

# **Design and Synthesis of Low-bandgap Polymers for Organic Photovoltaic Applications**

Link Energy Fellowship Final Report

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## **1. Introduction**

Organic photovoltaic (OPV) devices show great promise in low-cost, flexible, lightweight, large-area, energy-generation applications. In recent years, much work on designing new materials, device structures and processing techniques has been carried out to improve the power conversion efficiency of such devices. The key issues are how to design an electron-donor material (p-type semi-conductor) with a low energy bandgap to harvest more photons in the infrared region and with high quantum efficiency to convert photons to electrons efficiently.

My research at UCLA focused on the design and synthesis of novel conjugated polymers as the electron-donor material for photovoltaic devices. By careful molecular design both on the polymer backbone and the side chains, a series of low-bandgap conjugated polymers were synthesized for a variety of photovoltaic applications, including single junction and tandem polymer solar cells. In addition, I designed and synthesized a novel highly perfect polymer single crystal material via a visible light triggered topochemical reaction. This kind of materials shows high potential for application in solar cells and transistors, which we believe is a huge breakthrough in polymer science.

## 2. Results

In the first project, we synthesized conjugated polymer with selenium insertion on the side-groups of PTB7-Th (a previously reported high performance polymer),<sup>[1]</sup> namely PBDTSe-TT. Besides commonly observed red-shifted spectrum, selenium substitution on organic molecules usually improves the carrier transportation in the resulting electronic devices.<sup>[2,3]</sup> This improvement is believed to be a result of enhanced  $\pi$ - $\pi$  interaction between molecules brought by selenium atoms. Taking these advantages into account, we anticipate that a stronger stacking between polymer chains could be achieved through selenium substitution on the PTB7-based polymer, and thus the usage of solvent additives may not be necessary. Although the backbone selenium substitution on PTB7 has been previously reported, the polymer exhibits “too” strong of an inter-chain interaction thus the device performance turns out to be reduced as a result of improper phase separation.<sup>[4]</sup> Moreover, the synthesis of such molecules is rather complicated. The side-chain selenium modification is shown to be an effective way to address morphological issue of PTB7 related polymers. PBDTSe-TT, as we proposed, can achieve high performance of 8.8% PCE without any additives, such as 1,8-diiodooctane or 1-chloronaphthalene. Furthermore, it is shown that the newly synthesized polymer exhibits relatively improved thermal stability. When taking a further step to fabricate tandem device through identical PBDTSe-TT:PC<sub>71</sub>BM sub-cells, an ~10 % PCE was achieved.

In another project, we demonstrated a visible-light-triggered quantitative topochemical polymerization reaction based on a conjugated dye molecule. Macroscopic size, high quality polymer single crystals are obtained. Polymerization is not limited to single crystals but can also be achieved in highly concentrated solution or semi-crystalline thin films. In addition, we show that the polymer decomposes to monomer upon thermolysis, indicating that the polymerization-depolymerization process is reversible. The physical properties of the polymer crystals enable us to isolate single polymer strands via mechanical exfoliation, making it possible to study individual long polymer chains.

