Examples and applications

Chemiluminescence

(or CRET, chemiluminescence resonance energy transfer)

Chemiluminescence

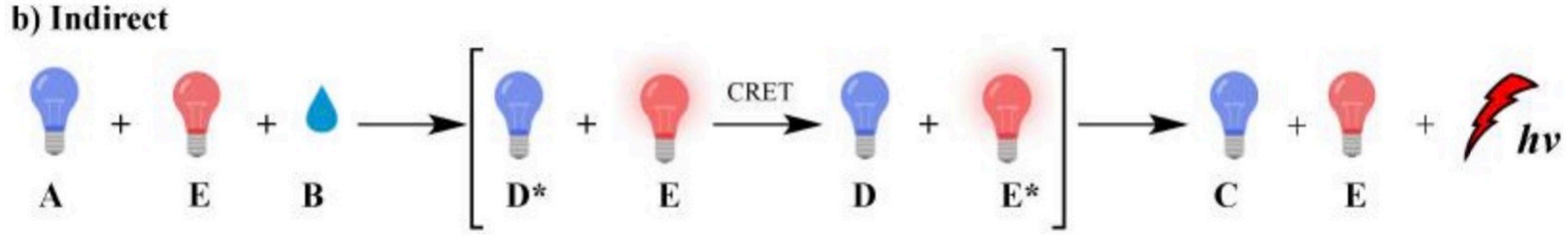
Table 9.1 ***Types of luminescence***

Type	Definition	Source of energy
Fluorescence	Electronic decay between allowed states	Ultraviolet and visible photons
Phosphorescence	Electronic decay between forbidden states	Ultraviolet and visible photons
Bioluminescence	Luminescence in a living organism	Gibbs energy of chemical reactions
Cathodoluminescence	Luminescence due to electron bombardment (cathode 'rays')	Electron kinetic energy
Chemiluminescence	Luminescence during a chemical reaction	Gibbs energy of chemical reaction
Electroluminescence	Luminescence resulting from the application of an electric field	Electrical potential energy
Photoluminescence	Luminescence after irradiation by visible or ultraviolet light	Ultraviolet and visible photons
Radioluminescence	Luminescence as a result of radioactivity	Energetic particles and γ rays
Tenebrescence	Reversible darkening under irradiation	Photon or particle energy
Thermoluminescence	Luminescence following an increase of temperature	Thermal energy
Triboluminescence	Luminescence following fracture or friction	Chemical bond energy

Colour and the Optical Properties of Materials, D. Tilley, Wiley

Chemiluminescence is light emitted as a result of a chemical reaction that leaves product molecules in a high energy state - from where they return to the ground state by the emission of photons.

