

## DOCTORAL THESIS

### Porphyrin-based materials for organic solar cells

Wang, Hongda

*Date of Award:*  
2015

[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

A series of novel porphyrin materials with push-pull framework were designed and synthesized for organic solar cells (OSCs). To start with, a brief overview on the background of OSC, including dye-sensitized solar cells (DSSCs) and bulk heterojunction (BHJ) solar cells, and the porphyrin based materials for OSC applications was presented in Chapter 1.

In Chapter 2, an efficient panchromatic light harvesting was demonstrated by the co-adsorption of a porphyrin molecule HD18 or HD19 and N719 in dye-sensitized solar cells. It is apparent that the porphyrin sensitizers show strong absorption in the Soret (400–500 nm) and Q bands (600–700 nm), while N719 shows efficient spectral response in the 500–600 nm (between the Soret and Q bands), and the combination of these two kinds of dye molecules might display strong spectral response in the full-colour region. Mechanistic investigations were carried out by various spectral and electrochemical characterizations. The best co-sensitized device based on HD18 + N719 shows considerably enhanced power conversion efficiency of 8.27%, while those individually sensitized by HD18 and N719 display efficiencies of 6.74% and 6.90%, respectively. Subsequently, an optimized co-sensitized device based on the porphyrin HD18 and organic dye PT-C6 was fabricated by a stepwise adsorption of HD18 and PT-C6. The best performance of  $J_{SC}/\text{mA cm}^{-2} = 19.61$ ,  $V_{OC}/\text{V} = 0.74$ ,  $FF = 0.69$  and  $\eta = 10.1\%$ , is superior to that of the individual device

made from either HD18 ( $\eta = 7.4\%$ ) or PT-C6 ( $\eta = 8.2\%$ ) under the same conditions of fabrication. The post-adsorption of PT-C6 on the porphyrin-sensitized TiO<sub>2</sub> anode surface not only enhances the spectral response of solar cells, but also greatly retards the back reaction between conduction-band electrons in TiO<sub>2</sub> and the oxidized species (I<sub>3</sub><sup>-</sup>) in the electrolyte.

In Chapter 3, a series of new donor- $\pi$ -acceptor (D- $\pi$ -A) porphyrin sensitizers with extended  $\pi$ -conjugation units were designed and synthesized for DSSC applications. Appending a phenothiazine (PTZ) donor moiety to the well-investigated porphyrin core and a variety of acceptors with electron deficient property at the opposite side can significantly red shift the absorption spectra to 700 nm in dyes (2-4). These different acceptor groups exert a significant influence on the electrochemical and photovoltaic properties of these sensitizers. These dyes have been evaluated in dye-sensitized solar cells, showing efficiencies of 0.90~7.29% with I<sup>-</sup>/I<sub>3</sub><sup>-</sup> based electrolytes. A detailed investigation on their physical, photophysical and electrochemical properties provided some important information on the factors affecting the main photovoltaic parameters.

In Chapter 4, we designed and synthesized another series of dyes based on the rigid 2-aryl-1*H*-imidazo[4,5-*b*]porphyrin donors, in which an electron-accepting group was incorporated at the position 2 of imidazo unit via an aromatic spacer. Their photophysical and electrochemical properties, theoretical calculations and dye-sensitized solar cell performances have been investigated. The

spectroelectrochemical data suggests the 1*H* imidazo unit can extend the conjugation length and lower the optical gap. As expected, the  $\pi$  conjugated substituents in all these dyes produced panchromatic absorption spectra over a wide range of wavelengths and IPCE spectra featuring a broad plateau in the region 430–650 nm. In addition, both DFT computational and electrochemical data indicate a smaller HOMO–LUMO energy gap for HD31Zn than that for dye **1**, suggesting that a slightly more facile conjugation between the porphyrin core and the diketopyrrolopyrrole (DPP) unit through the 1*H* imidazo unit in HD31. Both Dye **1** and HD31Zn exhibited strong solvation effect in different solvents. The effects of solvents and their structures on the photophysical and photochemical properties and device performance have been studied in detail. The results indicate that porphyrin fused heterocycle as an effective electron donor and a suitable spacer between the donor and the acceptor can reduce the molecular aggregation through solvation effects.

