:DCM=1:3	ODCB:DCM=1:1	ODCB:DCM=3:1
1 cm x 1 cm	198.17 nm	165.44 nm	120.27 nm
3 cm x 3 cm	75.63 nm	67.50 nm	47.83 nm

### 3.4 Other approach that may avoid aggregation

Since the aggregation is caused by the mismatch of solubility of pendant group to the backbone, a solution containing both polar solvent and non-polar solvent which is able to dissolve PTF(OMe)Ph may help to form a stable solution in relatively high concentration of polymer.

We dissolved 2 mg PTF(OMe)Ph in 1mL of ODCB, then dropwise add 2 mL ethanol (over 2 mL ethanol would cause precipitation). Then we add 2.5 eq fluoroboric acid diethyl ether complex and obtained a clear deep blue solution. It seems we have acquired a homogeneous solution. We kept this solution in room temperature for 2 days and no apparent aggregation was observed.

However, when we tried to use this solution for spin coating, most of the materials was removed during filtration of the sample through a 0.45 micron filter. It indicates, the polyions aggregate to form small particles that are invisible but still bigger than 0.45 micron. Thus, this is an effective method to reduce aggregation but still not good enough to prevent aggregation.

## 4. Conclusion

We can fabricate a partially converted PTFC-Ph film containing a small amount of free cations that are distributed on an insulator substrate. We are not able to measure charge carrier mobility or *in situ* conductivity but we can observe some other properties revealed by the cations.

The dielectric constant of less than 30% converted PTFC-Ph is 4.59, which is already higher than most polymers. Considering the limited free cations generated, the dielectric constant of a fully converted PTFC-Ph should be even higher. At least, it seems that to generating conjugated polyions via spinless doping is an effective way to increase the dielectric constant.

The band structure cannot be measured by cyclic voltammetry on a film because the CPI would dissolve into the electrolyte solution. The precursor solution can help us to fabricate an incompletely converted conjugated polyion PTFC-Ph. We have characterized the LUMO level of PTFC-Ph with less than 30 % conversion and was found to be 6.2 eV. From the cyclic voltammetry result of PTFC-Ph solution, the HOMO level is at 4.9 eV.

A mixed solution of ODCB and ethanol can help to reduce aggregation but still not good enough to help us fabricate a film. However, it is possible that other polar solvent instead of ethanol that can dissolve PTF(OMe)Ph better may be able to utilized to film preparation.

The conjugated polyion PTFC-Ph is a relatively green material that may have great properties and can be produced in scalable manner. However, it is difficult to process and characterize. For industrial application, further adjustment should be done to enable pendant groups dissolved into polar solvents.

## 5. Experimental part

### 5.1 Materials:

PTFK is synthesized by T.P. Voortman. [17] All other reagents and solvents are commercially available.  $\text{CH}_3\text{OH}$  was dried over  $\text{Na}_2\text{SO}_4$ , filtered, and distilled over sodium metal. Then, approximately 1M sodium metal was slowly added to dry  $\text{CH}_3\text{OH}$  and form 1M  $\text{CH}_3\text{ONa}$  in  $\text{CH}_3\text{OH}$ .

### 5.2 Characterization:

NMR spectra were measured using a Varian VXR300 (300MHz) or a VarianAMX400 (400MHz) instrument at 25 °C.

FT-IR spectra were recorded on a Nicolet Nexus FT-IR fitted with a Thermo Scientific Smart iTR sampler.

UV/Vis measurements were carried out on a Jenway 6715 spectrometer. Solution is contained in a 1 cm fused quartz cuvettes with concentrations of 0.01 mol/L. Films are fabricated by spin coating and loaded on glass.

Cyclic voltammetry measurements were carried out with an Autolab PGSTAT100 potentiostat. Cyclic voltammograms were recorded at 50 mV/s and conductivity traces were measured at 5 mV/s with a 40 mV offset between the two working electrodes in a 0.1 mol/L tetraethylammonium hexafluorophosphate propylene carbonate electrolyte solution.

The thickness of films is measured by AFM or Dektak.

