

DOCTORAL THESIS

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

Hua, Yong

Date of Award:
2014

[Link to publication](#)

General rights

Copyright and intellectual property rights for the publications made accessible in HKBU Scholars are retained by the authors and/or other copyright owners. In addition to the restrictions prescribed by the Copyright Ordinance of Hong Kong, all users and readers must also observe the following terms of use:

- Users may download and print one copy of any publication from HKBU Scholars for the purpose of private study or research
- Users cannot further distribute the material or use it for any profit-making activity or commercial gain
- To share publications in HKBU Scholars with others, users are welcome to freely distribute the permanent URL assigned to the publication

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. TiO₂) to produce electricity as 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 TiO₂ film. As a result, **Type 1** dyes have better light harvesting properties in contact with TiO₂ 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 TiO₂ 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 TiO₂ from the I⁻/I₃⁻ electrolyte. Under simulated AM 1.5G irradiation, the **PT-C₆** 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-C₆** with a porphyrin dye (**ZnP**) for DSSCs. Upon optimization, the device made of the **PT-C₆ + ZnP** system yielded $J_{sc} = 19.36 \text{ mA cm}^{-2}$, $V_{oc} = 0.735 \text{ V}$, $FF = 0.71$ and $\eta = 10.10\%$.

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 correlations 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 $J_{sc} = 19.18 \text{ mA cm}^{-2}$, $V_{oc} = 0.721 \text{ V}$, $FF = 0.712$ and $\eta = 9.84 \%$. 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.

Acknowledgements

First of all, I would like to express my profound gratitude and sincere thanks to my supervisor Prof. Rick Wai-Kwok Wong for his invaluable advice, inspiration and uninterrupted support throughout my studies. His guidance and encouragement are gratefully acknowledged. Moreover, I would like to give special thanks to Dr. Xunjin Zhu for his kind help, great discussing and invaluable advice throughout the research, and for his hardworking and patience when reviewing my manuscripts. A warm thank to Prof. Wai-Yeung Wong for his valuable contribution in revising manuscripts.

Great appreciation is extended to Dr. Tao Chen and his group members in the Chinese University of Hong Kong for their fruitful discussions and the fabrication of various DSSCs devices in my works. I would like to express my gratefulness to Dr. Wenjun Wu from the East China University of Science and Technology, Prof. Liyuan Han and Dr. Chunjiang Qin from the National Institute for Materials Science in Japan for their help on the fabrication of various DSSCs devices. Special thanks are given to Prof. Zhenyang Lin and his students from the Hong Kong University of Science and Technology and Prof. Jianzhang Zhao and his students of the Dalian University of Technology for molecular orbital calculations. I also gratefully thank all my research group members for their wonderful collaborations and helps. This group is really good to work and study for dye-sensitized solar cells.

Last but not least I wish to thank to my family for their endless love. My wife and my son who make me happy-thank you so much and I love you.

Table of Contents

| | |
|--|--------------|
| Declaration | i |
| Abstract | ii |
| Acknowledgements | v |
| Table of Contents | vi |
| List of Figures | xi |
| List of Tables | xvi |
| List of Schemes | xviii |
| List of Abbreviations and Symbols | xix |
| Chapter 1 Introduction | 1 |
| 1.1 Solar Light | 1 |
| 1.2 Dye-Sensitized Solar Cells | 2 |
| 1.2.1. Electron Injection | 5 |
| 1.2.2. Charge Recombination | 7 |
| 1.2.3. Dye Regeneration | 8 |
| 1.3. Key Efficiency Parameters of DSSCs | 9 |
| 1.3.1 Incident-Photo-Current Conversion Efficiency (IPCE) | 9 |
| 1.3.2. Open-Circuit Photocurrent (J_{sc}) | 10 |
| 1.3.3. Open-Circuit Photovoltage (V_{oc}) | 11 |
| 1.3.4. Fill Factor (ff) | 11 |
| 1.3.5. Solar Energy-to-Electricity Conversion Yield (η) | 12 |
| 1.4. Key Components of DSSCs | 12 |
| 1.4.1. Photo-anode | 12 |
| 1.4.2. Counter Electrode | 14 |
| 1.4.3. Electrolyte and Hole Conductors | 14 |
| 1.4.4. Sensitizers | 16 |
| 1.5. Objectives of the Thesis | 41 |
| 1.6. References | 42 |

