

DOCTORAL THESIS

Design, synthesis and characterization of A-D-A structural porphyrin small molecules for bulk heterojunction organic solar cell applications

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Abstract

Bulk heterojunction organic solar cells (BHJ OSCs) have been recognized as one of the most promising next generation green technology alternatives to inorganic solar cells because of the low-cost, lightweight, flexibility. Specifically, the use of small molecules instead of polymers as donors in BHJ OSC have been developed very fast recently because small molecules can be facilely synthesized and easily purified, and have a determined molecular structure without batch-to-batch variations. To date, those among the most efficient small molecules were constructed as acceptor-donor-acceptor (A-D-A) structural configuration from electron-rich units such as benzodithiophene (BDT), dithienosilole (DTS), oligothiophene units, and electron-deficient units such as benzothiadiazole (BT), diketopyrrolopyrrole (DPP), isoindigo (IID) and perylenediimide (PDI). Surprisingly, porphyrins were rarely studied either in polymers or π -conjugated small molecules as donor materials, though they have unique chemistry together with excellent photochemical and electrochemical properties, such as facile functionalization of the periphery and the variation of the central atom (metal ions), strong UV-visible absorption, ultrafast photoinduced charge separation in porphyrin-fullerene systems. In this research work, we design, synthesize and characterize new porphyrin-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 peripheral and backbone alkyl side-chains, π -conjugated linkers as well as electron-deficient ending units on the charge mobility, film morphology and solar cell performances.

In Chapter 1, a general review on the historic and recent development of BHJ OSCs was given first, including the major components and working principle of

OSC, the versatile organic semiconductors and their performances in OSCs.

In chapter 2, six A-D-A structural porphyrin small molecules were designed and synthesized, in which different peripheral alkyl substitutions are attached to the *meso*-position of porphyrin core (**CS-I**, **CS-II**, **CS-III**, **CS-4**, **CS-5** and **CS-6**), and 3-ethylrhodanine is used as terminal group. Their UV-visible absorption in solid, energy level, blend film morphology, charge mobility and cell performance are dependent on the different peripheral substitutions. The active layer consists of these six small molecules as donor materials and PC₇₁BM as the acceptor material with an optimized film thickness. Although all six molecules show similar optical spectrum in solutions, the introduction of linear alkyl side chains can promote thin-film nanostructural order, especially shown to shorten π - π stacking distances between backbones and increase the correlation lengths of both π - π stacking and lamellar spacing, leading to higher efficiency in this serial. Among them, the highest power conversion efficiency of 9.09% has been achieved by **CS-4** based devices.

In chapter 3, another two new A-D-A porphyrin small molecules (**PTTR** and **PTTCNR**) have been developed, which are similar in structure to **CS-I**, **II** and **III**, except that the linker is phenylethynyl in **CS-I**, **II** and **III**, whereas it is terthiophenylethynyl in **PTTR** and **PTTCNR**. The highest power conversion efficiency of 8.21% is achieved by **PTTCNR**, corresponding to a J_{SC} of 14.30 mA cm⁻², V_{OC} of 0.82 V, and FF of 70.01%. The excellent device performances can be ascribed to the conjugated structure of porphyrin with 3,3"-dihexyl-terthiophene and the aliphatic 2-octylundecyl peripheral substitutions, which not only effectively increase the solar flux coverage between the conventional Soret and Q bands of porphyrin unit, but also optimize molecular packing through

polymorphism associated with side-chain and the π -conjugated backbones, and form the blend films with [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) characteristics of bi-continuous, interpenetrating networks required for efficient charge separation and transportation.

