学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Suzuki–Miyaura cross-coupling based synthesis and characterization of fluorescent and chemiluminescent boron dipyrromethene dyes spanning near-infrared region

（近赤外領域にわたるボロンジピロメテン蛍光および化学発光色素の鈴木–宮浦クロスカップリングを活用した合成とその特性評価）

Fluorescence has been used extensively in diverse fields, such as clinical diagnostics, life science, materials, food analysis and environmental sciences. Compared to traditional measurement methods, fluorescence imaging offers an optional way which possesses incomparable merits, especially for cellular sensing and imaging of living systems. For instance, fluorescence imaging is a non-invasive measurement, and it does not consume or destroy the specimens, it is a safe detection method for both analytes and analysts.

As fluorophores, which correspond to convert the information of analytes to detectable fluorescence signals, are the essential elements of the fluorescence sensing systems. The rapid growth of using fluorescence technology call for design, development, and characterization of fluorophores featuring various properties.

In chapter 1, the advantages of near-infrared (NIR) dyes were stated as well as some representative examples. The properties of boron dipyrromethene (BODIPY) dyes and the way to design and synthesize NIR BODIPY dyes were illustrated.

In chapter 2, a series of red and near-infrared dyes derived from BODIPY were developed by introducing thiophene and its derivatives to the 3- and 5- positions of the dichloroBODIPY core. For the first time, cyclictriol boronates and N-methyliminodiacetic acid (MIDA) boronate were used as organoboron species to couple with 3,5-dichloroBODIPY via the one-step Suzuki–Miyaura cross-coupling. Six kinds of thieno-expended BODIPY dyes were synthesized in acceptable yields ranging from 31% to 79%. All six dyes showed different absorption and emission wavelengths spanning a wide range (c.a. 600–850 nm) in the red and NIR regions with relatively high quantum yields (19–85%).

In chapter 3, a series of three luminol-based NIR chemiluminescent BODIPY dyes were developed by conjugating a luminol part at the 2-position of the NIR fluorescent BODIPY dyes through a direct bond. By applying last-stage functionalization, the chemiluminescent dyes were synthesized in high reaction yields. The synthesized dyes emit different

chemiluminescence in the NIR region under identical reaction conditions, indicating that various NIR chemiluminescent dyes can be developed by simply exchanging the parent NIR BODIPY fluorescent dyes.

In chapter 4, to investigate the performance of synthesized NIR BODIPY dyes in practical application, biological studies were carried out. Cellular imaging of NIR fluorescent BODIPY dyes (dye **2.1-2.6**) was conducted using bovine cumulus cells. After incubation at 38 ^{o}C for specific time, the fluorescence microscopy images indicated that the dye **2.1-2.6** penetrated the membrane of the cells and was exclusively localized in the cytoplasm rather than the nucleus suggesting it could be utilized as a subcellular probe.

In chapter 5, the findings of each chapter were summarized, and a general conclusion was described.