DOCTORAL THESIS

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

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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 bands 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**:$PC_{70}BM$ (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**:$PC_{60}BM$ (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.

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

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