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DOCTORAL THESIS

Visible and near-infrared absorbing porphyrin-dimer based acceptor-donor-acceptor small molecules for organic solar cell applications

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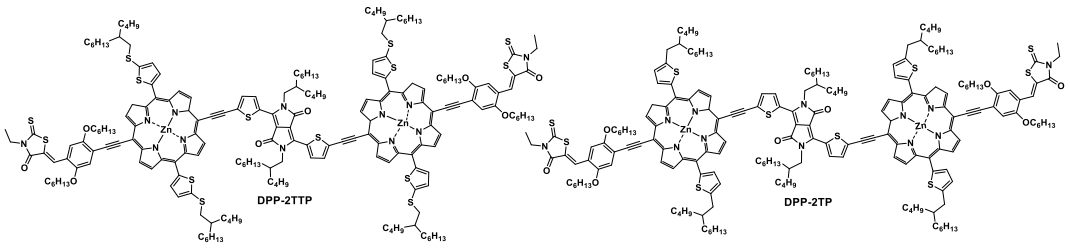
Abstract

Bulk heterojunction organic solar cells (BHJ OSCs) have been fascinated in recent years for the future green energy generation due to their most promising results of low-cost fabrication, great flexibility, and lightweight properties. Very recently small molecule donors in the BHJ active layers have shown prominent attention due to the synergistic advantages over the polymer counterparts, which possess easy purification, highly facile synthesis, and negligible batch-batch variations. To construct push-pull molecules for p-type semiconductors, acceptor-donor-acceptor (A-D-A) based backbone exalted so far. In addition, the most impressive small molecule electron-donor units (D) are like benzodithiophene (BDT), oligothiophene, 3-dithienosilole (DTS), and indacenedithiophene (IDT) and so on. Likewise, electron-acceptors (A), such as 3-alkylrhodanine, diketopyrrolopyrrole (DPP), and perylenediimide (PDI) have been utilized. Porphyrin derivatives show excellent photochemical and electrochemical properties. Interestingly, porphyrins can be easily modified by different substituents at the peripheral positions (meso- and β-) and metal insertions at the center of the porphyrin core. In this work, we design, synthesize and characterize visible-near infrared absorbing new porphyrin dimer based small molecules with acceptor-donor-acceptor (A-D-A) configuration for bulk heterojunction organic solar cells, and investigate their structure-property relationships, specifically the effect of conjugation and planarity of the backbone central units on the charge mobility, film morphology,

and solar cell performances.

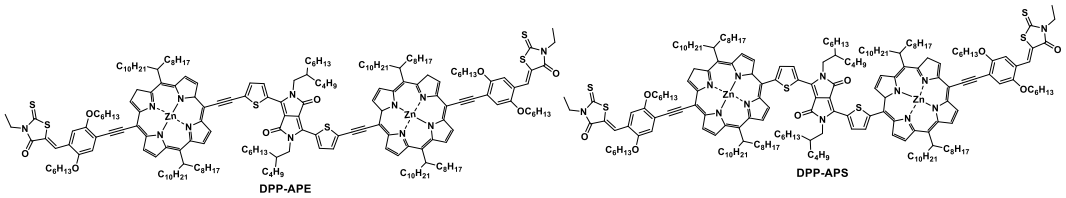
Chapter 1 deals with an overview of the past and recent development of BHJ OSCs, particularly the key principles and photovoltaic characteristics. Furthermore, we focus on the detailed classification of porphyrin-based small molecules and their performances in OSCs.

In chapter 2, two promising near-IR absorbing porphyrin-based dimeric small molecules were designed and synthesized, in which diketopyrrolopyrrole-ethynylene-bridged porphyrin dimers are capped with electron-deficient 3-ethylrhodanine (A_2) *via* a π-bridge of phenylene ethynylene, with an optimal A_2-π-D-A_1-D-π-A_2 architecture affording porphyrin dimers **DPP-2TTP** and **DPP-2TP**. They possess strong absorption in ranges of 400–550 (Soret bands) and 700–900 nm (Q bands). Their intrinsic absorption deficiency between the Soret and Q bands could be perfectly compensated by a wide bandgap small molecule DR3TBDTTF with absorption in 500–700 nm. Impressively, the optimal ternary device based on the blend films of **DPP-2TPP**, DR3TBDTTF (20 wt.%) and $PC_{71}BM$, shows a PCE of 11.15%, while the binary devices based on **DPP-2TTP**/$PC_{71}BM$ and **DPP-2TP**/$PC_{71}BM$ blend films exhibit PCEs of 9.30% and 8.23%, respectively. The high compatibility of the low bandgap porphyrin dimers with the wide bandgap small molecule provides a new threesome with $PC_{71}BM$ for highly efficient panchromatic ternary organic solar cells.