### 5.3 PTF(OMe)Ph synthesis:

Process of PTF(OMe)Ph synthesis is followed Thomas's method:

PTFK was added to 50 mL dry THF in a dried flask. After polymer has been dissolved, 1.4mL (1.6M) phenylmagnesium bromide is dropwise injected into flask. After complete addition the reaction mixture was refluxed overnight under strong stirring. Cooling down to room temperature, the now deep green suspension was quenched by adding freshly prepared 15 mL 1M CH<sub>3</sub>ONa in CH<sub>3</sub>OH. A clear orange solution is obtained and has been washed with CH<sub>2</sub>Cl<sub>2</sub> and water several times. 0.1M NaHCO<sub>3</sub> has been added dropwise to adjust pH from 13 to 8. Extreme dilute HCl with brine was then added to adjust pH from 8 to 6. Yellow solution has been obtained. The solvent was removed by rotary evaporation and redissolved in a minimal amount of hot THF. The hot solution was filtered to get rid of salt and then precipitated in stirring n-hexane. The precipitate was filtered over a Soxhlet thimble and extracted with n-hexane overnight. The polymer was collected by extraction with CF and dried in vacuum oven. The product of PTF(OMe)-Ph is yellow solid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62, 7.60, 7.54, 7.48, 7.44, 7.42, 7.34, 7.26, 7.20, 6.71, 3.02, 1.96, 1.61, 1.01, 0.72, 0.61 ppm. FT-IR (ATR) 3428, 3061, 3024, 2955, 2925, 2853, 1704, 1601, 1446, 1404, 1375, 1319, 1287, 1204, 1133, 1004, 882, 799, 752, 698, 650, 585, 545 cm<sup>-1</sup>.

### 5.4 Spin coating conditions

**Table 4 spin coating conditions used in this thesis**

	Stage 1			Stage 2		
	Spin speed (rpm)	Acceleration (rpm/s)	Time (s)	Spin speed (rpm)	Acceleration (rpm/s)	Time (s)
15 mg/mL	400	400	15	1000	400	60

PTF(OMe)Ph chlorobenzene solution						
Precursor solution (for UV-vis and UPS)	600	300	10	1200	600	80
Precursor solution (for device fabrication)	400	200	10	1000	200	80

## 5.5 Device fabrication

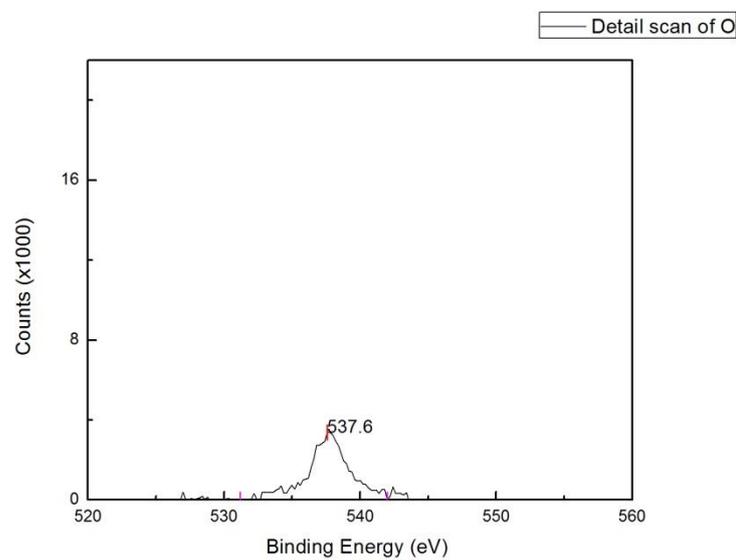
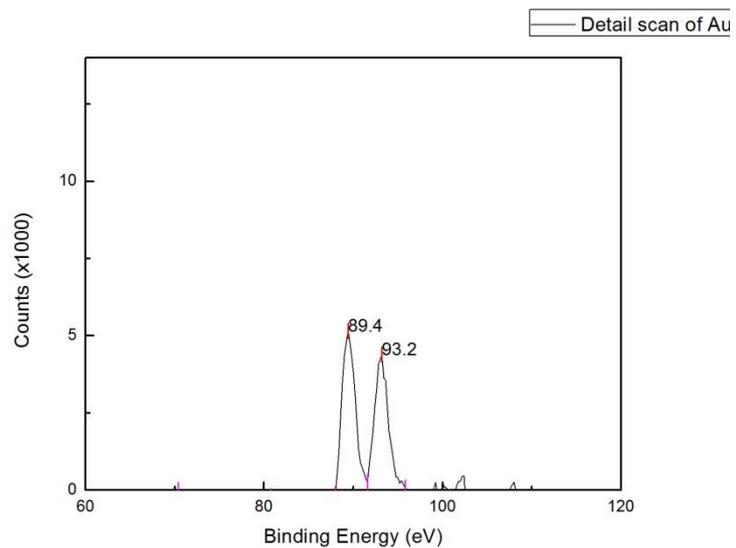
First, we scrubbed samples with warm demi-water and soap (10% heat in advance) for 5 minutes each to remove contaminations and spikes on ITO. Then the samples were brushed in demi-water in flow bath for 5 minutes, followed by ultrasonic cleaned in acetone. After ultrasonic, these substrates were brushed in demi-water again in flow bath for 5 minutes to remove remaining acetone. Then, they were cleaned by ultrasonic in isopropanol for 5 minutes. After dry spinning and dried in 120 °C oven 10 minutes, these samples were cleaned in Uv-ozon for 20 minutes to remove remaining organics.

