Ultrafused Dipyrromethene Borate Complexes for Deep NIR Applications

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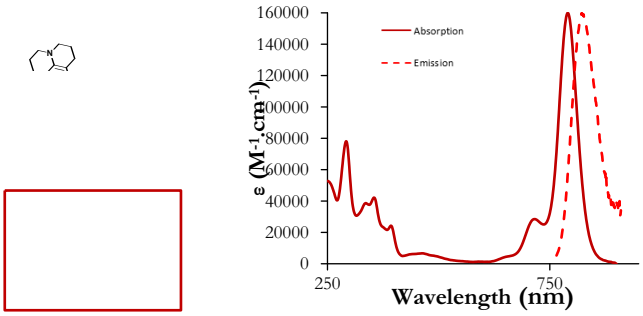
Biological imaging based on fluorescence has emerged as a powerful approach to non-invasively visualize dynamic, functional and molecular events in living organisms, without ionization and at low contrast agent concentration contrary to nuclear imaging and MRI[1]. Fluorescence imaging agents emitting in the visible and the close near-infrared I (650-1000 nm) have been well developed for imaging in living cells or tissues. However, a high resolution *in vivo* with these imaging agents is difficult to achieve due to scattering and interference in the tissue. The development of fluorescent imaging agents operating deeper in the NIR-I and -II (800-1000, 1000-1700 nm) is one strategy to overcome these obstacles[2]. Boron-dipyrromethene (BODIPY) dyes are widely used as small organic fluorescent probes in biological imaging thanks to their biocompatibility and tunable photophysical properties[3]. Recent studies shows that the emission wavelength of BODIPY dyes can be bathochromically shifted to the NIR-II region by a rational molecular design. Vinyl-bridged BODIPY oligomers[4], aza-BODIPY with strong electron-donating groups at the 1,3,5,7 positions of the core were developed with emission maximum (λ_{em}) in the NIR-II region but with moderate brightness[5,6]. While these examples have provided some clues for the construction and application of BODIPY dyes in the NIR, improvements still need to be sought, to go further into the deep NIR and improve the brightness.

With the aim to modulate photophysical properties of BODIPY to the NIR region, we synthesized ultrafused BODIPY by introduction of known strong electron-donating groups and extended of their π-system by cyclization of these groups. After pyrrole condensation to afford unsubstituted BODIPY which was then tetra-halogenated to gives the key intermediate involved in two subsequent Stille cross-coupling, various electron-donating groups were introduced on positions 2,3,5,6 and their impact on the photophysical properties of the BODIPY were studied. Oxidative cyclization of the tetra-substituted platforms allowed us to afford diverse ultrafused structures presenting strong bathochromic shift of their emission wavelengths into the NIR region.



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