Sampling Effects on the Photophysics of Oxyluciferin within the Luciferase Environment

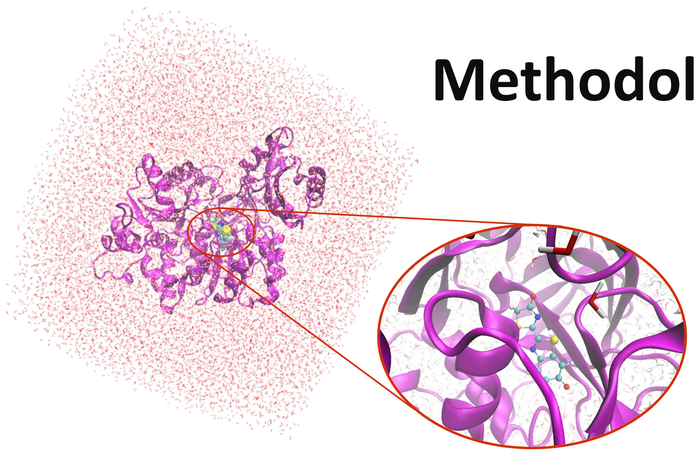
H. Mateo-delaFuente and J. J. Nogueira

Department of Chemistry, Universidad Autónoma de Madrid, 28049, Madrid, Spain

MoBioChem
Modeling Biology and Chemistry

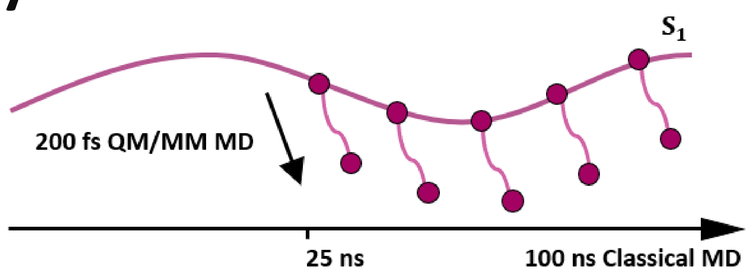
Motivation

- The oxyluciferin/luciferase complex has many applications in medicine[1]
- Goal: determine the impact of different computational factors on the properties of the electronic transitions



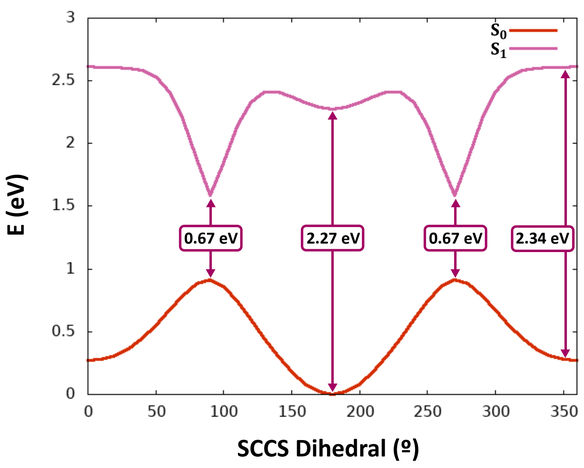
Methodology

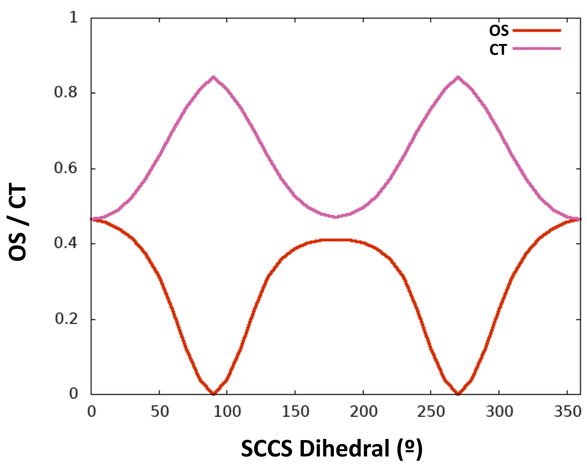
PDB ID: 4G37[2]



