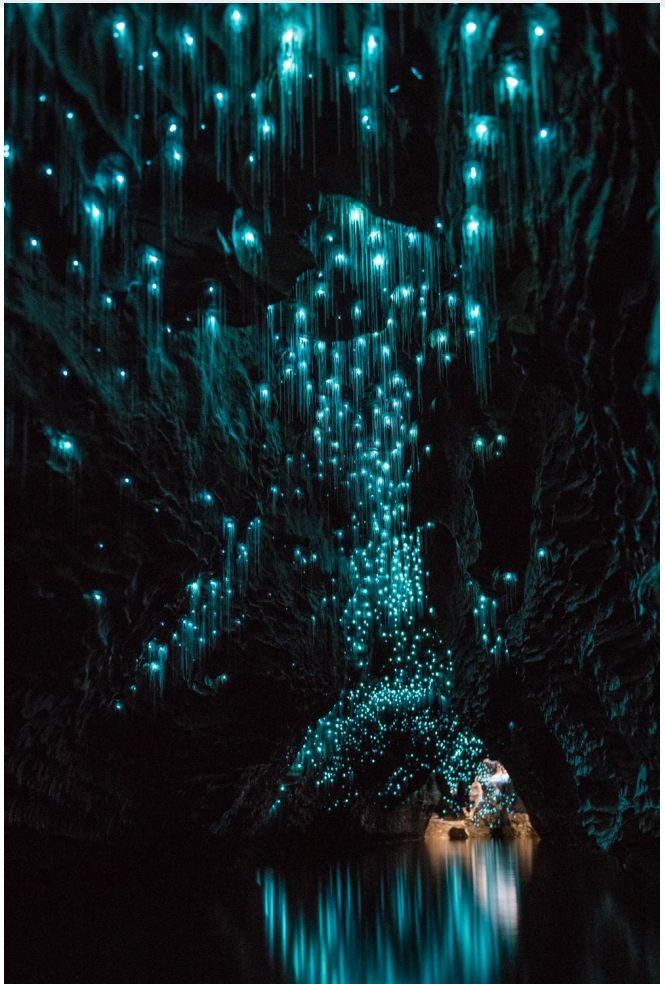
Bioluminescence from a (quantum) chemistry perspective

Keiran Rowell - USYD Theory Group Meeting - Nov 5th, 2020

Inspiration — Waitomo caves, NZ



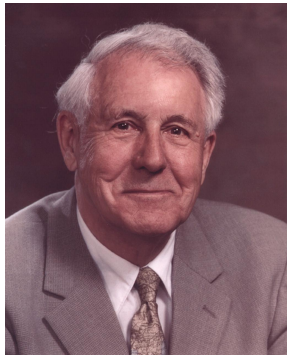
Acknowledgement

Accessible intro to bioluminescence:

- Survey across biology
- Several independent enzymes
- Found in diverse taxa
- Some species cultivate glowing bacteria (*angler fish lure*)

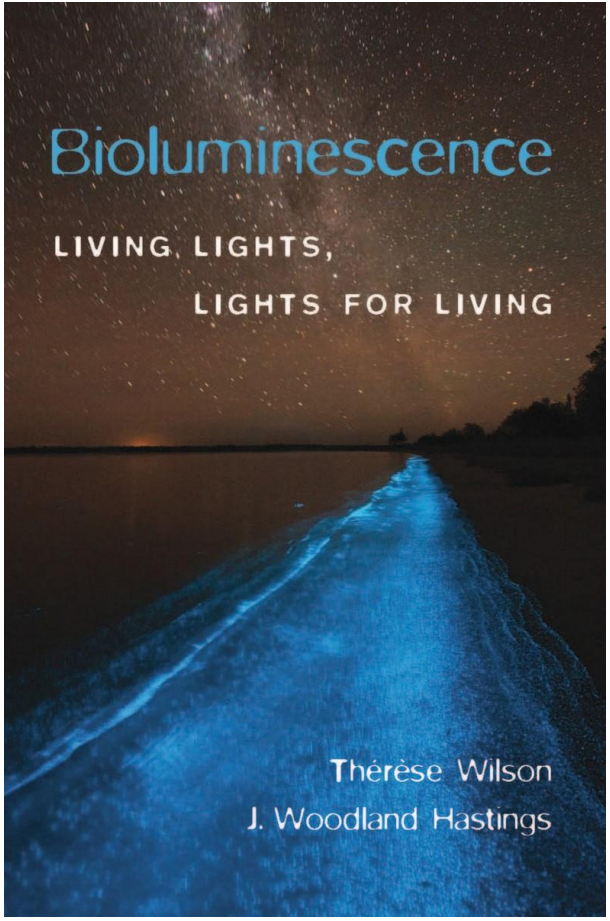
Thérèse Wilson

(1925–2014)



