

DOCTORAL THESIS

Conjugated polymer and small-molecule donor materials for organic solar cells

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Date of Award:
2014

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Abstract

This thesis is dedicated to developing conjugated polymer and small-molecule donor materials for solution-processable organic solar cells.

To begin with, a brief introduction of organic solar cells (OSCs) and an overview of donor materials development were presented in Chapter 1.

In chapter 2, we used carbon-carbon triple bonds as linkage of the TVT unit to develop a new building block, ATVTA. Small molecules **S-03**, **S-04**, and **S-05** with ATVTA as building block showed broad absorption spectra and low-lying HOMO energy levels. **S-01** with TVT unit and **S-02** with AT2 as building block were also synthesized for clear comparison. OSCs devices based on **S-01** and **S-02** showed a V_{oc} of 0.88 V and 0.89 V, respectively. The device based on **S-03** exhibited a high V_{oc} of 0.96 V, leading to a PCE of 2.19%. The devices based on **S-04** and **S-05** afforded a notable V_{oc} over 1.0 V. The results demonstrate that ATVTA unit is a promising building block for extending π conjugation of the molecules without pulling up their HOMO energy levels.

Chapter 3 focused on the development of 2D-conjugated small-molecule donor materials. The 2D-conjugated small molecule **S-06** possesses excellent solution processability, broad absorption feature, respectable hole mobility and good film-forming morphology. The conjugated thiophene side chain not only effectively extends the absorption spectrum, but also lowers the HOMO energy level, which is

desirable for obtaining high V_{oc} . The BHJ OSCs based on **S-06**:PC₇₀BM (1:0.5, w/w) afforded a high PCE of 4.0% and a notable FF of 0.63 without any special treatment needed. This preliminary work demonstrates that this kind of 2D-conjugated small molecules offer a good strategy to design new photovoltaic small molecule-based donor materials with high FF and V_{oc} for high-efficiency OSCs. The consistently developed two 2D-conjugated small molecules **S-07** and **S-08** also possess low-lying HOMO energy levels. OSC device based on **S-07**:PC₆₀BM (1:3, w/w) afforded a notable V_{oc} of 0.96 V, with a PCE of 2.52%. BHJ devices based on **S-08** will be fabricated and tested to investigate its photovoltaic properties in the near future.

We developed a series of oligothiophenes with platinum(II) as the building block in Chapter 4. These small metallated conjugated small molecules exhibited broad spectra and relatively low-lying HOMO energy levels in the range of -5.27 eV to -5.40 eV. Introducing platinum(II) arylene ethynylenes as building block can be considered as an approach to obtain small-molecule donors with satisfactory absorption features and HOMO energy levels. Nevertheless, due to the low FF, the PCEs of these donor materials based devices are lower than 2%. Fine tuning the film morphologies of this kind of metallated small-molecule donor materials should be carried out to improve their photovoltaic performance.

We addressed an efficient approach to improve the photovoltaic properties by side chain engineering in 2D-conjugated polymers in Chapter 5. Considering the fact that the V_{oc} of PBDTTT based devices is less than 0.8 V, we introduced alkylthio substituent on the conjugated thiophene side chains of the 2D-conjugated copolymer

to further improve the photovoltaic performance of the 2D-conjugated copolymers PBDTTTs. The weak electron-donating ability of the alkylthio side chains effectively down-shifted the HOMO energy level of **PBDTT-S-TT** by 0.11 eV in comparison to the corresponding polymer with alkyl substitution on the conjugated thiophene side chains. The PSC device based on **PBDTT-S-TT** showed an enhanced V_{oc} of 0.84 V, which is among the highest one in the reported copolymers based on BDT and TT units, leading to an enhanced PCE of 8.42%. The results indicate that molecular modification by introducing alkylthio side chain will be a promising strategy to broaden the absorption, down-shift the HOMO energy level and increase the hole mobility of the low band gap 2D-conjugated polymers for further enhancing the photovoltaic performance of PSCs. **PBDTT-O-TT-C** and **PBDTT-S-TT-C** were developed to further study the conclusion. We found that OSC device based on **PBDTT-S-TT-C** with alkylthio side chain also demonstrated a high V_{oc} of 0.89 V, with a PCE of 6.85% when processed with 3% DIO additive.

Acknowledgements

My deepest gratitude goes first and foremost to my supervisor Prof. Wai-Yeung (Raymond) Wong for his thoughtful pieces of advice, encouragement and undoubtful support. Prof. Wong set a good example to me about how to be an excellent scientist, a good advisor, and a generous supporter. He made my experience in HKBU enjoyable and unforgettable. He trained me how to properly write a manuscript, review a scientific paper, and give a public presentation.

I would also like to express my heartfelt gratitude to Prof. Yongfang Li (Institute of Chemistry, Chinese Academy of Sciences), who led me into the world of science. I spent more than two years in Prof. Li's research group during my Master period. Prof. Li taught me a lot not only in academic research, but also in the right attitude to failure. His motto is "try your best, let nature take its course". He made me realize that we should maintain peace of mind on the path to the heights of science.

Special thanks are also expressed to other collaborators. Prof. Christoph J Brabec and my friend Mr. Jie Min (Friedrich-Alexander-University Germany), Dr. Wallace Choy (The University of Hong Kong), and Prof. Zhiyuan Xie (Changchun Institute of Applied Chemistry, Chinese Academy of Sciences) contributed to the fabrication and testing of organic solar cells. Prof. Jianzhang Zhao (Dalian University of Technology), Prof. Zhenyang Lin and Dr. Man-Sing Cheung (The Hong Kong University of Science and Technology) contributed to the density functional theory calculations.

I would also like to show my appreciation to Prof. Wong's research group members, Dr. Cheuk-Lam Ho, Dr. Guiping Tan, Dr. Xinli Liu, Dr. Lai-Fan Lai, Dr. Yi Zeng, Mr. Yun Ma, Miss Jing Xiang, Mr. Zhengong Meng and Miss Yujie Dong etc. I am deeply indebted to their kind help. Kind gratitude is also shown to all scientific officers of the Department of Chemistry.

Finally, I owe a special debt of gratitude to my family for their continuous support and encouragement. They supported my every decision without the least hesitation. I would like to express my sincere gratitude to my friends who encouraged me a lot. Specifically, I also would like to thank my lover who has not shown up yet. Thanks to her lateness, I apparently could pay more attention to the research work.

“I leave no trace of wings in the air, but I am glad I have had my flight”.

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