

## Synthesis, spectroscopy and photophysical characterization of two meso-substituted tetramethyl borodipyrromethene (BODIPY) derivatives.

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**Introduction:** Fluorescence is a photophysical process that occurs in some compounds in excited electronic state, in which the return of the excited electron to lower energy orbitals is accompanied by luminescence emission. In the last decades, fluorescence-emitting compounds (fluorophores) have risen as an essential tool for academic and commercial researches; consequently, every year novel fluorescent compounds are synthesized and characterized. Borodipyrromethene (BODIPY) is a widely applied fluorescent scaffold, characterized by two pyrrolic units bridged by a sp<sup>2</sup> carbon, and a BF<sub>2</sub> unity complexed to the pyrrolic nitrogens. Herein we show the synthesis and characterization of two meso-substituted BODIPYs as a part of a new research project recently implemented in our group. **Objective:** Our objective was to synthesize BODIPY derivatives and determine their spectroscopic and photophysical characteristics. **Methods:** Reaction of 2,4 dimethylpyrrole with two different aromatic aldehydes (4-Fluorobenzaldehyde and 2-Thiophenecarboxaldehyde) followed by purification via classic chromatography yielded dipyrromethane derivatives. The respective dipyrromethenes were obtained through the reaction with equimolar quantities of DDQ (2,3-dichloro-5,6-dicyanobenzoquinone). Finally, without previous chromatographic purification, it was performed a reaction with BF<sub>3</sub> etherate catalyzed by triethylamine, and the desired products were obtained after chromatographic purification. Spectroscopic characterization was realized via High-Resolution Electrospray Ionization Mass Spectrometry (UltrTOF-Bruker), infrared spectroscopy (Perkin-Elmer 502), <sup>1</sup>H-NMR and <sup>13</sup>C-NMR (Bruker DRX-500). As for photophysical properties, absorption spectra were obtained in a spectrophotometer (Hitachi U-3501), emission and excitation spectra were obtained in a spectrofluorometer (Shimadzu RF5301PC). Quantum Yield was assayed through a comparative method using a solution of fluorescein in NaOH<sub>(aq)</sub> 0,1N as standard. **Results:** Two tetramethyl BODIPY derivatives were obtained: QHM-8, bearing a 2-thienyl substitution (yield = 25.9%), and QHM-13, bearing a 4 fluorphenyl substitution (yield = 21.0%). In mass spectrometry it was possible to observe the protonated and the sodiated molecule. In <sup>1</sup>H-NMR two methyl peaks were observed (singlets in ~ 2.5 and 1.5ppm) and also a singlet in 6.0ppm for the hydrogen atom directly bound to the BODIPY core. The other peaks referred to the aromatic substituents, and they were plausible for the designed structures. As for <sup>13</sup>C-NMR two methyl peaks were observed (~14.7 and 14.6ppm) and the expected aromatic peaks were also present. Regarding infrared spectroscopy it was mainly observed signals in the fingerprint region and in the region of C-H stretch. Both compounds showed small stokes shift and a slight bathochromic effect in their absorption and emissions when compared to non-mesosubstituted BODIPYs (QHM-8: λ<sub>abs</sub> = 512nm, λ<sub>em</sub> = 521nm and QHM-13: λ<sub>abs</sub> = 503nm, λ<sub>em</sub> = 510nm). Regarding quantum yield, QHM-13 shows a higher fluorescence (Φ = 91.0%) than QHM-8 (Φ = 7.5%). **Conclusion:** We obtained and characterized two BODIPY derivatives with an aromatic substituent in meso position. Extension of the length of the conjugated n-system seems to account for a slight bathochromic effect in both emission and absorption. Finally, thienyl substituent seems to hamper significantly quantum yield, while 4-fluorophenyl maintained the high quantum yield typical of BODIPY derivatives.

**Keywords:** BODIPY, Fluorophore, Organic synthesis, Fluorescence, Spectroscopy.

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