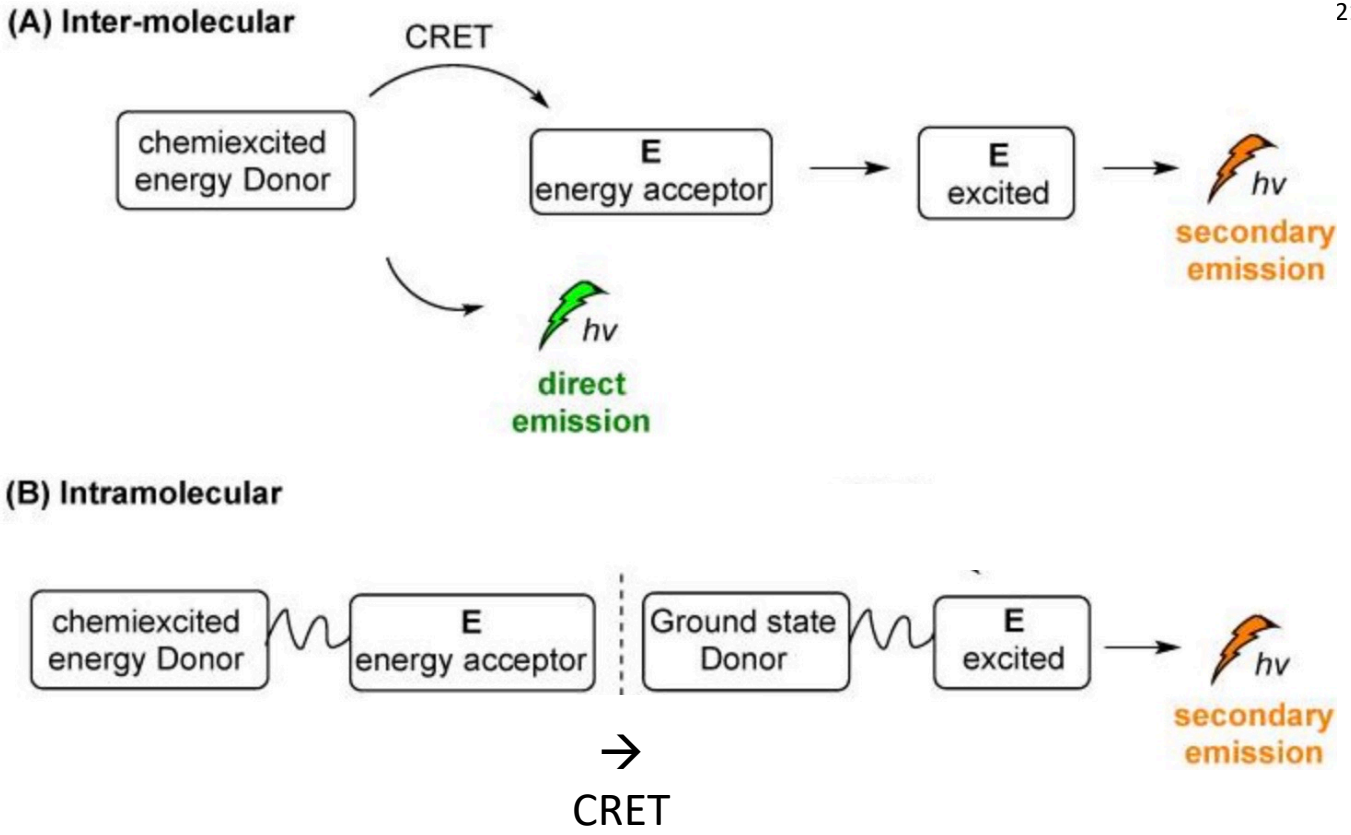
Chemiluminescence resonance energy transfer (CRET)



Molecules, 2021 Dec 17;26(24):7664

- "FRET" type of energy transfer!
- When donor molecule is photoexcited (D*), an oscillating dipole is generated
- If acceptor molecule is in close proximity to the donor (1 to 10 nm), the dipole of the donor induces a dipole in the acceptor molecule
- The same rules for the emission spectrum of the donor and the absorption spectrum of the acceptor as in FRET are valid
- Leads to the deactivation of the donor and the excitation of the acceptor

Chemiluminescence resonance energy transfer (CRET)



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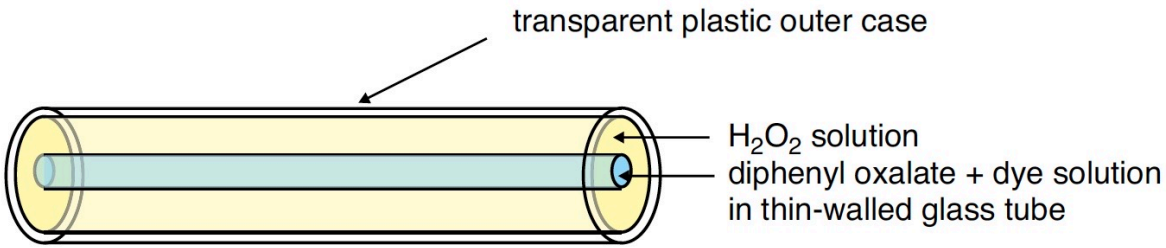
Bright emitters are good acceptor candidates:

