



Project 02: Scientific Progress – Fall 2009 to Fall 2015

The main objective of this project was to build a tandem organic device and characterize its properties. The polymers were to be selected with the help of quantum mechanical calculations. The goal was achieved and such device was made. The following is a scientific progress update for each collaborating investigator on the project at the 5-year point:

Steven Holdcroft

The change in morphology of the bulk heterojunction films is considered a major degradation mechanism in polymer solar cells. The active layer composed of a well-mixed polymer-fullerene blends undergoes large scale phase segregation whereupon fullerene aggregates appear in the films, and which greatly reduce charge separation and transportation processes; ultimately, resulting in a drastic reduction of photo conversion efficiency (PCE). This mechanism of degradation cannot be prevented by simple device engineering or encapsulation. The problem originates from the inherent thermodynamic instability of the film and thus has to be tackled from a molecular perspective. Holdcroft's contribution to this project has been to target a reduction in large scale phase segregation, thus preserving the optimal morphology, through the chemical modification of the polymers as well as the use of chemical crosslinkers. Two different functional groups – an azide and tetrahydropyran (THP) – have been employed: the former makes use of an increased rigidity of the polymer upon removal of such groups, the second utilizes an increased morphological stability of BHJ films by crosslinking the components.

Azides has been known and demonstrated to be able to crosslink with fullerene. Several modification strategies of introducing azides into the polymer have been attempted. Polythienothiophene benzodithiophene (PTB) was chosen as the polymer to demonstrate these strategies due to its high, reproducible performance in polymer solar cell applications. Holdcroft's first attempt was to synthesize a block copolymer consisting of PTB and azide-substituted polystyrene blocks. The diblock copolymer route had been proved to be effective in stabilizing the PCE of the poly-3-hexylthiophene/PCBM solar cells and the block copolymer structure was believed capable of helping the polymer fullerene to develop an optimized morphology. However, this approach using the PTB was proven to be synthetically to challenging and this approach was suspended. A revised plan eliminate the use of insulating polystyrene blocks and sought out a direct linkage between the polymer and fullerene by placing the azide groups on the end of the polymer side chains. The azide group was introduced onto the end of the side chain via post-functionalization PTB polymer with chlorine-terminated side chains. The synthesis was successful up to the point of polymerization, whereupon substitution of the azide for chlorine resulted in insoluble materials even for low azide contents. Although disappointing, this result has led to speculations that the azide may actually crosslink with polymer backbone. Hence, the project was further modified to using small molecule azide crosslinkers to stabilize the morphology of the active layer. An azide crosslinker, namely diazidoctane (DAzO), was readily synthesized. It appears as a slightly yellowish oil and was blended into the polymer-fullerene mixtures before casting. 13.3% w/w of DAzO was added to the PTB/PCBM mixture. 15 minutes of annealing at 150 °C was implemented after film casting to initiate the crosslinking in solid state. After deposition of the metallic cathode, films with and without DAzO were tested under 1 sun condition to evaluate their PV performance. Accelerated aging was performed inside

the inert atmosphere filled glovebox by heating the devices for up to 4 hours at 150 °C. Stability of the devices was evaluated by taking PV measurements of the devices after each hour of heating. The results show that those devices with DAzO added and initially annealed exhibit moderate but stable PCE over the entire course of the aging process, whereas those without DAzO quickly exhibited decreased efficiency and remained inefficient for the rest of the aging process. In the following study, the content of the DAzO and the initial annealing time was investigated. It was found that sufficient annealing time was required to initiate the crosslinking while the content of the crosslinker does not make an appreciable difference in PCE and stability. The degradation profiles of individual PV parameters revealed that the stabilization of the PCE can be attributed to the stabilization of short circuit current J_{sc} and fill factor FF, which indicates the stabilization of the active layer morphology, preserving efficient charge separation and charge transportation.