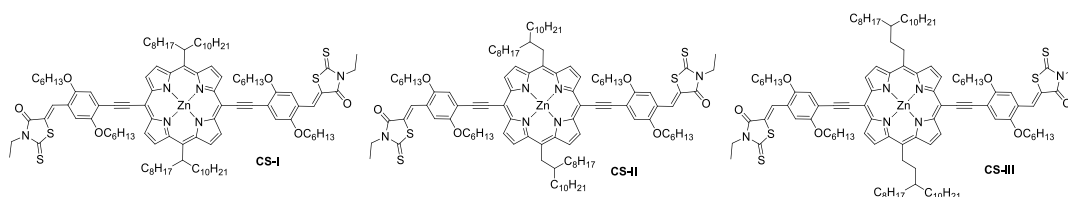
In chapter 4, we designed and synthesized a new dimeric porphyrin donor molecule (**CS-DP**) containing A- π_2 -D- π_1 -D- π_2 -A architecture by coupling of two zinc porphyrin cores through ethynyl linker. Interestingly, it can harvests the photons up to deep near-infrared (NIR) region in the absorption spectrum. From the past decades, it has been found that developing donor molecules with the absorption spectral in NIR region is a challenging key factor to get the high performance BHJ OSCs. Solar cell devices employing **CS-DP** as a donor exhibit a highest power conversion efficiency of 8.23%, corresponding to $J_{SC} = 15.14 \text{ mA cm}^{-2}$, $V_{OC} = 0.781 \text{ mV}$ and $FF = 69.8\%$ under AM 1.5G solar radiation. The high efficiency of this molecule is attributed to a panchromatic IPCE action spectrum from 300 nm to 1000 nm. Also, this performance is best for the reported deep NIR organic solar cells based on single small molecule and PC₇₁BM system so far. We envision that this new small bandgap dimeric porphyrin is very promising to use in ternary and multi-junction applications as well as NIR photodetectors.

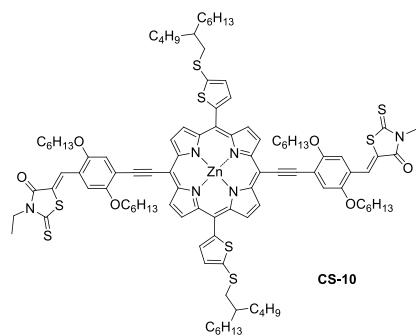
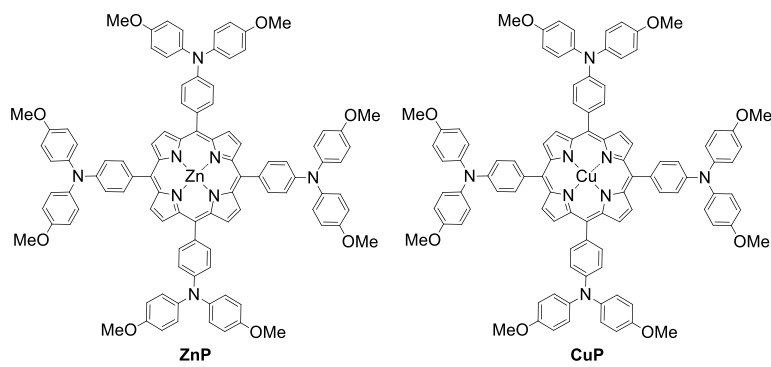
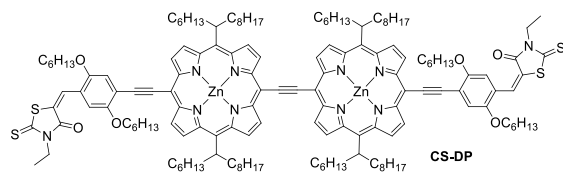
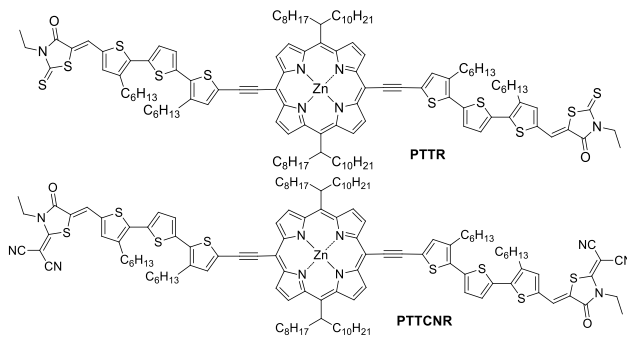
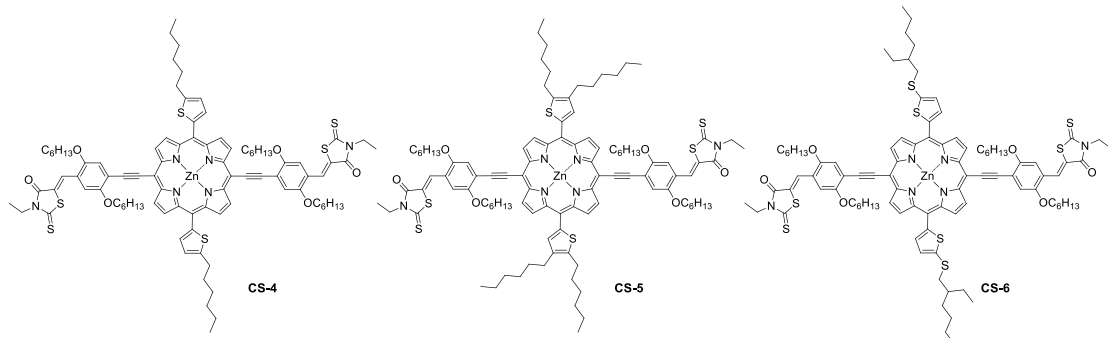
In chapter 5, a series of new A-D-A structural porphyrin small molecules (**CS-10**, **CS-11** and **CS-12**) have been prepared, that contain the same *meso*-thienyl-thioalkyl substituted porphyrin core and 3-ethylrhodanine ending unit, but varies with different numbers of phenylethynyl linker. Using them as donors for solution-processed organic solar cells, the device based on **CS-10** featuring single phenyl ethynyl π -linker exhibits high power conversion efficiency (PCE) of 7.0%. The results indicate that *meso*-thienyl-thioalkyl substitution and