- Organic dyes
- Quantum dots, gold nanoparticles
- Semiconducting polymers

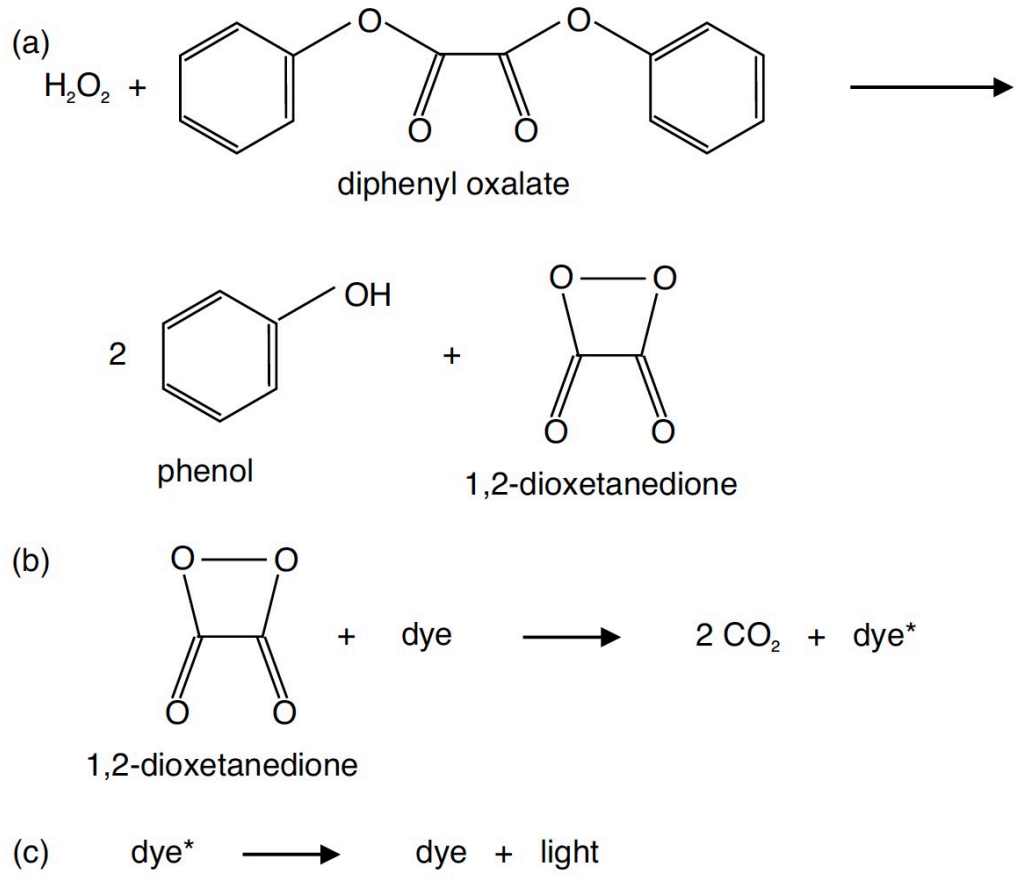
Glow sticks



- To activate the glowstick, the outer tube is twisted or bent in order to fracture the inner glass tube → the chemicals mix
- The energy produced in the resulting chemical reaction (= chemiexcited energy donor) excites dye molecules (energy acceptor) that are present in solution
- Molecules in a high energy state return to the ground state by photon emission

Glow sticks

- The reaction starting chemical is H_2O_2, contained in the outer part of the stick
- The glass tube contains diphenyl oxalate and the chosen dye
- H_2O_2 oxidizes the diphenyl oxalate to phenol and the very unstable intermediate 1,2-dioxetanedione, which decomposes immediately to CO_2, exciting the dye molecules in the process