John “Woody” Hastings

(1927–2014)

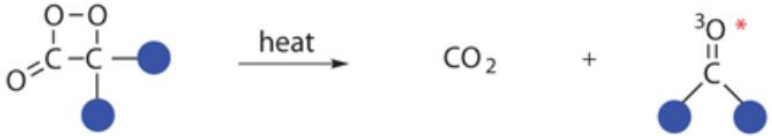


- Luciferase(s) evolved 2.5 billion years ago as antioxidant. Producing light was incidental!

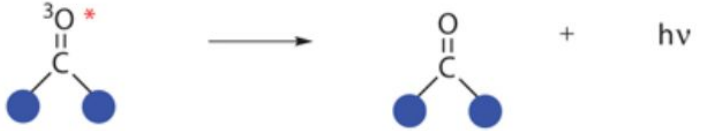
Making light — Bond energy → hv

Cyclic peroxide → CO_2 + $R_2C{=}O$,. E release

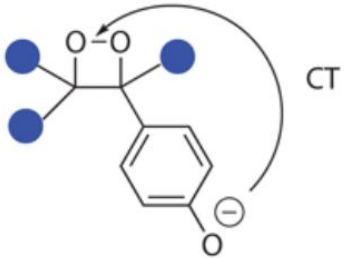
Triplet $R_2C{=}O$ generated



Quantum yields (QY) are low, and slow emission due to phosphorescence.



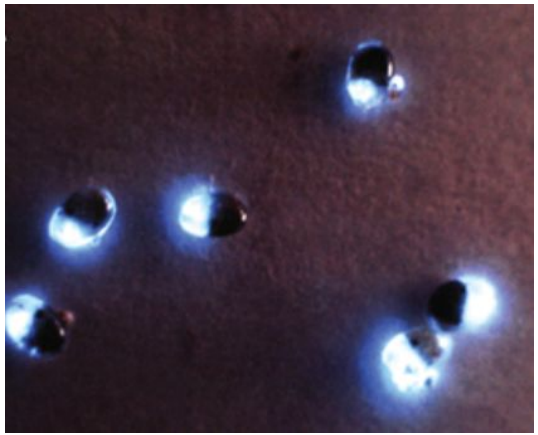
Charge transfer from negatively charged aromatic group generates excited singlets.



High QY and rapid luminescence.

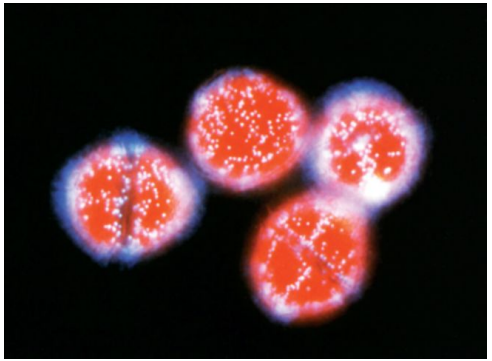
Enzyme and substrate — Luciferase + luciferin