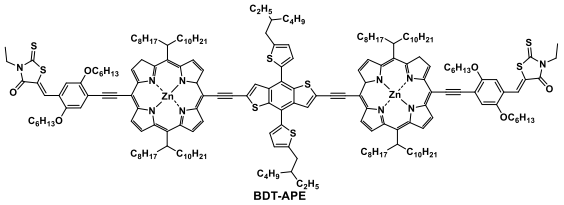
Chapter 3 describes another two new A-π-D-π-A structural porphyrin small molecules denoted as **TDPP-2P** and **TDPPE-2P** which are constructed from dimeric porphyrin linked by 2,5-bis(2-butyloctyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dion e (TDPP), and 2,5-bis(2-butyloctyl)-3,6-bis(5-ethynyl-2-thienyl)-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione (TDPPE), respectively, further π-extended symmetrically with electron-deficient 4-[(3-ethyl-4-oxo-2-thioxo-5-thiazolidinylidene)methyl]-phenylethynyl fragments. Compared to the absorption spectra of **TDPP-2P**, astonishingly **TDPPE-2P** improves the range of near-infrared over 1000 nm due to the enhanced coplanarity of the central core. Moreover, the intrinsic absorption deficiency (500-700 nm) is perfectly compensated by IT-M small molecule acceptor. Remarkably the blend film **TDPPE-2P**:IT-M accomplished panchromatic photo-current absorption from 400-900 nm, as a result, the device exhibits a prominent PCE of 5.69%. Whereas, the film **TDPP-2P**:IT-M shows comparatively low PCE of 4.12%. Finally, we believe that such a combination of **TDPPE-2P**:IT-M device demonstrates synergetic compatibility of donor/acceptor domain to promote the complementary absorption spectrum and enhances through higher hole mobilities and better crystallinity of the surface and interface for non-fullerene small-molecule organic

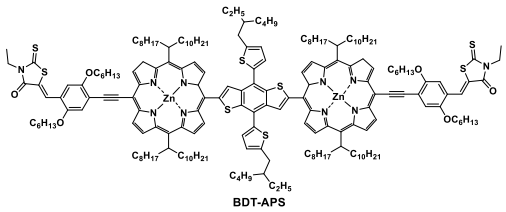
solar cells.



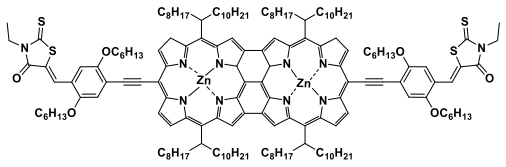
In Chapter 4, we further modified and synthesized a new series of A^*-π-D_2-D_1-D_2-π-A^* based porphyrin dimer (2P) (D_2) small molecules flanked by 4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-2,6-diethynylbenzo[1,2-b:4,5-b']dithiophen e (TBDTE) and 4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (TBDT) as **TBDTE-2P** and **TBDT-2P** respectively, in which benzodithiophene (BDT) (D_1) based analog was constructed as a central unit because of extended coplanarity conjugation length. Finally, TBDTE and TBDT units end-capped with 3-ethylrhodanine (A^*) *via* a π-bridge of phenyl ethynyl linker and 2-octyldodecan-1-al long alkyl chain was used on vertical meso-porphyrins to improve the material solubility for the solution-processed OSCs. The compound **TBDTE-2P** accomplishes absorption range from 400-800 nm in the vis-near-infrared region, whereas **TBDT-2P** compound absorbs 400-700 nm range. The higher absorption range of **TBDTE-2P** arises from more planar backbone orientation and strong intramolecular charge transfer (ICT) within the donor molecules. Further, we focus on the OPV performances of binary devices **TBDTE-2P** / **TBDT-2P**: IDIC under AM 1.5G 1-Sun and 300 lux LED illuminations. The champion device **TBDTE-2P**: IDIC was accumulated a PCE of

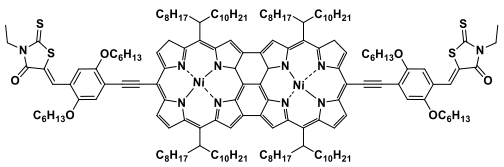
7.46% under 1-Sun whereas a PCE of 12.34% was obtained under indoor light illuminations. The exploit of superior properties, charge generation and collection, hole and electron mobilities, and atomic force microscopy (AFM) were also examined.





In Chapter 5, we synergistically designed and synthesized two new porphyrin dimer triply fused at *meso–meso*, *β-β* and *β′-β′* positions, from the corresponding *meso–meso* singly-linked porphyrin arrays. These fused porphyrin tapes differ by two metal atoms at the porphyrin core, such as zinc and nickel, termed as **F-C19ZnP** and **F-C19NiP**, respectively. With the purpose for design new acceptor-donor-acceptor small molecules for OSCs, the two fused porphyrin tapes were investigated in detail on the photophysical and electrochemical properties. Both fused porphyrins exhibit a strong and wide Soret-band absorption from 400-570 nm. Interestingly, the compound **F-C19ZnP** is recorded a larger red-shift absorption than the compound **F-C19NiP** consistent with cyclic voltammetry (CV) measurements, because the Zn-porphyrin attains more planar conjugated geometry.





Finally, the dissertation was completed with a summary in chapter 6.

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