D1CH9116 - MMCO
Molecular Modelling applied to organic chemistry

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 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 α, β or *meso* position, see Figure 1), to generate a large variety of structures.

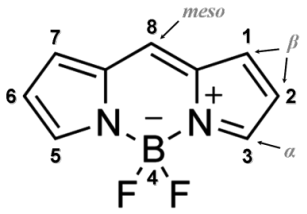
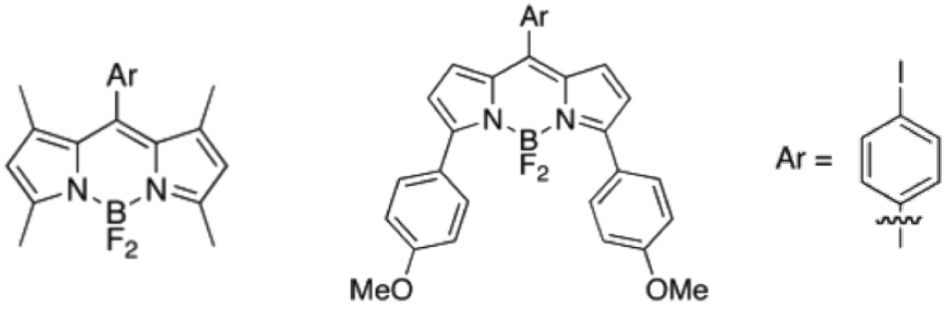


Figure 1: Structure and IUPAC numbering of the BODIPY core.

a/ Impact of substitution in α position

Calculate the absorption and emission wavelengths, as well as the associated Stocke shift (in 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.



λ_{abs} = 500 nm
λ_{em} = 510 nm
Φ = 0.64

λ_{abs} = 582 nm
λ_{em} = 626 nm
Φ = 0.42

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)]. Φ is the fluorescence quantum yield.

The absorption and emission properties of BODIPY derivatives **1** and **2** are gathered in Table 1. Compared to **1**, the addition of methoxy-phenyl groups in compound **2** results in a bathochromic shift of both the absorption and emission bands. At the SCI/AM1 level, the shifts amount to 29 nm and 64 nm for absorption and emission, respectively, in qualitative agreement with experimental results.

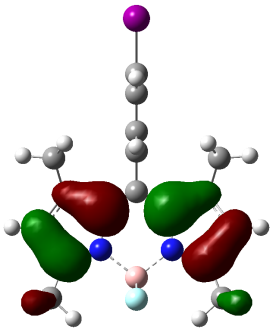
In both compounds, the first absorption band mainly results from a π–π^* electron transition between the HOMO and the LUMO. The shift of the band originates from the extension of the electron conjugation across the molecule, as characterized by the delocalization of the HOMO on the methoxy-phenyl substituents and of the LUMO on the iodophenyl group in meso position (Figure 3).

One also notes that the Stokes shift (i.e. the difference in the energy of the absorption and emission bands) is much larger in compound **2** than in compound **1**. This is due to the more important geometrical rearrangement of the first electronic excited state in compound **2**, as a consequence of its larger flexibility. Geometrical analyze shows that this effect mainly arises from the rotation of the methoxy-phenyl substituents, the related dihedral angle being reduced from 49° to 30° when relaxing the geometry of the excited state.

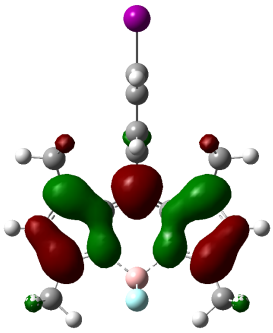
Table 1: Absorption and emission properties of BODIPY derivatives **1** and **2**.

	1	**2**
SCI/AM1 calculations		
λ_{abs} / nm	492	521
ΔE_{abs} / eV	2.522	2.379
f_{abs}	0.7316	0.9306
λ_{em} / nm	499	563
ΔE_{em} / eV	2.482	2.202
f_{em}	0.7347	0.9195
ΔE_{stokes} / eV	0.040	0.177
Experiments		
λ_{abs} / nm	500	582
ΔE_{abs} / eV	2.480	2.130
λ_{em} / nm	510	626
ΔE_{em} / eV	2.431	1.981
ΔE_{stokes} / eV	0.049	0.149

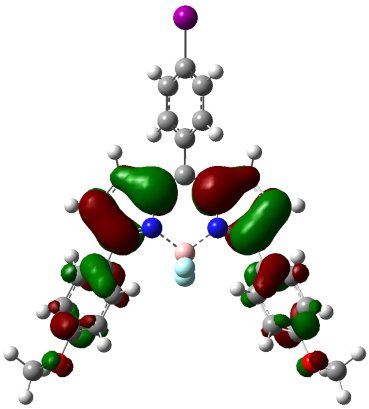
HOMO (**1**)



LUMO (**1**)



HOMO (**2**)



LUMO (**2**)

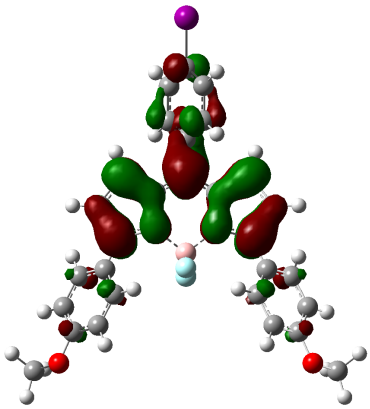


Figure 3: Frontier orbitals of compounds **1** and **2**.