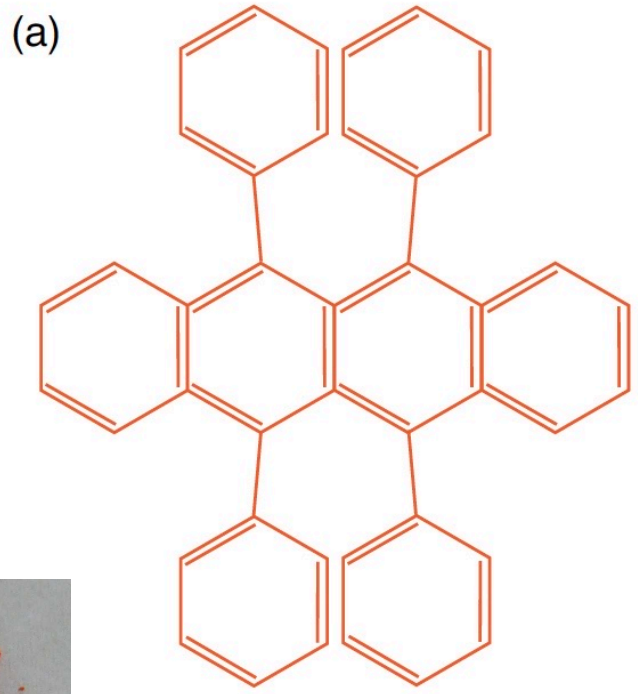


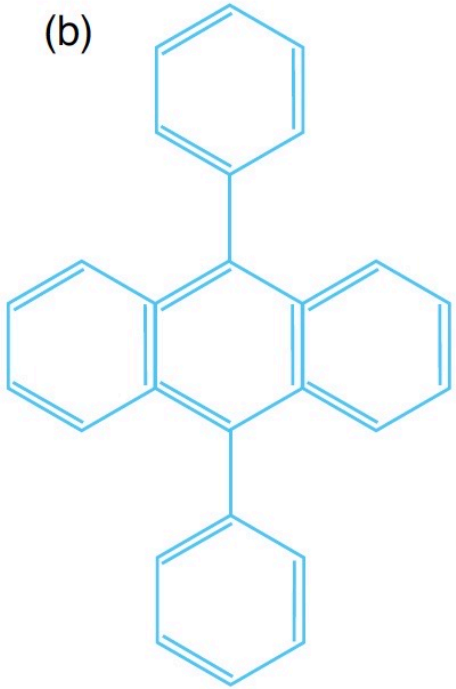
The concentrations of the chemicals and the temperature influence the length of time over which the glow stick is luminous.

Common dyes

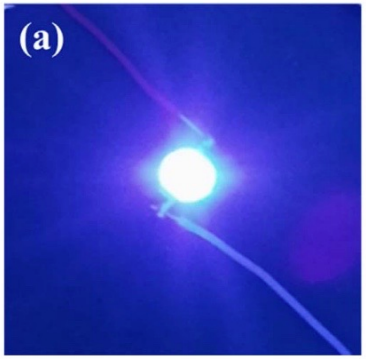
Rubrene
(5,6,11,12-Tetraphenylnaphthacene)
Also used in OLEDs!

9,10-diphenylanthracene
Used in blue OLEDs





https://commons.wikimedia.org/w/index.php?curid=16019452



Kim et al., *J. Lum. 190* (**2017**) 154–16

How to get a Nobel prize:

"In 1960, Osamu Shimomura wasn't trying to revolutionize science — if he had been, he might not have started by studying jellyfish. Shimomura was a young researcher with a simple question: What made the crystal jelly, Aequorea victoria, glow bright green when agitated?

His attempts to isolate a luminescent luciferase enzyme from the jellyfish were only partially working. After various tweaks in the lab, he was only able to produce a low glow from samples isolated from the jellyfish, so he dumped the samples into a sink to clean up for the day. When the fluid hit the sink, there was a sudden bright blue flash.

Shimomura quickly found that it wasn't the sink itself, but sea water — specifically the calcium in the sea water — that reacted with the samples from the crystal jelly to create the blue flash. But there was a further mystery: Crystal jellies glow green, not blue.

Shimomura hypothesized that there was an additional compound in the jellyfish that was absorbing the blue light and then emitting green light. This compound turned out to be a unique protein that Shimomura named Green Fluorescent Protein, "GFP" for short."

https://www.universityofcalifornia.edu/news/how-glow-dark-jellyfish-inspired-scientific-revolution

