

DOCTORAL THESIS

Metallated and metal-free molecular dyes for dye-sensitized solar cells

Siu, Chi Ho

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

The molecular design, synthesis and spectroscopic characterization of a series of ruthenium(II), metal-free and platinum(II) photosensitizers were discussed. The applications of some of these compounds in dye-sensitized solar were also outlined.

To start with, a brief overview on the background of dye-sensitized solar cells (DSSCs) was presented in Chapter 1.

In Chapter 2, a series of new thiocyanate-free ruthenium(II) cyclometalated complexes with different ligands were successfully synthesized and some of them were fully characterized by spectroscopic and computational methods. The nature of cyclometalating ligands effectively tunes the properties of the metal complexes and the resulting DSSC performance.

In Chapter 3, new di-anchoring organic dyes have been synthesized and characterized. This molecular design strategy can significantly enhance the η value because this successfully inhibits the undesirable charge combination and prolongs the electron lifetime. The discoveries open up a new avenue to the evolution of organic sensitizers and the optimization of bridged di-anchoring dyes for highly efficient co-adsorbent-free DSSCs.

In Chapter 4, a series of new thiophene-free platinum sensitizers for the application

of DSSCs was developed. Four unsymmetrical platinum(II) di-acetylide complexes containing phenothiazine moiety with different donor units were designed and synthesized. These photosensitizers were fully characterized by spectroscopic as well as computational studies and also successfully employed in DSSC fabrication. These findings provided positive evidence that platinum-acetylide complexes have a great potential and prospect for the use as promising metal-based photosensitizers in DSSC applications.

Finally, Chapters 5 and 6 present the concluding remarks and the experimental details of the work described in Chapters 2–4.

Acknowledgements

I would like to express my profound gratitude and sincere thanks to my supervisor Prof. Raymond W. Y. Wong for his invaluable advice, encouragement and uninterrupted support throughout my study. His precious comments and opinion in the preparation of this thesis at the time he was very busy are gratefully acknowledged. His erudite advices always open up new horizons for me and his devoted attitude in research has influenced me a lot and made my study a truly rewarding experience.

Wordless thanks go to Mr. L. T. L. Lee and Prof. T. Chen (Department of Physics, The Chinese University of Hong Kong) for the fabrication and testing of DSSCs; Prof. J. Zhao (State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian) for the density functional theory calculations.

Special thanks are given to Prof. T. Chen (Department of Physics, The Chinese University of Hong Kong) for giving me a chance to explore the fabrication of DSSCs.

I would like to show my kind gratitude to our research group members especially Dr. C. L. Ho. for their genuine care, guidance, support and encouragement. I am indebted to all clerical and scientific officers of the Department of Chemistry.

I would like to acknowledge the financial support from Hong Kong Research Grants Council (HKBU203011).

Last but not least, I would like to thank my parents and my love Joyi Ho for their continuous support during my PhD study and encouragement throughout my life.

Table of Contents

DECLARATION		i
Abstract		ii
Acknowledgements		iv
Table of Contents		vi
List of Tables		xiv
List of Figures		xvii
List of Schemes		xxiii
List of Abbreviations and Symbols		xxv
Formula Index		xxviii
Chapter 1	Introduction	1
1.1	Dye-Sensitized Solar Cells (DSSCs)	1
1.1.1	Background	1
1.1.2	Operating Principles of the DSSCs	3
	1.1.2.1 Steps 1 and 2: Electron Injection and Decay of Excited State	5
	1.1.2.2 Step 3: Regeneration of the Excited/Oxidized Dyes	6

1.1.2.3	Transportation of Electron through the Semiconducting Oxide Film	6
1.1.2.4	Steps 5 and 6: Recombination of Electrons in the Semiconductor with Oxidized Dyes or Redox Species in Electrolyte	7
1.1.2.5	Step 7: Reduction of Oxidizing Agent in an Electrolyte at the Counter Electrode	7
1.1.3	Structure of DSSCs	8
1.1.3.1	Photoanode	8
1.1.3.2	Electrolyte	10
1.1.3.3	Counter Electrode	11
1.1.3.4	Photosensitizers (Dyes)	12
1.1.3.4.1	Standard Ruthenium(II) Dyes	13
1.1.3.4.2	Recent Efficiency Advances Using New Heteroleptic Ruthenium Complexes	14
1.1.3.4.3	New Paradigm, Thiocyanate-free Cyclo-metalated Ruthenium Complexes	16
1.1.3.4.4	Organic Photosensitizers with One Anchoring Group	18

