



# Chemistry at Boron: Synthesis and Properties of Red to Near-IR Fluorescent Dyes Based on Boron-Substituted Diisoindolomethene Frameworks

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Auteur	Ulrich, Gilles [1], Goeb, Sébastien [2], De Nicola, Antoinette [3], Retailleau, Pascal [4], Ziessel, Raymond [5]
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Résumé en anglais

A general method for the synthesis of difluorobora-diisoindolomethene dyes with phenyl, *p*-anisole, or ethyl-thiophene substituents has been developed. The nature of the substituents allows modulation of the fluorescence from 650 to 780 nm. Replacement of the fluoro ligands by ethynyl-aryl or ethyl residues is facile using Grignard reagents. Several X-ray molecular structures have been determined, allowing establishment of structure-fluorescence relationships. When the steric crowding around the boron center is severe, the aromatic substituents  $\alpha$  to the diisoindolomethene nitrogens are twisted out of coplanarity, and hypsochromic shifts are observed in the absorption and emission spectra. This shift reached 91 nm with ethyl substituents compared to fluoro groups. When ethynyl linkers are used, the core remains flat, and a bathochromic shift is observed. All the fluorophores exhibit relatively high quantum yields for emitters in the 650–800 nm region. When perylene or pyrene residues are connected to the dyes, almost quantitative energy transfer from them to the dye core occurs, providing large virtual Stokes shifts spanning from 8000 to 13 000  $\text{cm}^{-1}$  depending on the nature of the dye. All the dyes are redox active, providing the Bodipy radical cation and anion in a reversible manner. Stepwise reduction or oxidation to the dication and dianion is feasible at higher potentials. We contend that the present work paves the way for the development of a new generation of stable, functionalized luminophores for bioanalytical applications.

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## Liens

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