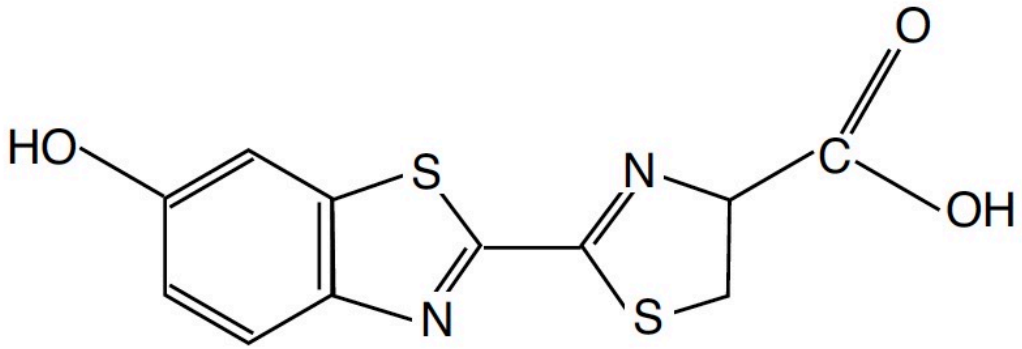
Bio-CRET

Jellyfish A. Victoria

+Ca^{2+}

(a) luciferin + O_2 + luciferase → oxyluciferin* → oxyluciferin + light **(407 nm)**
(excited) (ground state)

(b)



Light (407 nm) + Green fluorescent protein →

https://www.universityofcalifornia.edu/news/how-glow-dark-jellyfish-inspired-scientific-revolution

Applications

- Bioimaging and sensing
- Cancer treatment therapy

Advantages:

- Because CRET depends on the intermolecular distance and energy level, subtle changes of molecules can be characterized by CRET, such as the conformation transition of proteins and the specific recognition of antigen and antibody
- **No need for external light source, avoiding autoluminescence of the background!**
- CRET can avoid the photobleaching (of the donor or of the background), making it more sensitive in sensing and imaging

Example of H_2O_2 imaging *in vivo*

- Overproduction of H_2O_2 is implicated in numerous diseases (e.g. cancer)
- Great interest in developing contrast agents that can image H_2O_2 *in vivo*
- Imaging H_2O_2 *in vivo* has been difficult because of its low concentration and low reactivity in comparison with other reactive oxygen species