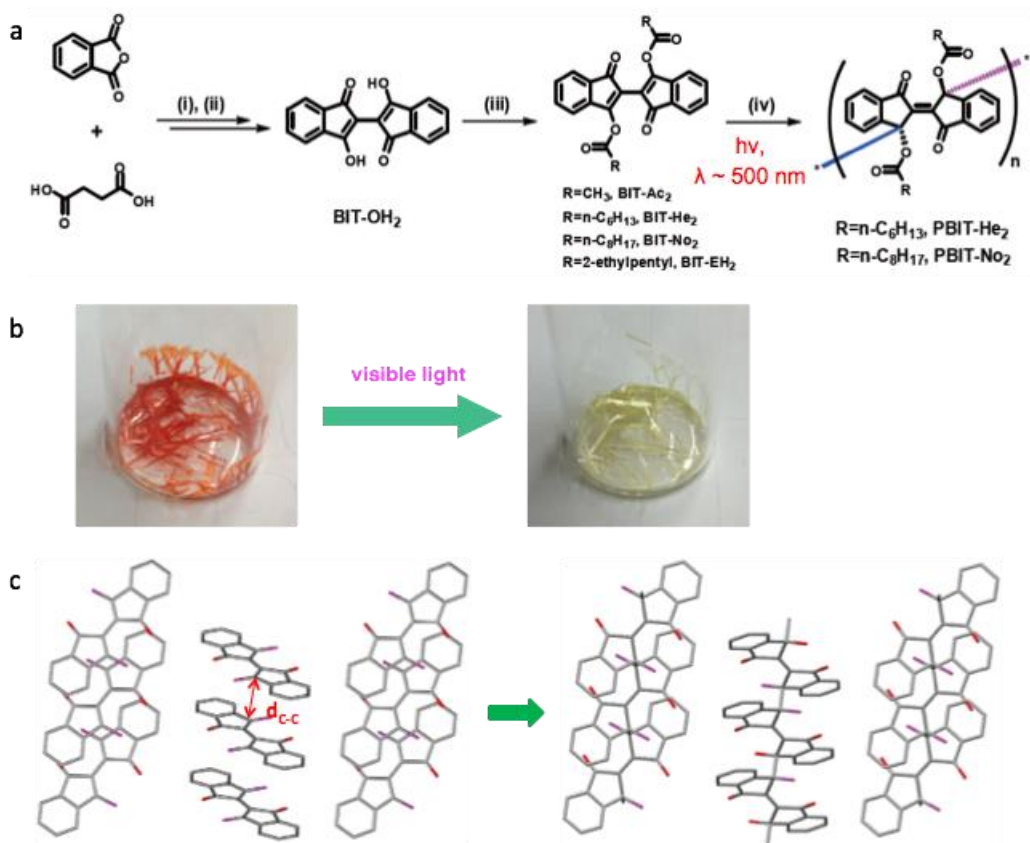


Figure 1. Synthesis of single crystalline polymers.

Figure 1a shows the synthesis of the monomers and polymers. Figure 1b shows the images of the crystal before and after polymerization. The gross morphology of the polymers is the same as the monomers. Figure 1c shows the crystal structure of monomers and polymers, characterized by single crystal X-ray diffraction technique. It can be seen that after polymerization, the carbon atoms in the 3, 3' positions changed from  $sp^2$  to  $sp^3$  hybridization and there is a single bond formed between the 3 and 3' positions of adjacent monomers. The length of the bond is 1.590 Å, slightly larger than that of a conventional C – C single bond ( $\sim 1.54$  Å). The polymer crystal shares the same space group with the monomer, slightly larger cell angle  $\beta$  (104.422 v.s. 100.086 degree), slightly smaller cell volume and slightly smaller  $\pi - \pi$  stacking distance. The perfect alignment of the monomers in the crystals and the short distance of the two active carbon atoms ( $d_{C-C}$ , 3.2 ~ 3.3 Å) are necessary to ensure that topochemical reaction will occur with concomitant high quality polymer crystal formation (R factor  $\sim 5\%$ ).

### **3. Significance, impact, and future directions**

The results from first project indicate that selenium-substitution is a promising way to enhance the photovoltaic performance of the low bandgap polymers. And the results from the second project open the door to prepare single crystalline polymers using a straightforward chemistry for a variety of electronic devices. Our research represents an important step forwards in the commercialization of polymer solar cells, which is a very promising way to use the solar energy to solve the energy crisis problem.

#### **References:**

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#### **List of publications in which the support of the Link Foundation Energy Fellowship is acknowledged:**

- [1] W.-H. Chang, L. Meng, L. Dou, C.-C. Chen, Y. Yang, *Macromolecules* **2015**, *48*, 562-568.
- [2] L. Dou, Y. Zheng, X. Shen, G. Wu, K. Fields, W. Hsu, H. Zhou, Y. Yang, F. Wudl, *Science* **2014**, *343*, 272.

#### **Utilization of Discretionary Funds:**

The fund was mainly used as the fellow's stipend during the summer and fall quarters of 2013. Due to the earlier graduation of the fellow, the fellowship was terminated in 2014. And the rest of the fund was returned to the institute of Link Energy Foundation.

**Impact of the Fellowship on the Fellow's Academic and Professional Development:**

The fellowship provided me great opportunities to pursue science and technology that can benefit our society, and it helped to create a new direction of research at UCLA. Winning the fellowship enhanced my commitment to working on clean energies, and made me feel that it is a lifelong passion and mission. I believe that the prestigious Link Foundation Energy Fellowship will have long-lasting impacts on my opportunities for professional career.