Studies on Synthesis of NIR aza-BODIPY Analogues Based on the Push-Pull Strategy and Their Optoelectronic Properties

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論 文 名　：　Studies on Synthesis of NIR aza-BODIPY Analogues Based on the Push-Pull Strategy and Their Optoelectronic Properties（プッシュ·プル戦略に基づく近赤外aza-BODIPY類縁体の合成と光電気化学的特性に関する研究）

区　　分　：甲

論　文　内　容　の　要　旨

Near-Infrared (NIR) dyes are designed to absorb and emit light in the NIR, typically between 700 and 2500 nm. Because the NIR light of such a range can penetrate deeper into tissues without causing damage or discomfort, potential applications of the NIR dyes in photoacoustic imaging and photothermal therapy are highly expected. In addition, the NIR dyes can also potentially be used in telecommunications, organic light-emitting diodes (OLEDs), and organic photovoltaics (OPVs), where they are used to improve the efficiency of solar cells by converting absorbed NIR light into electrical energy.

Pyrrolopyrrole aza-BODIPYs (PPABs), dimeric aza-BODIPY analogues, exhibit intense absorption and fluorescence in the far-red region and electron-accepting ability. Moreover, PPABs can be easily synthesized by a Schiff base forming reaction of diketopyrrolopyrrole (DPP) and azaarylamines.

The prominent optical properties of PPABs can be shifted into the NIR region by creating donor-acceptor (D-A) systems. Appropriate D-A combination can effectively adjust the HOMO and LUMO energy levels of molecules, resulting in tunable bandgap while maintaining certain stabilities of the molecular systems. In this thesis, the author focused on using PPAB as acceptor groups and investigated a series of symmetric and asymmetric D-A PPABs to develop novel NIR dyes. This thesis provides insights into their photophysical and electronic properties.

Chapter 1 outlines the importance of the NIR dyes based on small organic molecules and the main strategies for constructing NIR dyes with special emphasis on the advantages of the D-A strategy. Then this chapter focuses on PPAB chemistry and progress in the structural modification toward the creation of the NIR dyes. A design idea to use PPAB as an acceptor in the D-A combination was also proposed.

Chapter 2 introduces a series of D-A-D NIR PPABs comprising thienyl and phenyl linkers.

This design strategy enabled high brightness by optimizing donors and adjusting the π-spacer between the D-A components. Remarkably, a unique NIR emission at 862 nm with a high fluorescence quantum yield of 15% arising from the hybridized locally excited and charge transfer (HLCT) excited state emission was achieved.

Chapter 3 describes the multi-modal D-A system based on PPAB and explained its panchromatic absorption. The incorporation of tetracyano-1,3-butadiene (TCBD) groups significantly stabilized the LUMO energy level and enhanced the electron-accepting nature, resulting in the redshifts of the PPAB absorption into the NIR region. In addition, TCBD-appended PPABs (TCBD-PPABs) exhibited an intense ICT band due to the transition from the triphenylamine donor units to the electron-accepting TCBD-PPAB moieties. The resultant panchromatic absorption and low-lying LUMO certify their promising applications in OPV studies.

Chapter 4 details the author's efforts to extend the optical absorption of the PPAB-based D-A system into the longer NIR region. This goal was pursued by the asymmetric multi-module D-A systems bearing one TCBD or TCNQ group. The UV/vis/NIR spectrum and theoretical calculations revealed that PPAB can serve as an acceptor and π-spacer to expedite the ICT throughout the system. This approach can potentially extend the absorption properties of the monomeric PPAB-based D-A systems into the NIR II region.

Overall, this thesis discloses the substantial potential of the PPAB-based D-A system as a NIR dye. Further studies on the structure-property relationships of PPAB will enable PPAB-based NIR dyes with suitable optical and electrochemical properties for respective applications. PPABs bearing appropriate donors and π-spacers, as described in Chapter 2, exhibit high fluorescence brightness, which can potentially be applied to OLEDs and bioimaging. The multi-modal PPABs, which demonstrated panchromatic absorption in the UV/vis/NIR region and held promise for extension into the NIR II region, are appropriate candidates for OPVs and photothermal therapies. Further development along these research directions will be achieved in future research.