

Studies on the Optical and Electrochemical Properties of Pyrrolopyrrole-aza-BODIPY-Based Donor-Acceptor Molecules and Their Organic Photovoltaic Applications

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論 文 名：Studies on the Optical and Electrochemical Properties of Pyrrolopyrrole-aza-BODIPY-Based Donor-Acceptor Molecules and Their Organic Photovoltaic Applications (ピロロピロール-aza-BODIPY を基体としたドナー・アクセプター分子の光および電気化学物性と有機太陽電池への応用に関する研究)

区 分：甲

論 文 内 容 の 要 旨

Pyrrolopyrrole aza-BODIPY (PPAB) is a novel far-red/NIR chromophore. Because its absorption and emission wavelengths can be controlled by the aryl-substituents and heteroaromatic ring moieties in the structure, various application studies of PPAB have been investigated in the fields of bioimaging, sensor, therapeutics, and organic electronics to achieve aggregation-induced emission enhancement (AIEE), two-photon absorption (TPA), photoacoustic imaging, photothermal cancer therapy, electrogenerated chemiluminescences (ECLs). Although PPAB has been expected as a far-red/NIR chromophore for the organic photovoltaics (OPV) since the initial study on this molecule, their OPV performance has remained low due to the narrow absorption of PPAB and poor solubility of the PPAB dimers.

Considering the intense solar irradiance spectrum in the far-red/NIR regions, there is still room to develop PPAB-based chromophores toward the NIR OPV application. Donor-Acceptor (D-A) architecture is one of the established structural motifs to tune the HOMO and LUMO energy levels and the optical band gaps. In this work, the author designed and synthesized D-A type PPAB oligomers and polymers to improve both solubility and absorption properties in the vis/NIR regions. In addition to the functionalization of PPAB toward OPV application, the author also focused on the Schiff base forming reaction of PPAB because not only PPAB but also other types of aza-BODIPY analogues can be synthesized using this reaction. To further broaden the substrate scope, a new aza-BODIPY was synthesized using 1,4-dihydroquinoxaline, and its optical properties were revealed.

Chapter 1 outlines a brief overview of the OPV study and PPAB chemistry, mainly focusing on the history, principle, device structure, and conventional OPV chromophores, and the structural-optical property relationship of PPAB. The basic questions why the OPVs are important, how the OPVs work, what the optimal device structure is, and what kind of p-type and n-type materials are suitable for OPVs, is discussed. The chapter also reveals the development of structural modification of PPABs toward NIR chromophores.

In Chapter 2, panchromatic A-D-A small molecules comprising diketopyrrolopyrrole (DPP) or PPAB or both as acceptors and cyclopentadithiophene (CPDT) as a donor are presented. By replacing DPP with PPAB, the role of PPAB as an acceptor unit on the absorption spectra is revealed. The absorption in the UV/vis/NIR regions becomes broad, and the molar absorption coefficients increases. Owing to the panchromatic absorption and high absorptivity of the PPAB-based triad, the OPV performance with the highest PCE of

3.88% and J_{sc} of 11.73 mA cm⁻² is achieved. This result demonstrates that the A–D–A structural motif using PPAB as an acceptor is an effective approach to realize panchromatic photovoltaics with high PCE values.

In Chapter 3, the effect of donor units on the optical properties and OPV performance of A-D-A PPAB-based triads is described. Thienothiophene (TT) and 3,3'-difluoro-2,2'-bithiophene (DFBT) as new donors displays significant stabilization of the HOMO energy levels and slight stabilization of the LUMO energy levels, leading to the blue-shifts of the absorption spectra compared with that of the triad with CPDT as a donor. Owing to the deeper HOMO energy levels, larger V_{oc} values than that of the CPDT-triad are achieved. Meanwhile, J_{sc} values decrease in the same order due to narrower absorption compared with the CPDT-triad. Ultimately, the moderately high PCE of 3.11% is attained using TT as a donor. These results ensure that PPAB-based A–D–A triads are potential candidates for designing OPV chromophores in the NIR region.

In Chapter 4, motivated by the moderately high OPV performance of the PPAB-based A-D-A triads, a series of D-A polymers comprising DPP or PPAB or both as acceptors are synthesized, and their OPV performance are investigated. Upon replacement of DPP with PPAB, the optical bandgap decreases from 1.30 to 1.08 eV due to the stronger electron accepting nature of PPAB than DPP. Consequently, PPAB-based polymers exhibit the panchromatic absorption extending to 1200 nm. Despite the small E_{loss} value below 0.6 eV, which generally causes inefficient charge generation, PPAB-based polymer solar cells (PSCs) exhibit moderately high NIR photoresponse. Considering the D-A polymers with NIR photoresponse have still been on its infant stage, the small E_{loss} achieved using the PPAB-based polymers and PC₇₁BM is highly promising for further application in the NIR PSCs.

In Chapter 5, in terms of the broad substrate scope of the Schiff base forming reaction, a new asymmetric aza-BODIPY analogue is synthesized using 1,4-dihydroquinoxaline as a precursor. This aza-BODIPY exhibits intense fluorescence in solution and fluorescence quenching in a film state due to the self-absorption caused by large overlap of absorption and emission.

Overall, this thesis discloses the great potential of PPAB-based D-A molecules as p-type materials for OPV application. D-A architecture based on PPAB is an effective approach to achieve the NIR photovoltaics with high PCE values. In addition, a new aza-BODIPY is obtained using the Schiff base forming reaction, which further broadens the scope of this reaction.