Unravelling the Emissive Behavior of 8-Formyl-BODIPY Molecules in Methanol

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Fluorogenic probes, during their reaction with analytes, produce measurable changes in photophysical properties. These probes can be used for monitoring and determining the concentration of small molecular mass compounds and metal ions. A fluorogenic boron-dipyrromethene (BODIPY) probe, FormylBDP (Figure 1), bearing a formyl group, was successfully demonstrated to have a linear fluorescence intensity versus methanol concentration dependency[1], thereby allowing for determination of methanol concentration in samples. Additionally, it was found that upon reaction with methanol (Figure 1), the determined excited state lifetime of FormylBDP decreases approximately by a factor of two[2]. In this work, we theoretically characterize this probe and compare it to the molecule functionalized with phenyl groups at the 2, 6 positions of the BODIPY fragment (Figure 1, DPhFormylBDP) by exploring the potential energy profiles for this reaction and the possible excitation energy dissipation pathways. In addition, radiative and non-radiative decay constants are calculated, since they are crucial for the theoretical description of the excited state dynamics of fluorogenic probes. It is expected that the 2,6-functionalized probe is not likely to react with methanol due to an increase in the reaction energy barrier caused by the phenyl groups. Therefore, finding a computational method that would reflect changes in the energy barrier for the reaction and in the excited state decay rate is important for characterizing new fluorogenic probes.

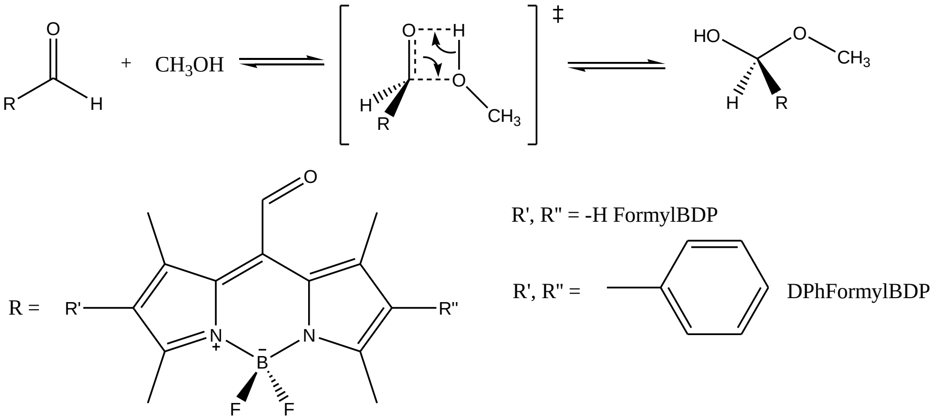

Figure 1 FormylBDP and DPhFormylBDP reaction with methanol scheme and molecular structures

All calculations were performed using the Orca 5.0.3 quantum chemistry package. Structures corresponding to extrema points along the potential energy profile were optimized. Ground state optimizations were done using Density Functional Theory (DFT), and excited state calculations were done using time-dependent DFT (TD-DFT) with the ωB97X-D3 functional. For a better description of the region near the conical intersection, the spin-flip DFT/B3LYP/cc-pVDZ level of theory was used. Radiative constants were calculated using the time-dependent formalism based on Fermi's Golden Rule with the Vertical Gradient (VG) approximation. The calculation results show that the energy barriers for the reaction with methanol do not differ much for FormylBDP and DPhFormylBDP molecules, while non-radiative relaxation rate constants agree only qualitatively.

Acknowledgements
Computations were performed on resources at the supercomputer "VU HPC" of Vilnius University in Faculty of Physics location.

References

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