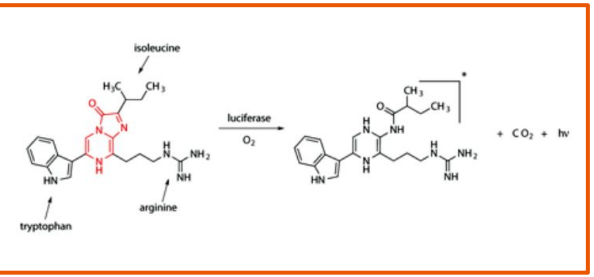
Crustaceans

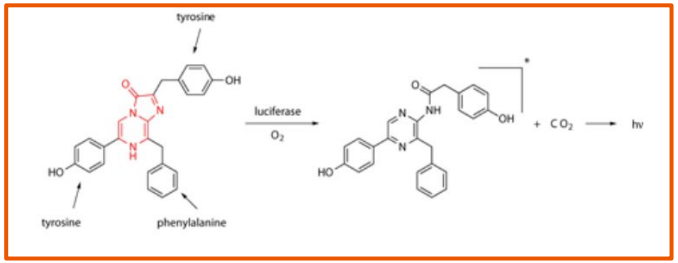


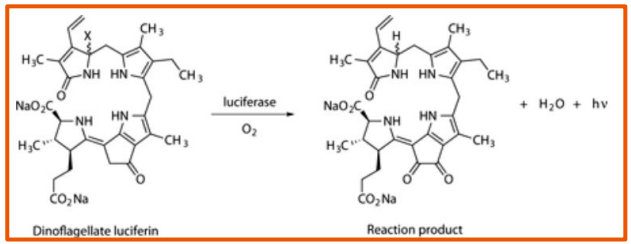
Jellyfish

Algae

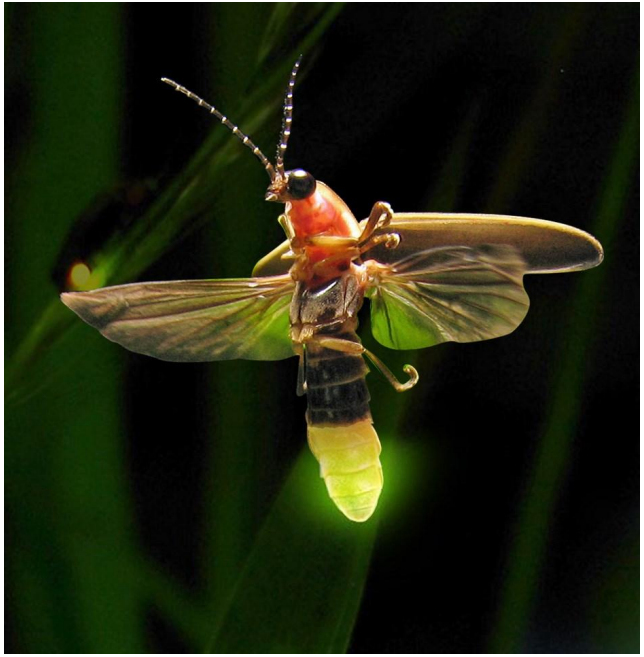


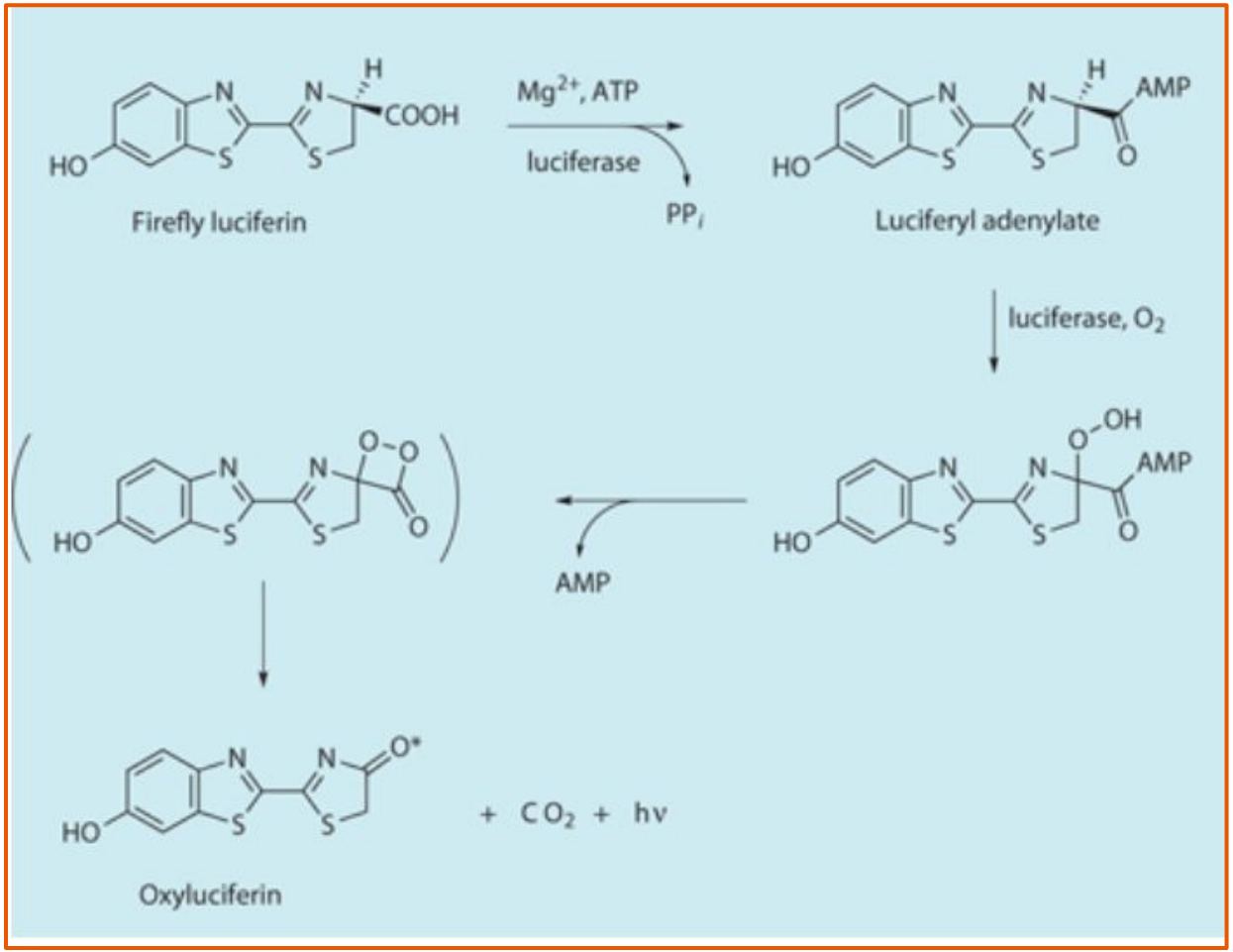






Firefly luciferin



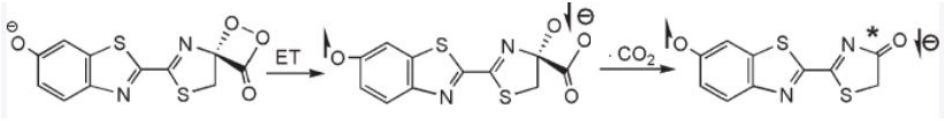