| | |
|--|-----------|
| Chapter 2. New Phenothiazine-based Dyes for Efficient Dye-Sensitized Solar Cells: Positioning Effect of a Donor Group on the Cell Performance | 53 |
| 2.1 Introduction | 53 |
| 2.2 Results and Discussion | 56 |
| 2.2.1. Synthesis and Characterization | 56 |
| 2.2.2. UV-vis Absorption Spectra | 58 |
| 2.2.3. Electrochemical Properties | 60 |
| 2.2.4. Molecular Calculations | 62 |
| 2.2.5. Photovoltaic Properties of DSSCs | 64 |
| 2.3. Conclusions | 68 |
| 2.4. Experimental Section | 69 |
| 2.4.1. Materials and Characterization | 69 |
| 2.4.2. Photophysical and Electrochemical Characterization | 75 |
| 2.4.3. Theoretical Calculations | 76 |
| 2.4.4. Fabrication of Dye-Sensitized Solar Cells | 76 |
| 2.4.5. Characterization of Dye-Sensitized Solar Cells | 77 |
| 2.5. References | 78 |
| Chapter 3. Co-sensitization of the Simple Phenothiazine-Based Dye and a Porphyrin Dye for Efficient DSSCs | 83 |
| 3.1 Introduction | 83 |
| 3.2. Results and Discussion | 86 |
| 3.2.1. Synthesis and Characterization | 86 |
| 3.2.2. UV-Vis Absorption Properties. | 87 |
| 3.2.3. Electrochemical Properties | 89 |
| 3.2.4. Theoretical Calculation | 91 |
| 3.2.5. Photovoltaic Performance | 93 |

| | |
|---|-----|
| 3.2.6. Photophysical, Photocurrent–Voltage Characteristics of Cosensitized DSSCs | 99 |
| 3.3. Conclusions | 103 |
| 3.4. Experimental Section | 104 |
| 3.4.1. Materials and Characterization | 104 |
| 3.4.2. Fabrication and Characterization of Cells | 118 |
| 3.4.3. Theoretical Calculation | 119 |
| 3.5. References | 120 |
| Chapter 4 Molecular Engineering of Simple Phenothiazine-based Dyes to Modulate Dye Aggregation, Charge Recombination and Dye Regeneration in Highly Efficient Dye-Sensitized Solar Cells | 124 |
| 4.1. Introduction | 124 |
| 4.2. Results and Discussion | 127 |
| 4.2.1. Synthesis and Characterization | 127 |
| 4.2.2. Spectroscopic Studies | 128 |
| 4.2.3. Electrochemical Properties. | 131 |
| 4.2.4. Theoretical Studies | 134 |
| 4.2.5. Photovoltaic Performance | 136 |
| 4.2.6. Electrochemical Impedance Spectroscopy | 139 |
| 4.2.7. Transient Photovoltage Measurement | 142 |
| 4.3. Conclusions | 144 |
| 4.4. Experimental Section | 145 |
| 4.5. References | 158 |
| Chapter 5 Simple 3D Bulky Organic Phenothiazine Dyes for Highly Efficient Cosensitized Solar cells | 161 |
| 5.1. Introduction | 161 |
| 5.2. Results and Discussion | 164 |
| 5.2.1. Synthesis and Characterization | 164 |
| 5.2.2. UV-Vis Absorption Properties | 165 |

| | |
|---|-----|
| 5.2.3. Electrochemical Properties. | 167 |
| 5.2.4. Theoretical Calculation | 170 |
| 5.2.5. Photovoltaic Performance | 172 |
| 5.2.6. Electrochemical Impedance Spectroscopy (EIS) | 175 |
| 5.2.7. Photophysical, Photocurrent–Voltage Characteristics of Cosensitized DSSCs | 177 |
| 5.3. Conclusions | 181 |
| 5.4. Experimental Section | 182 |
| 5.5. References | 196 |
| Chapter 6 New Simple Panchromatic Dyes based on Thiadiazole[3,4-c]pyridine for Dye-Sensitized Solar Cells Applications | 201 |
| 6.1. Introduction | 201 |
| 6.2. Results and Discussion | 204 |
| 6.2.1. Synthesis and Characterization | 204 |
| 6.2.2. Photophysical Properties | 205 |
| 6.2.3. Electrochemical Properties | 207 |
| 6.2.4. Molecular Calculations | 209 |
| 6.2.5. Photovoltaic properties of DSSCs | 210 |
| 6.2.6. Electrochemical Impedance Spectroscopy Analysis | 213 |
| 6.3. Conclusions | 214 |
| 6.4. Experimental Section | 215 |
| 6.5. References | 222 |
| Chapter 7 Structure-Function Relationships in Thiadiazole[3,4-c]pyridine-Based Organic Dyes for Dye-Sensitized Solar Cells | 225 |
| 7.1. Introduction | 225 |
| 7.2.1. Photophysical Properties | 228 |
| 7.2.2. Electrochemical Properties | 231 |
| 7.2.3. Molecular Calculations | 233 |

| | |
|--|-----|
| 7.2.4. Photovoltaic Properties of DSSCs | 235 |
| 7.2.5. Electrochemical Impedance Spectroscopy Analysis | 238 |
| 7.3. Conclusions | 240 |
| 7.4. Experimental Section | 241 |
| 7.5. References | 260 |
| Chapter 8 General Conclusions and Outlook | 264 |
| Curriculum Vitae | 268 |
| List of Publications | 269 |