

Studies on the Synthesis, Structures, and Properties of Aza/BODIPY Analogues and Their Application as a Functional Chromophore

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論 文 名 : Studies on the Synthesis, Structures, and Properties of Aza-BODIPY Analogues and Their Application as a Functional Chromophore (aza-BODIPY 類縁体の合成、構造、および物性と機能性色素としての応用に関する研究)

区 分 : 甲

論 文 内 容 の 要 旨

Owing to the rapid growth of the research fields of bioimaging and organic optoelectronics such as dye-sensitized solar cells, thin-layer organic photovoltaics (OPV), and organic light emitting diodes (OLED), design and creation of new functional dye molecules have been intensively investigated. In this thesis, the author investigated pyrrolopyrrole aza-BODIPY (PPAB) and subphthalocyanine (SubPc) as a NIR fluorophore and a building block of mechanically interlocked molecules (MIMs), respectively.

The structure of PPAB has two aryl substituents, which can perturb optical and electrochemical properties. Thus, as for PPAB, the author firstly revealed their substituent effects. The author started the research from π -extensions of the aryl substituents through thienyl and phenyl linkages, and properties of PPABs with thienyl- and phenyl-linked fluorenes were compared. The significant red-shift of absorption and emission indicated that the thienyl linkage allowed efficient interactions, whereas the role of the phenyl linkage was found to be rather segregation of the interactions. With this information in hand, the longest absorption and fluorescence were achieved by both π -extension and introduction of electron-donating substituent through the thienyl linkage. Meanwhile, the unique CT emission was realized by introducing strong electron donating groups through the phenyl linkage. Secondly, the author extended this insight to a PPAB dimer. As with the PPAB monomers, a bithienyl linkage enabled the intramolecular interaction, whereas a biphenyl linkage segregated interactions between the monomer units. The bithienyl-linked dimers exhibited unique dual emission, which was significantly dependent on the solvent polarity and viscosity. The observed panchromatic absorption of the bithienyl-linked dimer was explained by the rotational isomerism. The theoretical calculation on the rotational isomers well reproduced the experimental results. The OPV application of the bithienyl-linked dimer was also achieved.

The Schiff base forming reaction is a key step of the PPAB synthesis. By changing a combination of starting materials, the author successfully synthesized a novel aza-BODIPY analogue with a helical π -conjugated structure. The resulting structure could be regarded as an azabora[6]helicene, which showed fluorescence not only in the solution but also in the film state. The cyclic voltammogram indicated possibility of oxidative cyclization to afford an antiaromatic macrocycle.

SubPc has a unique bowl-shaped structure with an axial ligand. Despite this unique structure in terms of supramolecular chemistry, no MIM such as a rotaxane has not been reported yet. Thus, the author also described the synthesis of SubPc-stoppered [2]rotaxanes. The unsubstituted SubPc-stoppered axle can go through the ring unit, whereas such threading behavior was not observed for the perfluorinated SubPc

stopper. The small size difference between the two stoppers of only 0.62 Å was critical, and the size threshold for the slippage of the ring unit lies between the sizes of unsubstituted SubPc and perfluorinated SubPc. The kinetics study revealed that the activation Gibbs free energies for the slipping-on and -off were determined to be 19.5 and 22.1 kcal mol⁻¹, respectively

As for PPAB molecules, the structure-property relationships of PPAB revealed in this thesis will help molecular design to endow optical and electric properties required for the optoelectronic applications. Although application studies of PPAB rapidly grew in recent years, there is still large room to be investigated. The OPV study of PPAB dimers described in this thesis showed a potential of PPAB oligomers as a NIR-absorbing OPV material. PPAB monomers bearing triphenylamines, which showed high fluorescence quantum yields, were also attractive as a NIR emitter in the OLED application.

Aza-BODIPY synthesis using diamine emerged the novel azabora[6]helicene, which can be further converted to antiaromatic macrocycles. Antiaromatic compounds are recently gaining much attention because of not only scientific interests but also their potential applications in organic electronics such as organic thin-film transistor and battery.

This thesis also gave disclosed the unique slippage behavior of the SubPc-stoppered [2]rotaxanes, which can be used for the high-yielding slippage synthesis. The choice of solvent or slight modification of the SubPc structure may enable the slippage synthesis. The SubPc-stoppered [2]rotaxanes have opened the door of SubPc to MIMs.