Tetrahydropyran (THP) is a well-known alcohol protecting group, which deprotects the hydroxyl group when heated mildly in the presence of acid. This feature has been exploited in the manipulation of the solubility of conjugated polymer. THP can be incorporated into the side chain of polymer, and subsequently cleaved leaving the polymer with shortened side chains and decreased solubility. Initially, a high band gap polymer F(THP)T2 was developed with the view of utilizing its reduced solubility following deprotection to construct tandem solar cells in conjunction with a low band gap, secondary layer directly deposited on it. However, the fabrication of useful tandem cells proven difficult many months of effort. The goal of the project then modified to investigated the stabilization effect in single layer polymer solar cells using the THP groups. Single layer devices using F(THP)T2 as the polymer were fabricated. F(THP)T2 absorbs within 300 – 500 nm and TGA analyses show that this polymer loses THP groups when heated to 210 °C, or 140 °C in the presence of trace acid. The polymer was rendered insoluble and possessed an absorption profile that was unchanged. Deprotection of the polymer deposited on devices was realized by thermal annealing for 1 hour at 150 °C in the presence of an organic acid, camphorsophonic acid (CSA). The PCE of the devices after deprotection degraded relatively less quickly (from 1.5 % to 0.3 %) than those prepared from F(THP)T2 prior to deprotection demonstrating the concept of stabilizing PV performance using THP thermal cleavable side chains. Based on the results above, the synthesis and characterization of a THP-protected low bandgap polymer based on the PTB was carried out. Again, PTB(THP) displayed similar absorption spectrum of the unmodified PTB polymers which remained unchanged after thermal cleavage of the THP groups. Devices using PTB, PTB(THP), and deprotected PTB(THP) were fabricated. To cleave the THP group from the deprotected polymers, 5-10 mins of thermal annealing at 150 °C with CSA as the catalyst was performed before the deposition of the cathode. In subsequent aging tests, model PTB devices exhibited a drastic drop in PCE from 3.2% to 0.6% after the first hour of accelerated aging. A similar trend was observed for the PTB(THP) devices (from 3.4% to 0.6%). However, the deprotected PTB devices stabilized at 1.6% after 6 hours of aging. The result clearly shows that the thermal cleavable THP group has the potential of improving the longevity of the polymer solar cells. In support of this conclusion, the microscopic and X-ray scattering studies were performed for the PTB(THP) systems. From analyses of optical microscopy, deprotected PTB(THP)/PCBM films do not develop PCBM aggregates after 6 hours of annealing, unlike the model PTB/PCBM films and the untreated PTB(THP)/PCBM films, which show high population of PCBM

aggregates after annealing. Results from grazing incident wide angle X-ray scattering (GIWAXS) was also used to support the microscopic findings. The high q range ($0.02 \text{ \AA}^{-1} - 0.1 \text{ \AA}^{-1}$) in the integrated data along the horizontal line in the 2D-GIWAXS result represents the well-mixed donor and acceptor phases. The gradual decrease in high q range intensity of PTB/PCBM films is consistent with the slow aggregate appearance in the optical microscopic images. In contrast, PTB(THP)/PCBM displayed a sudden drop of high q range intensity, in agreement with the observation of early onset of PCBM aggregation observed under optical microscopy. However, deprotected PTB(THP)/PCBM film did not show high q range intensity decrease. In fact, the overall intensity of the full spectrum increased after the thermal annealing without change of the pattern. Overall, the PV and morphological studies of the PTB(THP)/PCBM films demonstrated that by cleaving off the THP, the stabilization of the morphology of the polymer fullerene film can be enhanced, hence the PCE can be stabilized. An attempt is being made to merge the high band gap F(THP)T2 and low band gap PTB(THP) work together and to publish this work as a whole. Similar morphological studies are planned for the azide crosslinker work in the summer. The results will be assembled for the final half year update due September.

To sum up, two projects have been carried out in Holdcroft group through the funding period of the PV innovation network. Both the azide crosslinker and THP thermal cleavable side chain are proven to be effective in stabilizing polymer solar cell efficiencies. The stability in efficiency is a result of the stabilization of the active layer morphology as evidenced by microscopy and X-ray scattering studies. Further experiments will be performed to complete these projects.