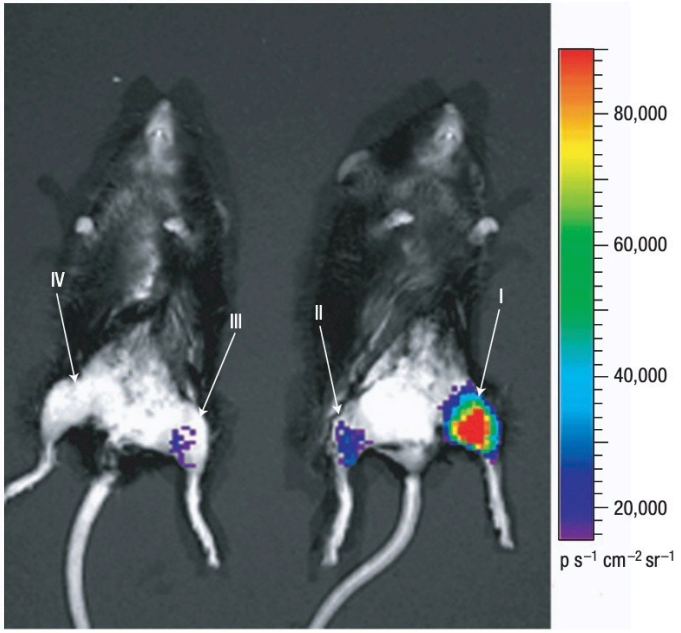
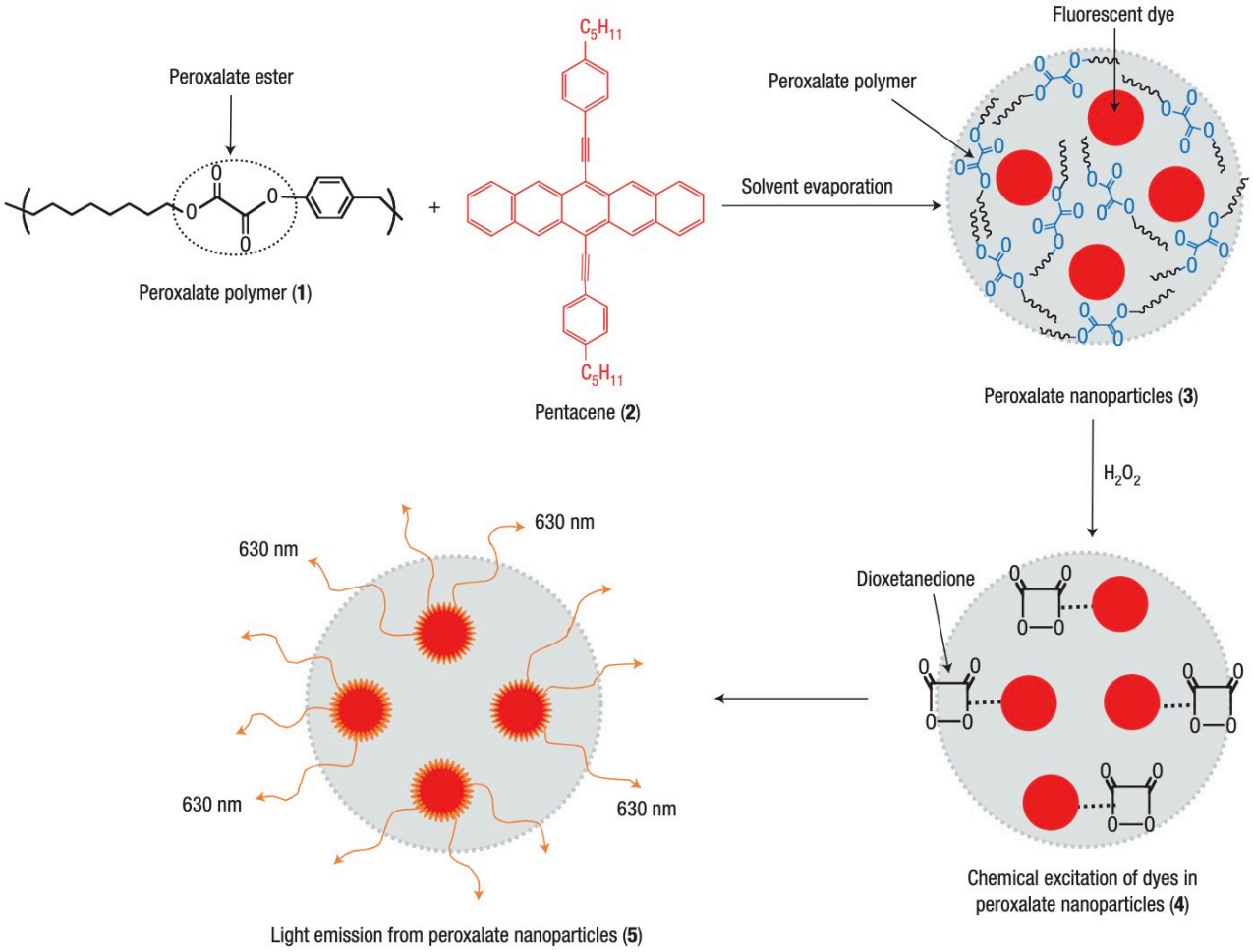


Figure 3 ***In vivo*** **imaging of exogenous hydrogen peroxide using peroxalate nanoparticles.** Peroxalate nanoparticles were mixed with various concentrations of hydrogen peroxide and injected, intramuscularly, into the leg, and then imaged in an IVIS imaging system. (I) Peroxalate nanoparticles + 10 μM of hydrogen peroxide; (II) peroxalate nanoparticles + 1 μM of hydrogen peroxide; (III) peroxalate nanoparticles only; (IV) negative control.

Nature Mater **6**, 765–769 (2007). https://doi.org/10.1038/nmat1983

Example of H_2O_2 imaging *in vivo*



Same reaction as glow sticks here!

Figure 1 Peroxalate nanoparticles—a new strategy for imaging hydrogen peroxide *in vivo*. Peroxalate nanoparticles (**3**) are formulated from the peroxalate polymer (**1**) and a fluorescent dye (**2**), in this case pentacene. Hydrogen peroxide reacts with the peroxalate ester of **3** to produce a high-energy dioxetanedione intermediate within the nanoparticles (**4**), which then chemically excites the encapsulated dye, leading to light emission from the nanoparticles and the imaging of hydrogen peroxide (**5**).

Nature Mater **6**, 765–769 (2007). https://doi.org/10.1038/nmat1983