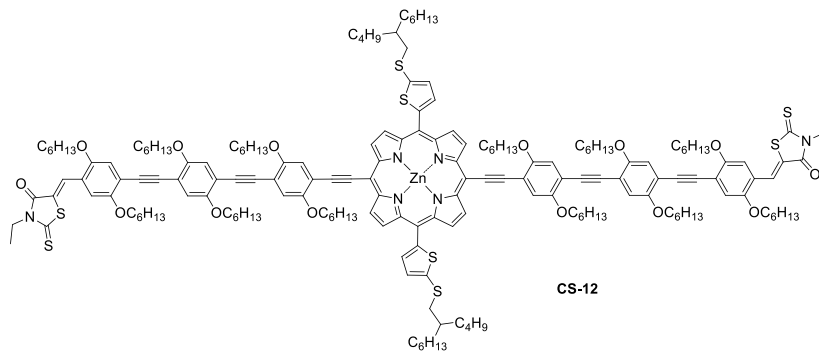
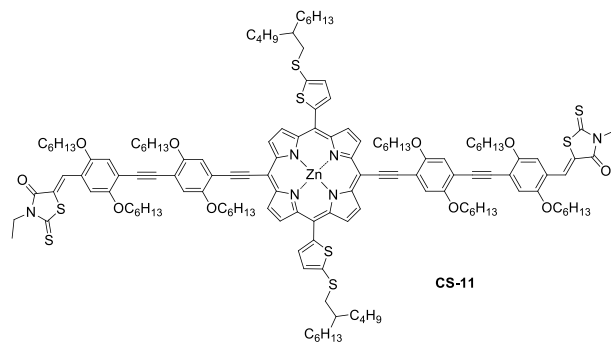
controlled π -linker length is beneficial to tune the optoelectronic properties, film morphology and consequently performance of porphyrin-based BHJ OSCs.

In chapter 6, two symmetrical tetra-*meso*-substituted porphyrin molecules (**ZnP** and **CuP**) have been prepared in gram-scale through the direct condensation of pyrrole and 4-[bis(4-methoxyphenyl)amino]benzaldehyde. Its Zn(II) and Cu(II) complexes exhibit excellent thermal and electrochemical stability, specifically, high hole mobility and very favorable energetics for hole extraction that render them attractive for implementation as new hole transporting materials in organometallic halide perovskite solar cells (PSCs). As expected, the use of **ZnP** as HTM in PSCs affords a competitive PCE of 17.78%, which is comparable to the most powerful HTM of Spiro-OMeTAD (18.59%) under the same working conditions. Meanwhile, the metal centers affect somewhat the photovoltaic performances that **CuP** as HTM produces a relative lower PCE of 15.36%. Notably, the perovskite solar cells employing **ZnP** show longer stability than that of Spiro-OMeTAD. Moreover, the two porphyrin-based HTMs can be prepared from relatively cheap raw materials with a facile synthetic route. The results demonstrate that **ZnP** and **CuP** can be a new class of HTMs for efficient and stable perovskite solar cells. To the best of our knowledge, this is the highest performance for porphyrin-based perovskite solar cells with PCE > 17%.

The dissertation was completed with conclusions and outlooks in chapter 7. Furthermore, the molecular structures of all the porphyrin small molecules developed in this research work are shown below:







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