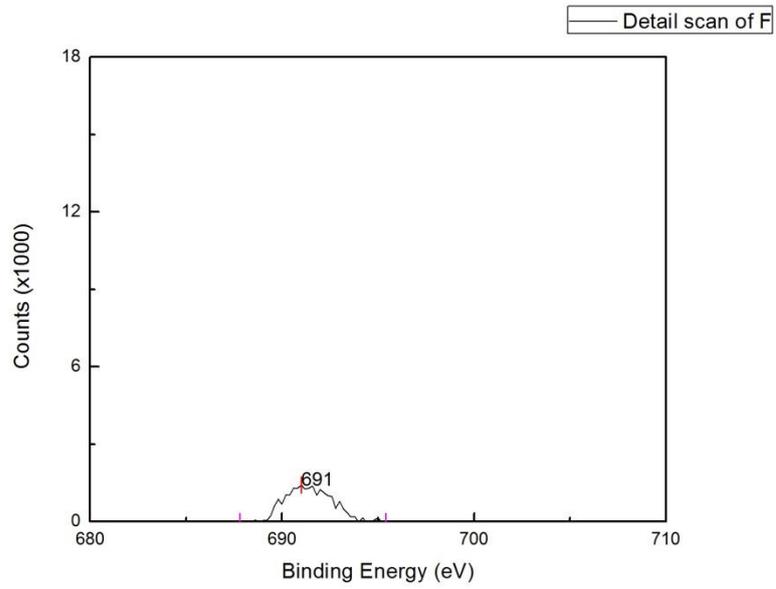
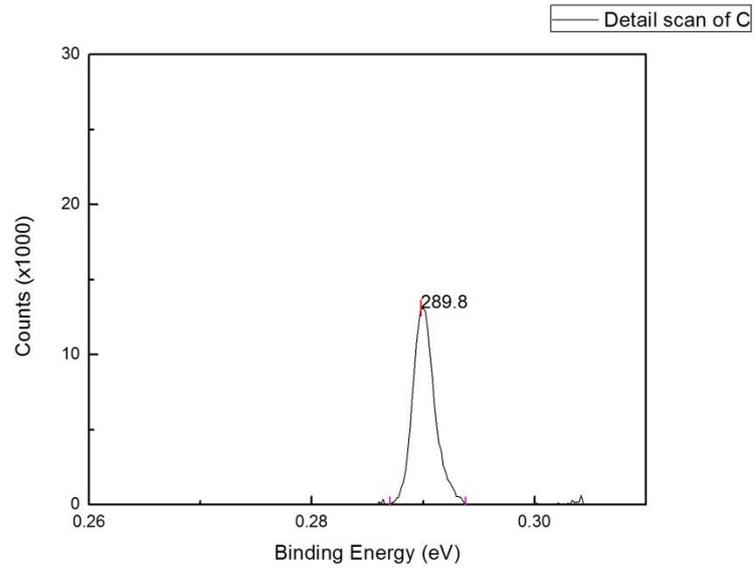
We spin coated a layer of PEDOT:PSS on the cleaned substrate and then dried them in oven for 10 minutes again. In the next step, we spin coated PTFC-Ph on PEDOT:PSS layer and then deposited a layer of Al in the pattern of electrode.

