

Development of near infrared fluorescent dyes based on BODIPY with a pyridyl group

(ピリジル基を有する BODIPY を用いた近赤外蛍光色素の開発)

Hokkaido University, Graduate School of Environmental Science,
Division of Environmental Science Development,
Course in Environmental Adaptation Science.

張帥 (Shuai Zhang)

It is widely accepted that near infrared region (NIR) fluorescent dyes are favored for various applications in biology, but so far, maintaining high fluorescent quantum yield have been quite difficult. The aims of this study were (1) to synthesize a novel NIR fluorescent dye which linking a pyridyl at 8-position and thienyl/phenylthienyl group at 3,5-positions of BODIPY (4,4-difluoro-4-bora-3a,4a-diaz-s-indacene, well known as difluoroboron dipyrromethene) which shows higher potential and has remarkably heightened in popularity among the numerous classes of fluorescent dyes; (2) to compare the difference between chlorination and bromination that are used to facilitate Suzuki coupling, on the synthesis yield and spectral properties of BODIPY, and (3) to investigate the effect of the expansion of the conjugated system on BODIPY optical performances.

Synthetic approaches of the BODIPY started with the acid-catalyzed condensation of 2-formylpyridine and pyrrole to yield a dipyrromethane. The 3,5-dibrominated/dichlorinated dipyrromethane was then obtained through the electrophilic aromatic substitution (S_{EAr}) of bromine and chlorine. Additionally, the dipyrin was afforded through oxidation of halogenated dipyrromethane with DDQ (2,3-dichloro-5,6-dicyano-*p*-benzoquinone). Finally, the BODIPY derivatives were synthesized via Suzuki-Miyaura cross-coupling reaction after subjecting the oxidized dipyrin to base and boron trifluoride etherate. The products obtained were basically analyzed and evaluated by ^1H NMR, MS, and spectroscopy.

The results showed that the NIR fluorescent dye BODIPY with a pyridine at the *meso*-position has been synthesized. Furthermore, the synthesis of BODIPY core turned out that the yield of bromination is significantly higher than that of chlorination (from 5% to 20%). And the effect of extension of the π -conjugated framework mainly in terms of thiophene and phenylthiophene on the spectral properties can be observed, which suggested that the long conjugated system leads to longer wavelength, that would be far-reaching significance for the development of NIR fluorescent dyes.