In Chapter 5, a series of conjugated D– $\pi$ –A small molecules (YJ1–YJ6, YJ13–YJ15 and YJ16–YJ19) for bulk heterojunction solar cells (BHJSCs) were prepared by the Sonogashira cross coupling of the electron rich porphyrin units with electron deficient benzothiadiazole (BT), DPP, or 3-ethylrhodanine moieties. The peripheral side chains on the porphyrin units like alkoxy phenyl, alkyl, and (triisopropylsilyl)ethynyl (TIPS) can alter the solubility, conformation, and electronic properties of the obtained D– $\pi$ –A small molecules, allowing the tuning of their photovoltaic properties when

blended with fullerene derivatives. The presence of these side chains groups on porphyrin donor units affects the torsion angles between the side chains and the conjugated main chain, but resulting in only slightly different energy levels for the highest occupied molecular orbital (HOMO) for these molecules. Their performance in solution-processed solar cells is under studying.

In Chapter 6, we reported the synthesis, electrochemical properties, and optical properties of seven novel BODIPY based  $\pi$ -conjugated materials. These dyes were synthesized via the Stille coupling reactions between the BODIPY units and electron donating groups (EDGs), such as 4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (BDT), 9,9-dioctyl-9*H*-fluorene (FL) or thieno[3,2-b]thiophene (TH). These donors were rationally chosen based on their gas phase ionization potential (IP) values estimated by density functional theory (DFT) calculations. Cyclic voltammetry of these dyes in dichloromethane solutions reveals that HOMOs of the resulting dyes correlated well with the ionization potentials (donor strength) of the donors. On the contrary, the lowest unoccupied molecular orbital (LUMO) energy levels of all dyes are fairly invariant, independent of the donors used. This suggests that the BODIPY moiety provides the primary influence on the LUMO levels of the materials. Two series of YJ9–YJ11 and YJ21–YJ23 show strong visible absorption in the red region. In addition, we presented the first example of a donor-acceptor BODIPY-containing conjugated copolymers, HDP6 and HDP7, with absorption over

the entire spectrum of visible light and part of near infrared region (300–900nm) making them suitable as additive for light-harvesting antenna. These dyes provide us with a toolset to tune the frontier molecular orbital energy levels, while retaining the low band gap and broad absorption of these dyes. Overall, these BODIPY molecules exhibited appropriate lower lying LUMO levels ( $-3.70 \sim -3.86$  eV) when compared with that of the P3HT, indicating their potential as acceptors for many donor materials in BHJSCs.

## List of Contents

<b>Declaration</b>		i
<b>Abstract</b>		ii
<b>Acknowledgements</b>		vii
<b>List of Contents</b>		viii
<b>List of Schemes</b>		xiii
<b>List of Tables</b>		xiv
<b>List of Figures</b>		xv
<b>Abbreviations and Symbols</b>		xxii
<b>Chapter 1</b>	<b>Introduction</b>	<b>1</b>
1.1	Background	1
1.2	Porphyrins as sensitizers in DSSCs	2
1.2.1	DSSCs	2
1.2.2	The advantages and performances of porphyrin-based dyes	4
1.2.2.1	Linkers at $\beta$ -positions	4
1.2.2.2	Linkers at <i>meso</i> -positions	6
1.2.2.3	Porphyrins with extended spectral feature	8
1.2.2.4	Enveloping porphyrin	15
1.3	Porphyrin-based material for organic photovoltaics	21
1.3.1	Soluble porphyrin donor materials for small molecule BHJ solar cells	22