## 5.6 XPS analysis

After an overview scan, we identified peaks of Au, C, F and O. We had ten scans for each

representing region. We added these scan up to minimize the influence of noise. Then we calculated the integrate of peaks, corrected them with atomic sensitive factors (6.250 for Au, 0.296 for C, 0.711 for O and 1.000 for F) to obtain the ration of each elements.





**Figure 22 detail scan of each peaks of XPS**

## 6 Acknowledgements

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I would also like to thank Gang Ye for his help in lab. He has given me a lot of useful advices about CV and in-situ conductivity measurements

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## 7 Reference

- [1] Chochos C L, Choulis S A, How the structural deviations on the backbone of conjugated polymers influence their optoelectronics properties and photovoltaics performance, *Prog. Polym. Sci.*, 2011, 36: 1326-1414
- [2] Shirakawa H, Lowis J, Macdiarmid A G, et al., Synthesis of electrically conducting organic polymers: Halogen derivatives of polyacetylene, (CH)<sub>x</sub>. *J. Chem. Soc. Chem. Commun.*, 1977, 13: 578-580
- [3] Green M. A. Emery K., Hishikawa Y. Warta W. *Progress in photovoltaics: Research and applications*, 2011, 19, 84-92
- [4] F. Machui, L. Lucera, G. D. Spyropoulos, J et al., Large area slot-die coated organic solar cells on flexible substrates with non-halogenated solution formulations, *Sol. Energ. Mat. Sol.* 128, 441 (2014).
- [5] C.-C. Chen, W.-H. Chang, K. Yoshimura, et al., An efficient triple-junction polymer solar cell having a power conversion efficiency exceeding 11%, *Adv.Mater.* 26, 5670 (2014).
- [6] Y.-J. Hwang, B. A. E. Courtright, A. S. Ferreira, S. H. Tolbert, and S. A. Jenekhe, 7.7% efficient all-polymer solar cells, *Adv.Mater.* 27, 4578 (2015).
- [7] R. C. Chiechi and J. C. Hummelen, Polymer electronics, quo vadis? *ACS Macro Lett.* 1, 1180 (2012).
- [8] L. J. A. Koster, S. E. Shaheen, and J. C. Hummelen, Pathways to a new efficiency regime for organic solar cells, *Adv. EnergyMater.* 2, 1246 (2012).
- [9] Thunemann A F. *Adv, Mater.*, 1999, 11(2); 127-130
- [10] Patil A O, Ikenoue Y, Wudl F, Heeger A J, *J. Am. Chem. Soc.*, 1987, 109: 1858-1859.

- [11] Chang S C, Bharathan J, Yang Y, Appl, Phys, Lett., 1998, 73 (18):2561-2563
- [12] S. Link and M. El-Sayed, Atlanta: J.Phys. Chem.B, 1999, Vol. 103.
- [13] F. Wudl, R. O. Angus, F. L. Lu, P. M. Allemand, D. Vachon, M. Nowak, Z. X. Liu, H. Schaffer, and A. J. Heeger, Poly-pphenyleneamineimine: synthesis and comparison to polyaniline, J. Am. Chem. Soc. 109, 3677 (1987).
- [14] R. C. Chiechi, G. Sonmez, and F. Wudl, A robust electroactive n-dopable aromatic polyketone, Adv. Funct. Mater. 15, 427 (2005).
- [15] Thomas P. Voortman, et al. J.Mater. Chem. C. 2, 3407 (2014)
- [16] Thomas P. Voortman, et al. ACS Appl. Mater. Interfaces, 51, 28006 (2015)
- [17] Thomas P. Voortman, et al. Macromolecules 48, 7007 (2015)
- [18] I. Horcas, et al. Rev, Sci, Instrum, 78, 013705 (2007).