DOCTORAL THESIS

Design and synthesis of new organic dyes for highly efficient dye-sensitized solar cells (DSSCs)

Hua, Yong

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Abstract

Dye-sensitized solar cell (DSSC) has attracted increasing interest as a promising hybrid organic-inorganic solar cell. At the heart of the device is a photosensitizer, which is anchored onto a wide-bandgap semiconducting metal oxide. It harvests solar light and transfers the energy via electron transfer to a suitable material (e.g. TiO_2) to produce electricityas opposed to chemical energy in plant. The topic of this thesis focuses on the design and synthesis of metal-free organic dyes for applications in DSSCs. Specific attention has been paid to the correlation between the molecular structures and physical properties, as well as their performances in DSSCs.

Chapter 1 presents the major components and working principle of DSSC, following by a brief overview of the development of organic dyes and their application in DSSCs.

In chapter 2, we have designed two types of new phenothiazine-based dyes to investigate the positioning effect a donor group on the cell performance. The structural features of a donor aryl group at the C(7) position of phenothiazine core extend the π-conjugation of the chromophore and efficiently suppress the dye aggregation on TiO_2 film. As a result, **Type 1** dyes have better light harvesting properties in contact with TiO_2 films, and give much better photovoltaic performance than **Type 2** dyes.

Chapter 3 presents the synthesis and characterization of a series of simple phenothiazine-based dyes, in which, a linear electron-rich (4-hexyloxy)phenyl group at C(7) of the phenothiazine periphery as the donor, and an alkyl chain with

different length at N(10). The dye molecules show a linear shape which is favorable for the formation of a compact dye layer on the TiO_2 surface, while their butterfly conformations can sufficiently inhibit molecular aggregation. Moreover, the alkyl substituents with different chain length at N(10) could further optimize the performance through complete shielding the surface of TiO_2 from the I^-/I_3^- electrolyte. Under simulated AM 1.5G irradiation, the **PT-C$_6$** based DSSC produces a short-circuit photocurrent of 15.32 mAcm^{-2}, an open-circuit photovoltage of 0.78 V, a fill factor of 0.69, corresponding to a power conversion efficiency (PCE) of 8.18%. Moreover, we designed a stepwise approach for co-adsorption of the organic dye **PT-C$_6$** with a porphyrin dye (**ZnP**) for DSSCs. Upon optimization, the device made of the **PT-C$_6$** + **ZnP** system yielded J_{sc} = 19.36 mA cm^{-2}, V_{oc} =0.735 V, FF = 0.71 and η = 10.10%.

In chapter 4, we further developed five organic dyes appended with **T**, **TT**, **E**, **ET**, or **EE** (**T** and **E** denote thiophene and 3,4-ethylenedioxythiophene (EDOT), respectively) on the C(7) atom of phenothiazine core as electron donors. We have also analyzed the structure-performance corelations of dye molecules in the aspect of dye aggregation, electron injection, dye regeneration and interfacial charge recombination of electrons with electrolytes and/or oxidized dye molecules, through DFT calculation, impedance analysis and transient photovoltage studies.

In chapter 5, we extended our studies by using phenothiazine as a building block to construct 3D bulky organic dyes. We systematically investigated the influence of 3D bulky substituents on dye aggregation and charge recombination, as well as photovoltaic performance of DSSCs. The molecular design strategy demonstrates that high V_{oc} can be realized by employing 3D-phenothiazine dyes featuring a bulky substituent, such as, hexylcarbazole and dihexylfluorene units. Impressively, the co-adsorbent-free DSSCs based on dye **TP3** exhibits a photovoltaic performance with efficiency up to 8.00 %. In order to realize a panchromatic absorption and further enhance the energy conversion efficiency of DSSCs, we also designed a stepwise approach for co-adsorption of the organic dye **TP3** with a NIR dye **YR6** for co-sensitized DSSCs. Upon optimization, the device made of the **TP3** + **YR6** system yielded J_{sc} = 19.18 mA cm^{-2}, V_{oc} =0.721 V, FF = 0.712 and η = 9.84 %. The power-conversion efficiency is the highest reported efficiency for a squaraine dye-based co-sensitized panchromatic DSSCs.

From chapters 6 and 7, a series of new simple panchromatic dyes based on thiadiazolo[3,4-*c*]pyridine (**PyT**) have been designed for panchromatic DSSCs. These new organic dyes exhibit broad absorption spectrum in the range of 300~850 nm and high molar extinction coefficients. The electrochemical analyses demonstrate that the incorporation of the auxiliary electron-deficient thiadiazole[3,4-*c*]pyridine unit can fine-tune the HOMO and LUMO energy levels and red-shift the absorption spectra to NIR region. The overall conversion efficiencies of liquid-electrolyte DSSCs based on these sensitizers range from 0.46 to 6.30 %.

We draw some conclusions in chapter 8 together with the outlooks in DSSCs.

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