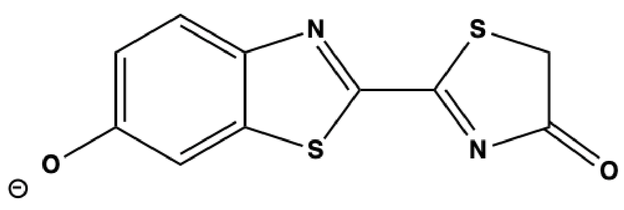
- TD-B3LYP/MM excitation energies

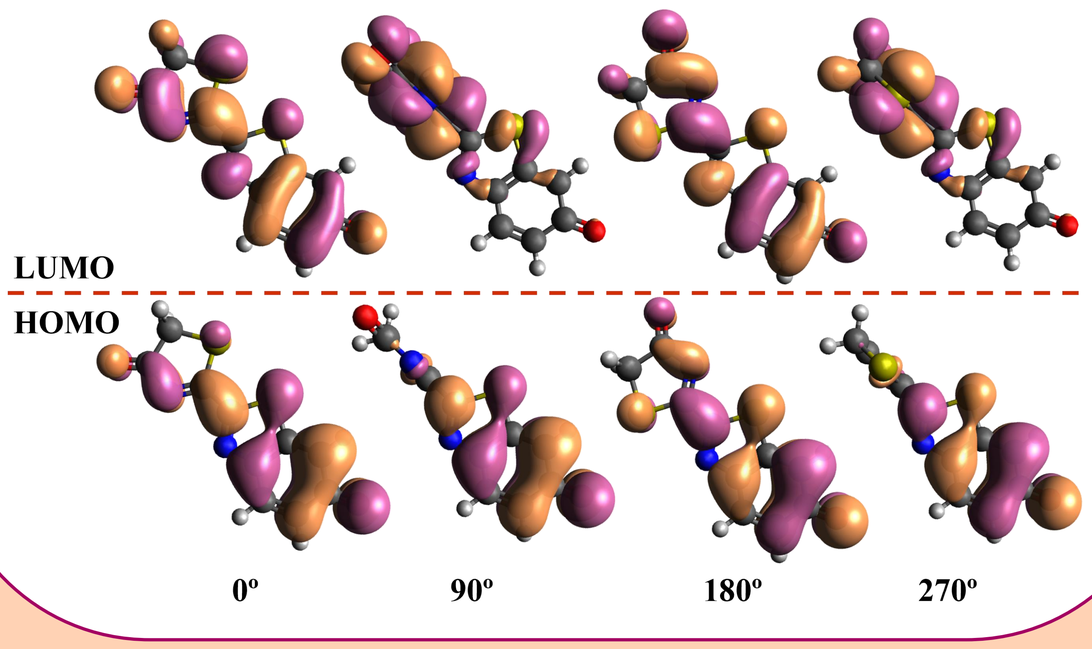
Torsion around the C-C single bond



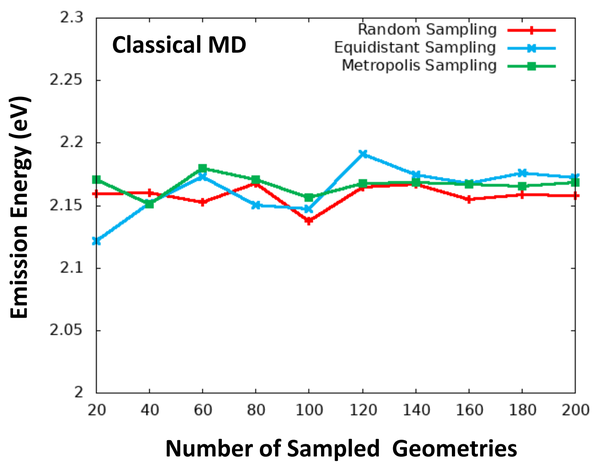


- Huge variation of the excitation energy
- Breaking of planarity results in higher CT and lower intensity

