

# Computational Characterization of the Relevance of the Luciferase Environment on the Electronic Properties of the Oxyluciferin Bioluminescent System

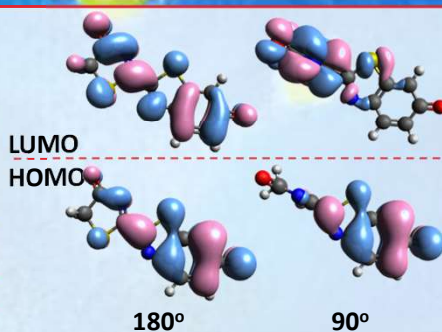
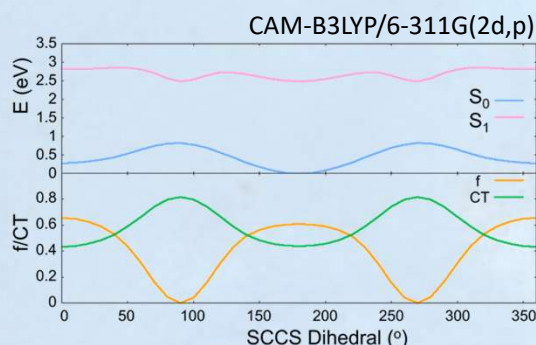
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## Motivation

- The oxyluciferin/luciferase complex has many applications in bioimaging<sup>1</sup> and biosensing<sup>2</sup>
- Goal:** to determine the structural characteristics that affect the electronic transition properties of the oxyluciferin/luciferase system

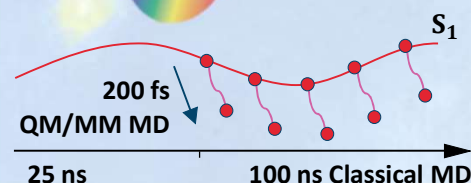
## In vacuum Static Picture



Torsion produces dark charge transfer states with lower transition energy

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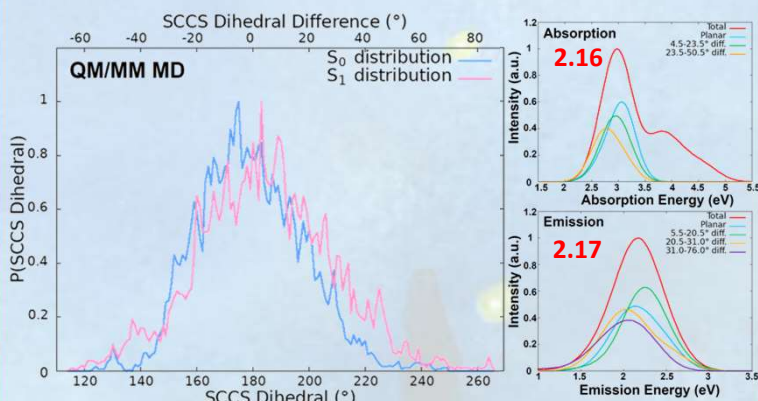
## MD Methodology



- TD-B3LYP/6-311G(2d,p) single point

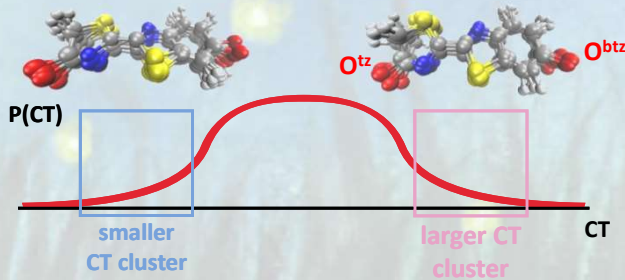
## Intramolecular Degrees of Freedom

### Probability Distribution of the SCCS Dihedral



- Q/M/M emission is similar to experiments (2.21 eV)<sup>3</sup>
- Q/M/M MD presents the expected red-shift and hypochromism

### Geometrical Relation with the CT

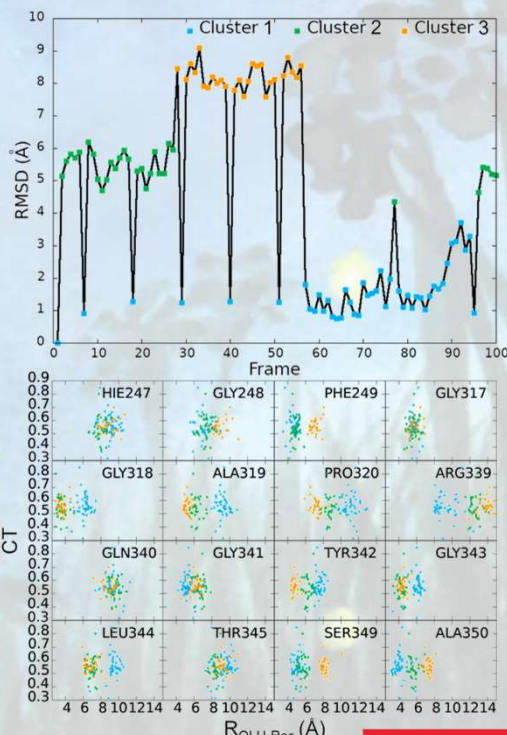


0.41 ± 0.16 ← 0.33 → 0.41 ± 0.17 RMSD

Larger differences within each cluster than between them

## Intermolecular Degrees of Freedom

### Closest amino acids



- 3 different poses depending on the closest amino acids
- No correlation of the CT with the presence of any specific amino acid

### Polarity of the Environment

More polar environments (larger number of H bonds) lead to larger CT values

Cluster	<CT>	Protein + H <sub>2</sub> O		
		O <sup>tz</sup>	O <sup>btz</sup>	Total
Small	0.45	0.1	0.6	0.7
Large	0.66	0.4	0.7	1.1

## Conclusions

- The torsional motion of the OLU is hampered by the enzyme, reducing the intramolecular CT nature of the emitting state.
- The presence of a polar environment around the OLU enhances the charge transfer character of the emitting state.

## Bibliography

- Teleman F1000Prime Rep. 2015, 7, 1
- J. Microbiol. Methods, 2001, 47, 159
- Nature, 2006, 440, 372
- PCCP, 2023, DOI: 10.1039/d3cp01387a