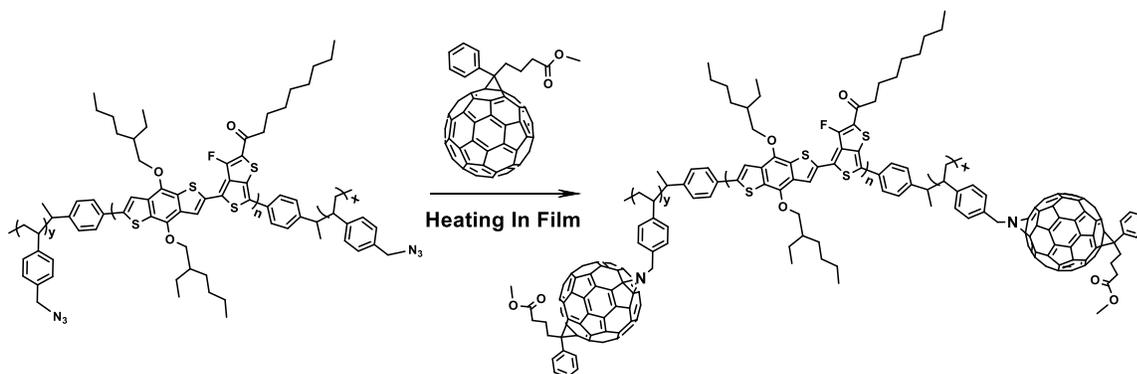


Figure 1. The crosslinking scheme of the originally proposed PTB-polyazidostyrene triblock copolymer.

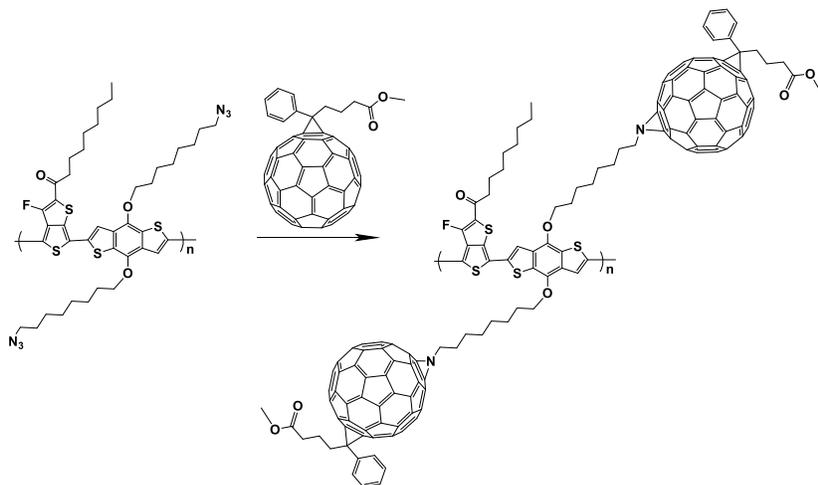


Figure 2. The crosslinking scheme of the modified project: PTB bearing azide functionalized side chains.

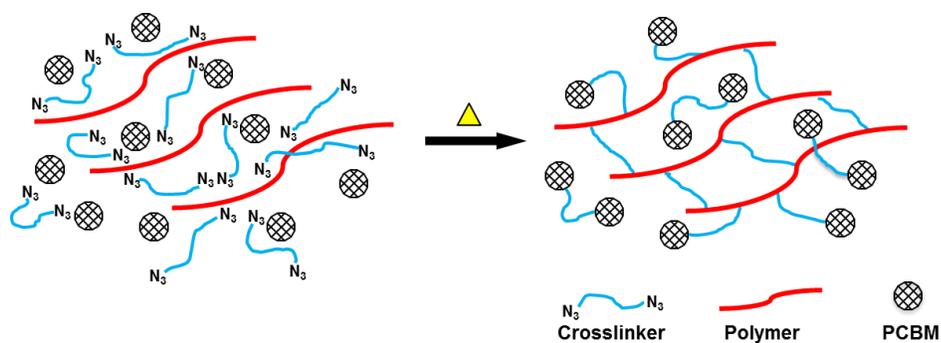


Figure 3. The crosslinking scheme that utilizes a much simple approach: a diazide crosslinker

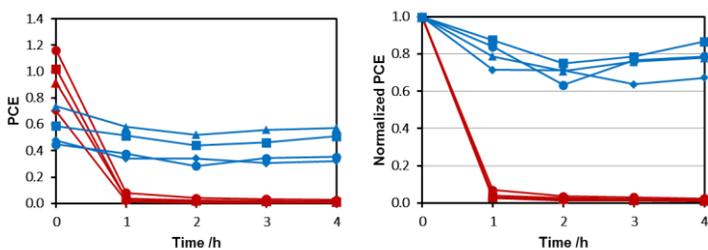


Figure 4. The PCE degradation profiles of the PTB/PCBM devices with and without the addition of DAZO. Devices were subjected to 150 °C annealing in inert atmosphere before tested again at each hour.