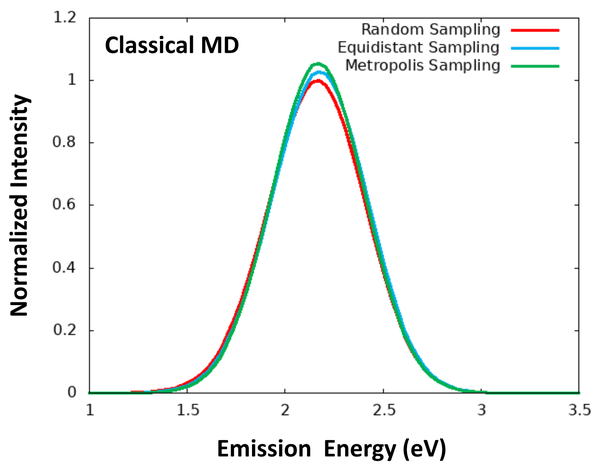




Impact of the sampling

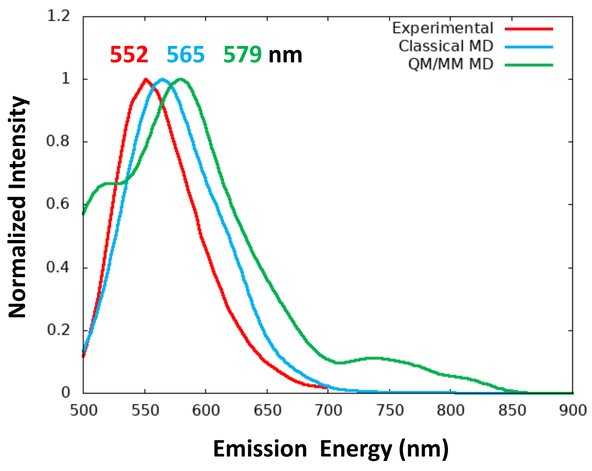


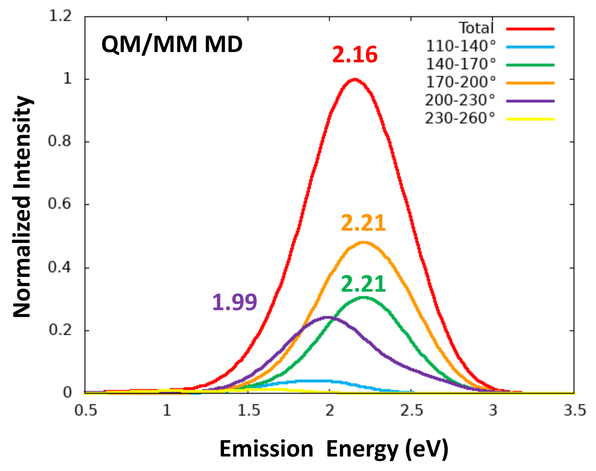
$$\langle E_{exc} \rangle = \frac{\sum_i E_{exc,i} f_i}{\sum_i f_i}$$



- Similar convergence
- Emission: 2.17 eV

Impact of the potential energy model





- Both models reproduce the experimental[3] result
- Deviation from planarity (180º) induces red shift

Conclusions

- The rotation around the C-C single bond strongly affects the properties of the electronic transition
- The sampling criterion does not affect the shape of the band
- Equidistant sampling results in a worse convergence
- Classical MD result is closer to the experimental band
- QM/MM MD sampling results in a wide torsion distribution leading to a low energy tail in the spectrum

1) Kaskova, Z. M.; Tsarkova, A. S.; Yampolsky, I. V. *Chem. Soc. Rev.* **2016**, 45, 6048–6077.
2) Sundlov, J. A.; Fontaine, D. M.; Southworth, T. L.; Branchini, B. R.; Gulick, A. M. *Biochemistry* **2012**, 51, 6493–6495.
3) Mofford, D. M.; Reddy, G. R.; Miller, S. C. *J. Am. Chem. Soc.* **2014**, 136, 13277-13282.