Xin Li, Lung Wa Chung, Keiji Morokuma, "Modelling Photobiology Using QM and QM/MM Calculations", *Chapter 12*, in "Computational Methods for Large Systems", Ed. Jeffery R. Reimers, **2011**

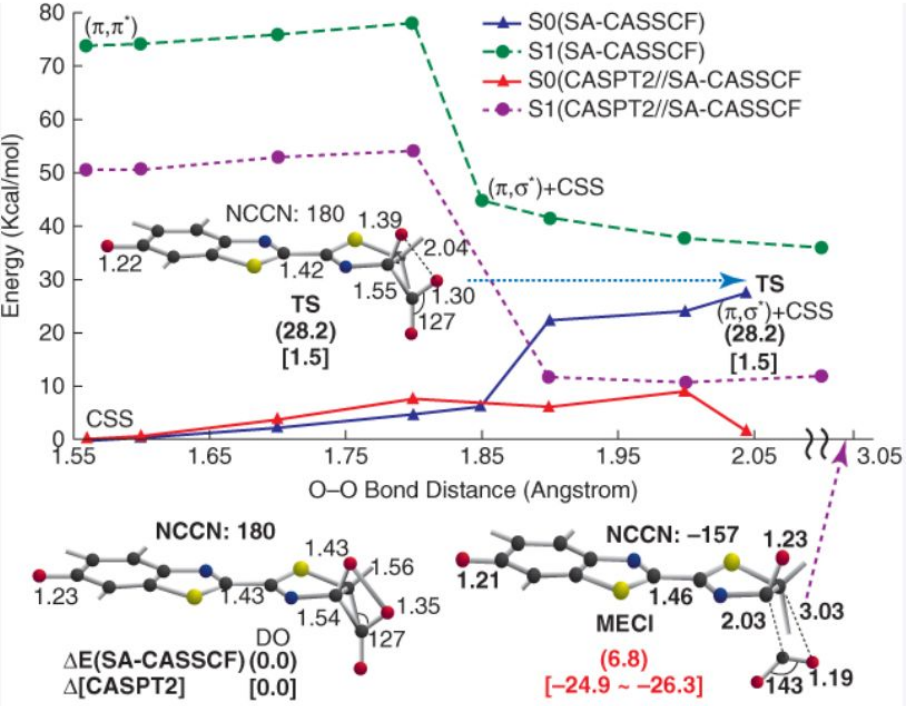
Other review: Isabelle Navizet *et al.*, "The Chemistry of Bioluminescence: An Analysis of Chemical Functionalities", *ChemPhysChem*, **2011**, *12*, 3064–3076