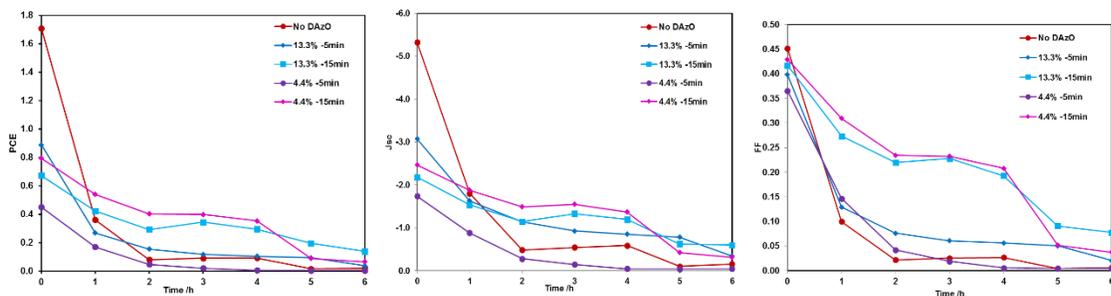


Figure 5. The degradation profiles of the devices with different content of diazidooctane, different initial annealing time, and their long term performance over the 6 hour accelerated aging at 150 °C.

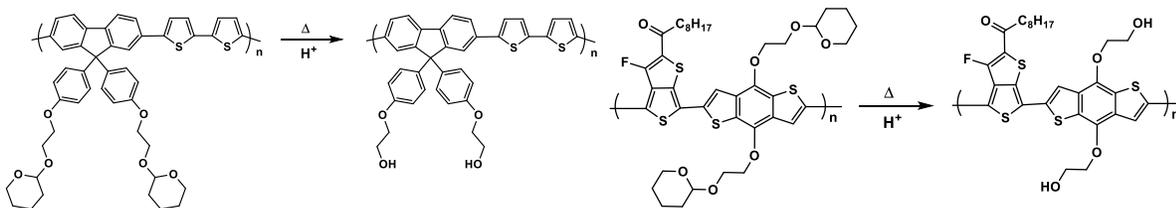


Figure 6. The thermal cleavage process of F(THP)T2 (top) and PTB(THP) (bottom).

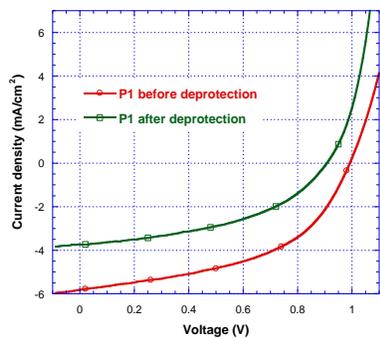


Figure 7. The PCE degradation profiles of F(THP)T2/PCBM and deprotected F(THP)T2/PCBM

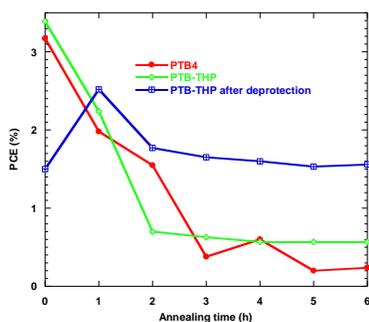
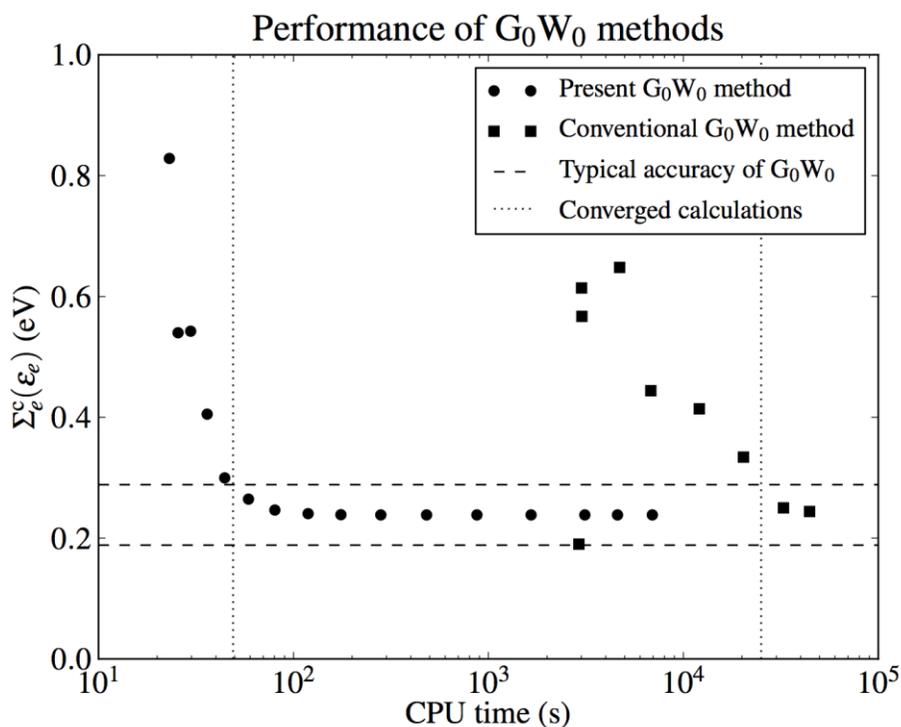