1.1.3.4.5	Bridged-Dianchoring Organic Photosensitizers	20
1.1.4	Efficiency Measurements	22
1.1.4.1	Measurement of Overall Conversion Efficiency	22
1.1.4.2	Measurement of IPCE	23
1.2	Scope of the Thesis	24
	References	25
Chapter 2	Thiocyanate-free Ruthenium(II) Complexes for Dye-Sensitized Solar Cells	31
2.1	Synthesis and Characterization of Pyridine-Based Thiocyanate-Free Ruthenium(II) Dye Photosensitizers	31
2.1.1	Introduction	31
2.1.2	Synthesis and Characterization	35
2.1.3	Results and Discussion	42
2.1.3.1	Photophysical Properties	42
2.1.3.2	Electrochemical Properties	45
2.1.3.3	Computational Studies	47
2.1.4	Applications in DSSCs	49

2.1.4.1	Preparation of DSSC Devices	49
2.1.4.2	Photovoltaic Performance of DSSCs	51
2.2	Synthesis and Characterization of Thiazole-Based Thiocyanate-Free Ruthenium(II) Dye Sensitizers	55
2.2.1	Introduction	55
2.2.2	Synthesis and Characterization	57
2.2.3	Results and Discussion	64
2.2.3.1	Photophysical Properties	64
2.2.3.2	Electrochemical Properties	66
2.2.3.3	Computational Studies	67
2.2.3.5	Thermal Properties	70
2.2.4	Applications in DSSCs	71
2.2.4.1	Preparation of DSSC Devices	71
2.2.4.2	Photovoltaic Performance of DSSCs	72
2.3	Concluding Remarks	76
	References	78
Chapter 3	Bridged Organic Dyes with Di-anchoring Groups for Efficient Dye-sensitized Solar Cells	84

3.1	Fluorene-Bridged Organic Dyes with Di-anchoring Groups for Efficient Co-Adsorbent-Free Dye-Sensitized Solar Cells	84
3.1.1	Introduction	84
3.1.2	Synthesis and Characterization	87
3.1.3	Results and Discussion	90
	3.1.3.1 Photophysical Properties	91
	3.1.3.3 Electrochemical Properties	93
	3.1.3.4 Computational Studies	94
3.1.4	Applications in DSSCs	108
	3.1.4.1 Preparation of DSSC Devices	108
	3.1.4.2 Photovoltaic Performance of DSSCs	110
3.2	Diacetylide-Bridged Di-anchoring Phenothiazine-based Organic Dyes for Highly Efficient Dye-sensitized Solar Cells	119
3.2.1	Introduction	119
3.2.2	Synthesis and Characterization	122
3.2.3	Results and Discussion	127
	3.2.3.1 Photophysical Properties	127

	3.2.3.3 Electrochemical Properties	129
	3.2.3.4 Computational Studies	131
	3.2.4 Applications in DSSCs	132
	3.2.4.1 Preparation of DSSC Devices	132
	3.2.4.2 Photovoltaic Performance of DSSCs	134
3.3	Concluding Remarks	142
	References	144
Chapter 4	Phenothiazine-based Platinum(II)-Acetylide Sensitizers for Efficient Dye-sensitized Solar Cells	149
4.1	Introduction	149
4.2	Synthesis and Characterization	153
4.3	Results and Discussion	156
	4.3.1 Photophysical Properties	156
	4.3.2 Electrochemical Properties	160
	4.3.3 Computational Studies	161
4.4	Applications in DSSCs	169
	4.4.1 Preparation of DSSC Devices	169
	4.4.2 Photovoltaic Performance of DSSCs	171

4.5	Concluding Remarks	177
	References	178
Chapter 5	Concluding Remarks and Future Work	186
Chapter 6	Experimental Details	193
6.1	General	193
6.2	Materials	194
6.3	Experimental Details for Chapter 2	195
6.3.1	Experimental Details for Ligands L1–L22	195
6.3.2	Experimental Details for D1–D22	214
6.4	Experimental Details for Chapter 3	225
6.4.1	Experimental Details for Aldehyde Precursors L23–L26 in Chapter 3.1	225
6.4.2	Experimental Details for Aldehyde Precursors L27–L33 in Chapter 3.2	234
6.4.3	Experimental Details for Dyes D23–D33	239
6.5	Experimental Details for Chapter 4	244
6.5.1	Experimental Details for Aldehyde Precursors L34–L37	244

6.5.2 Experimental Details for Dyes D34–D37	248
References	251
CURRICULUM VITAE	254