DFT & CAS calculations

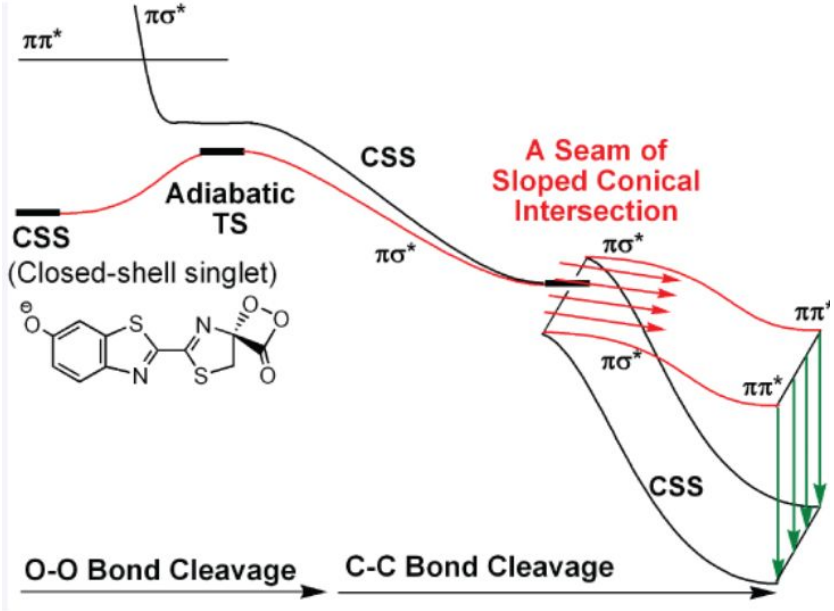
Electron-exchange luminescence proposal — B3LYP gives (π,σ*) ground state



Charge-transfer mechanism — CAS calculations

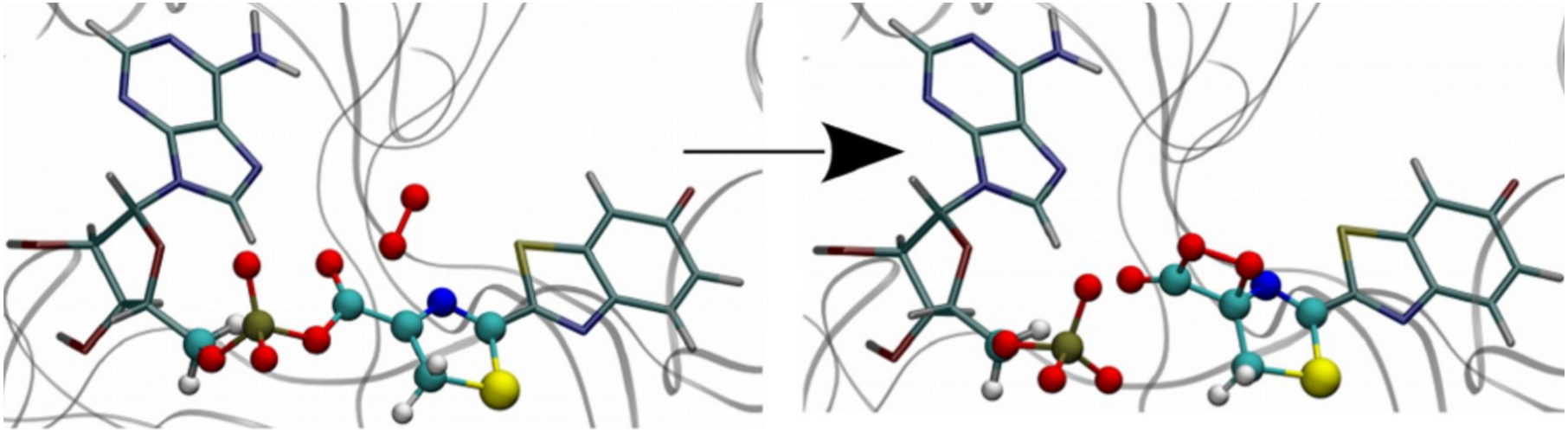


Conical Intersection — (π,σ*) avoided crossing creates TS



Romain Berraud-Pache, Roland Lindh, Isabelle Navizet, "QM/MM Study of the Formation of the Dioxetanone Ring in Fireflies through a Superoxide Ion", *J. Phys. Chem. B*, **2018**, *122*, 5137−5182

QM/MM Calculations — Luciferin + Luciferase



- O_2 enters protein barrierlessly.
- Substrate deprotonates to nearby histidine.
- Substrate e^--transfer for O_2^-
- Formation of cyclic peroxide concurrent with AMP-loss
- Singlet/triplet favour different C-O bonds forming first
- Luciferin/luciferase system dictates triplet formation is uphill

Thank you!