DOCTORAL THESIS

Synthesis and characterization of novel thienoacene-based semiconductors for transistors and dye-sensitized solar cell applications

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Abstract

Organic field-effect transistors (OFET) have attracted considerable interests as a promising technology for the next-generation flexible electronics. Thioacenes have recently emerged as potential semiconducting materials for OFETs. On the other hand, Photovoltaic (PV) technology is regarded as a prospective alternative for green and renewable energy source. Recently, dye sensitized solar cells (DSSCs) have drawn intensive attention and showed great potential for practical application. Herein, the research in this thesis would include the synthesis and characterization of novel thioacene-based semiconductors for OFET and DSSC applications.

To begin with, a general review on the current status of organic semiconductors for OFET and DSSC applications was presented in Chapter 1.

In chapter 2, a series of novel benzodithieno[3,2-*b*]thiophene derivatives (**BDTT-n**) with different lateral alkyloxy groups were designed and synthesized. In addition, alkyloxy-substituted benzo[2,1-*b*:3,4-*b*’]bis-[1]benzothiophenes derivatives (**BBBT-n**) were also synthesized. The performances of OFETs based on **BDTT-n** and **BBBT-n** have been fully investigated. Among them, **BDTT-4** based OFET exhibited the highest hole mobility of 1.74 $cm^2/(Vs)$ with a current on/off ratio above 10^7 without annealing.

In chapter 3, a novel series of naphthodithiophene-based oligomers with D-A-D-A-D structure motif were designed and synthesized. All these oligomers have been fully characterized by NMR and mass spectrometry. The hole mobility properties of these oligomers were determined in OFETs as fabricated by drop-coating technique. These oligomers exhibited typical p-type semiconducting behavior. A mobility of 1.6×10^{-2} $cm^2/(Vs)$ was demonstrated by **ENBT** based OFET with a current on/off ratio in the range of 10^{5-7} after annealing at 160 °C.

Besides, in chapter 4, a novel π-bridge, namely naphthodithienothiophene was developed and employed to explore photosensitizers for DSSC application. In this work, four novel photosensitizers with D-A-π-A or D-π-A structure motif were designed and synthesized in which the carbazole or triphenylamine derivative was used as a donating group and benzothiadiazole was applied as auxiliary accepting group. The performances of DSSCs based on these photosensitizers have been fully investigated. Among them, **CB-NDTT-CA** based device exhibited the highest power conversion efficiency (PCE) of 7.29%. Meanwhile, the interfacial properties of these photosensitizers anchored on TiO_2 have also been studied by *ab*-initio simulation and Gaussian calculations.

In chapter 5, another novel series of photosensitizers with benzodithienothiophene as the π-bridge would be presented, in which different donors, auxiliary acceptors, and structures were incorporated into the frameworks

of D-π-A motif to investigate the relationship between the structure and properties. The performances of DSSCs based on these photosensitizers have been fully investigated, and **BD-5** based device exhibited the best power conversion efficiency (PCE) of 4.66%. Furthermore, it was demonstrated that molecular engineering was an efficient way to modulate the performance of the DSSCs in which benzothiadiazole was used as an effective auxiliary accepting group in constructing photosensitizers with D-A-π-A structure motif. The di-anchoring approach was also found to be a promising method to design photosensitizers with improved performance.

Key words: organic semiconductors, organic field-effect transistor, photosensitizers, DSSCs, naphdithienothiophene, benzodithienothiophen, naphdithiophene.

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