1.3.2	Soluble BODIPY donor materials for small molecule BHJ solar cells	34
1.4	References	38
<b>Chapter 2</b>	<b>Molecular engineering of co-sensitizers for efficient panchromatic dye-sensitized solar cells</b>	<b>45</b>
2.1	Introduction	45
2.2	Panchromatic light harvesting by N719 with zinc porphyrin molecules	47
2.2.1	Molecular design and synthesis	47
2.2.2	Optical and electrochemical properties	47
2.2.3	DFT calculations	49
2.2.4	Photovoltaic performance	50
2.3	Conformational engineering of co-sensitizers to retard back charge transfer	57
2.3.1	Molecular design	57
2.3.2	Optical properties and photovoltaic performance	57
2.4	Conclusion	65
2.5	Experimental Section	66
2.6	References	70
<b>Chapter 3</b>	<b>Structural engineering of new porphyrin sensitizers with various acceptors for dye-sensitized solar cell applications</b>	<b>73</b>
3.1	Introduction	73
3.2	Results and discussion	76
3.2.1	Molecular design and synthesis	76



3.2.2	UV–visible absorption and fluorescence spectra	77
3.2.3	Electrochemical properties	78
3.2.4	DFT calculations	81
3.2.5	Photovoltaic properties	83
3.2.6	Electrochemical impedance spectroscopy	84
3.3	Conclusion	85
3.4	Experimental section	90
3.5	References	93
<b>Chapter 4</b>	<b>Suppression of dye aggregation for novel zinc imidazo[4, 5-b]porphyrin-based sensitizers via solvation effects</b>	<b>97</b>
4.1	Introduction	97
4.2	Synthesis and characterization of novel zinc Imidazo[4, 5-b]porphyrin-based organic dyes for dye-sensitized solar cells	99
4.2.1	Design and synthesis	99
4.2.2	Optical properties	100
4.2.3	Electrochemical properties and DFT calculation	103
4.2.4	Photovoltaic performance	105
4.2.5	Electrochemical impedance spectroscopy	106
4.3	Synthesis and characterization of imidazo[4,5-b]porphyrin-based sensitizers (HD31, HD31Zn and HD32) for DSSC applications	107
4.3.1	Design and synthesis	107
4.3.2	Optical properties	109

4.3.3	Electrochemical properties	110
4.3.4	Photovoltaic performance	112
4.4	Conclusion	115
4.5	Experimental section	116
4.6	References	124
<b>Chapter 5</b>	<b>Soluble porphyrin donors for small molecule bulk heterojunction solar cells</b>	129
5.1	Introduction	129
5.2	Synthesis and characterization of $\pi$ -extended porphyrin derivatives	131
5.2.1	Design and synthesis	131
5.2.2	Optical and electrochemical properties	134
5.2.3	Conclusions	136
5.3	Comparable studies of porphyrin-based small molecules with <i>meso</i> -aryl or alkyl substituents for OSCs	137
5.3.1	Molecular design	137
5.3.2	Synthesis and characterization	138
5.3.3	Optical and electrochemical properties	139
5.3.4	Conclusion	142
5.4	Porphyrin-based panchromatic A–D–A type small molecules for OSCs	142
5.4.1	Molecular design	143
5.4.2	Synthesis and characterization	144
5.4.3	Optical and electrochemical properties	145

5.4.4	Conclusion	147
5.5	Comparable studies of porphyrin-based small molecules with bulky solubilizing (triisopropylsilyl)ethynyl (TIPS)-substituted porphyrin	148
5.5.1	Molecular design	148
5.5.2	Optical properties	149
5.5.3	Electrochemical properties	150
5.5.4	Conclusion	153
5.6	Experimental section	153
5.7	Reference	179
<b>Chapter 6</b>	<b>New dipyrromethene-based materials for applications in organic photovoltaic devices</b>	<b>183</b>
6.1	Introduction	183
6.2	Results and discussion	185
6.2.1	Synthesis and characterization	185
6.2.2	Optical properties	190
6.2.3	Electrochemical properties	192
6.3	Conclusion	196
6.4	Experimental section	196
6.5	Reference	204
	<b>Appendices</b>	<b>207</b>
	<b>CURRICULUM VITAE</b>	<b>233</b>