Figure 8. The PCE degradation profiles of polymer/PCBM films: PTB, PTB(THP), and deprotected PTB(THP).

Michel Côté

One of the main objectives of on the theoretical side was to implement a new approach to analyse organic materials. This was achieved in the GW approach. This method has been used for many years to calculate the properties of inorganic materials but it was numerically too demanding for organic materials. We completely revised the approach to make it suitable. The graph below shows the comparison between the conventional implementation and the new one, called present.



We have applied this method to small molecules and the results were published in the article:

Laflamme Janssen, J., Rousseau, B., Côté, M. « Efficient dielectric matrix calculations using the Lanczos algorithm for fast many-body G_0W_0 implementations. » *Phys. Rev. B* **91**, 125120 (2015).

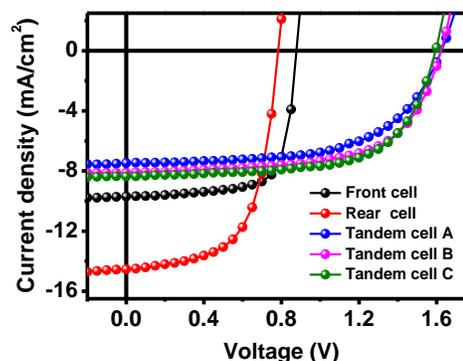
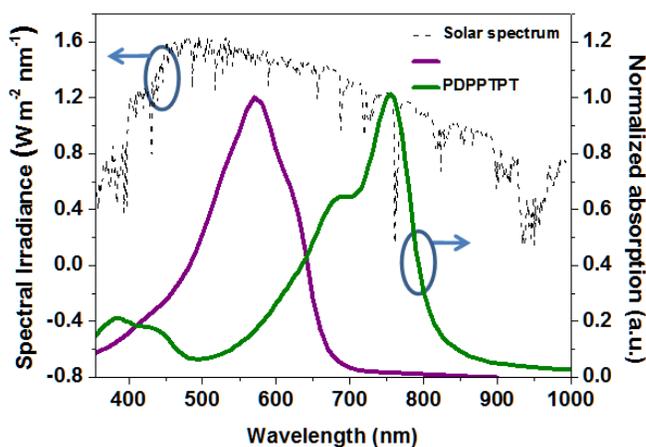
Mario Leclerc

The main objective of the project was the production of a tandem solar cell. This was achieved by the Leclerc's group.

On the basis of the single device results, the polymer identified as PDPPTPT, exhibits great potential for making **tandem solar cells**. Typically, large bandgap polymers, such as poly(3-hexylthiophene) (P3HT) and poly[N-9''-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-

benzothiadiazole)] (PCDTBT) have been widely used in the fabrication of high efficiency tandem cells. Here, we introduce another large bandgap material (P2) which has shown excellent performance with J_{sc} over 10 mA cm^{-2} , high $V_{oc} = 0.92 \text{ V}$, as well as high $FF = 63\%$. Combined with the PDPPTPT, these two polymers exhibit complementary absorption spectra from 350 nm to 850 nm, see the figure below.

Power conversion efficiency up to **8.58%** was reached for this device indicating that PDPPTPT is an excellent low bandgap material for the fabrication of high-efficiency solution-processed tandem solar cells.



Device structure	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
Front cell	0.88	9.7	73	6.18
Rear cell	0.78	14.5	62	7.04
Tandem solar cell A	1.62	7.5	60	7.23
Tandem solar cell B	1.61	8.0	62	8.04
Tandem solar cell C	1.60	8.4	64	8.58