

## Practical 6: Simulation of the optical properties of organic molecules – emission

## A/ BODIPY derivatives

Boron-dipyrromethene derivatives, abbreviated as BODIPY, are a class of fluorescent dyes composed of dipyrromethene complexed with a disubstituted boron atom, typically a  $\text{BF}_2$  unit. BODIPY dyes possess outstanding chemical, thermal and photochemical stability, high quantum yield and extinction coefficient, as well as quasi insensitivity to solvent polarity and pH. Their versatility originates from the broad range of possible functionalisations on the BODIPY core (either in  $\alpha$ ,  $\beta$  or *meso* position, see Figure 1), to generate a large variety of structures.



Figure 1: Structure and IUPAC numbering of the BODIPY core.

a/ Impact of substitution in  $\alpha$  position

Calculate the absorption and emission wavelengths, as well as the associated Stokes shift (in  $\text{cm}^{-1}$ ) for the two BODIPY derivatives schematized in Figure 2 at the AM1/CIS level with an active space of 20 molecular orbitals. Comment on the impact of the 3,5-substitution on the spectroscopic properties.

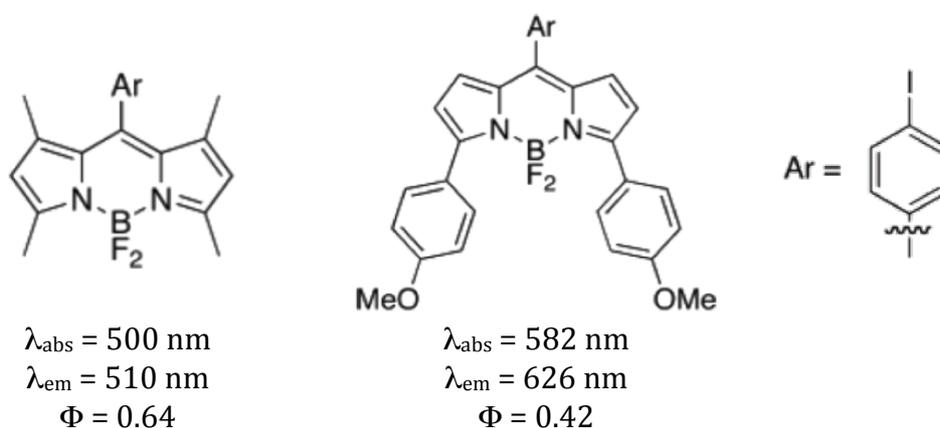


Figure 2: Illustration of the 3,5-substitution effects on the absorption and emission properties, from [A. Loudet, K. Burgess, *Chem. Rev.* 107, 4891 (2007)].  $\Phi$  is the fluorescence quantum yield.

b/ Impact of conformational constraints

Calculate the absorption and emission wavelengths, as well as the associated Stokes shift (in  $\text{cm}^{-1}$ ) for the three BODIPY derivatives schematized in Figure 3 at the AM1/CIS level with an active space of 20 molecular orbitals. Comment on the impact of increasing the conformational restrictions through ring annulation within the **1**  $\rightarrow$  **2**  $\rightarrow$  **3** series.

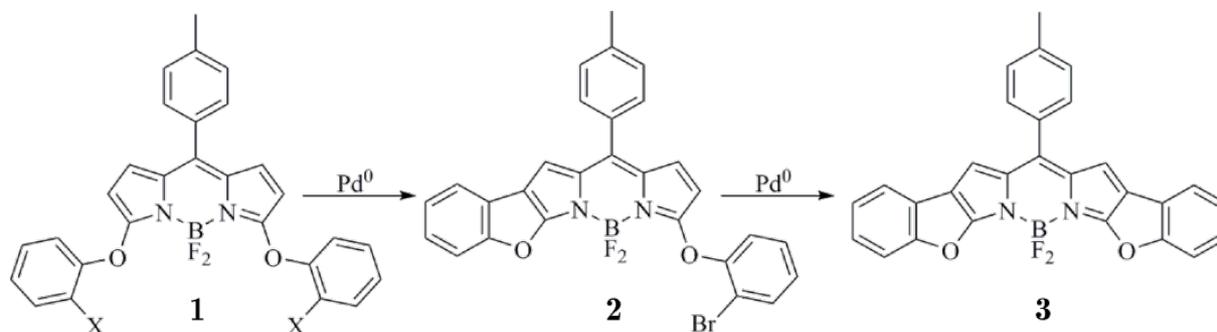


Figure 3: Structures of the BODIPY dyes series with reaction conditions of transition metal catalyzed annulation.