The Chemistry Behind Glow Sticks

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March, 2012

Introduction

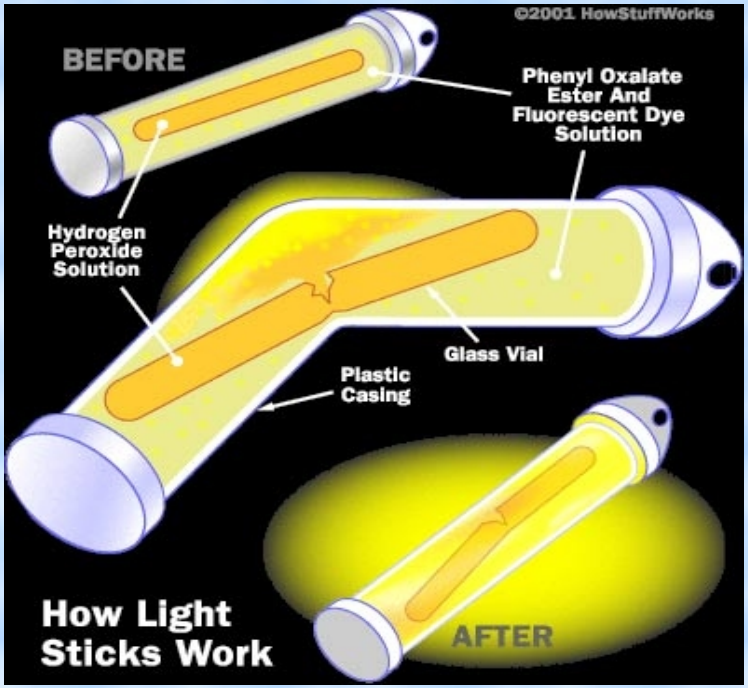
Last summer, I traveled to Maryland. After dark, fireflies were everywhere, and glowed a yellow-green light from time to time. Such small flies seemed to glow extremely bright. They must use their energy very efficiently! How? This amazing sight made me recall glow sticks, which I played with when I was young. I enjoyed them, and always wished that they would glow longer. However, I either got a bright one which glowed briefly,or a dim one which seemed to last forever! Back then, I was happy to see them glow, but I did not bother asking why. When I watched those fireflies, *all of them, to me, never quit glowing, and were also bright!* It is a weird combination I have seldom seen. This made me wonder why?

After some research, I found out that the glowing process in fireflies is called bioluminescence, which is a form of chemiluminescence. A substrate - luciferin reacts with an enzyme - luciferase to make the glow. Fireflies have organs to produce these chemicals. As long as their bodies provide the chemicals, they can keep glowing. Then, what make glow sticks glow? Can they be like those fireflies - glowing brightly “forever”? If so, how? From that point, my adventure begins.

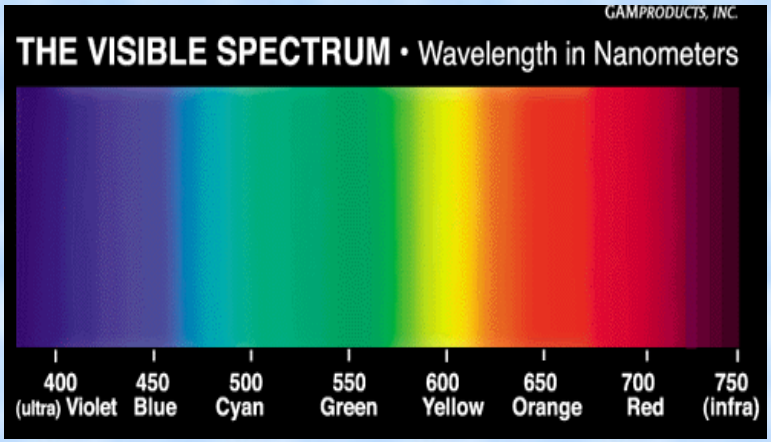
How Does a Glow Stick Work?

When you get a glow stick – a plastic tube, it does not glow. you have to bend it and break something inside (a glass tube) the tube to make it to glow. Typically, the key chemicals are TCPO (or other similar chemicals), a fluorescence dye, and H_2O_2. TCPO and the dye are dissolved in an organic solvent (e.g. DEP). Initially, all the chemicals are mixed in one compartment, but not H_2O_2, which is kept in a separate tube. When the tube is broken, it allows H_2O_2 to enter the system. It then reacts with TCPO to release energy. When the florescent dye absorbs the energy, it's electrons are excited and jump to higher energy levels and then jump back to their original energy level to emit the visible light. In the process called chemiluminescence.

A glow stick comes in many colors because different dyes emit different colors of light.



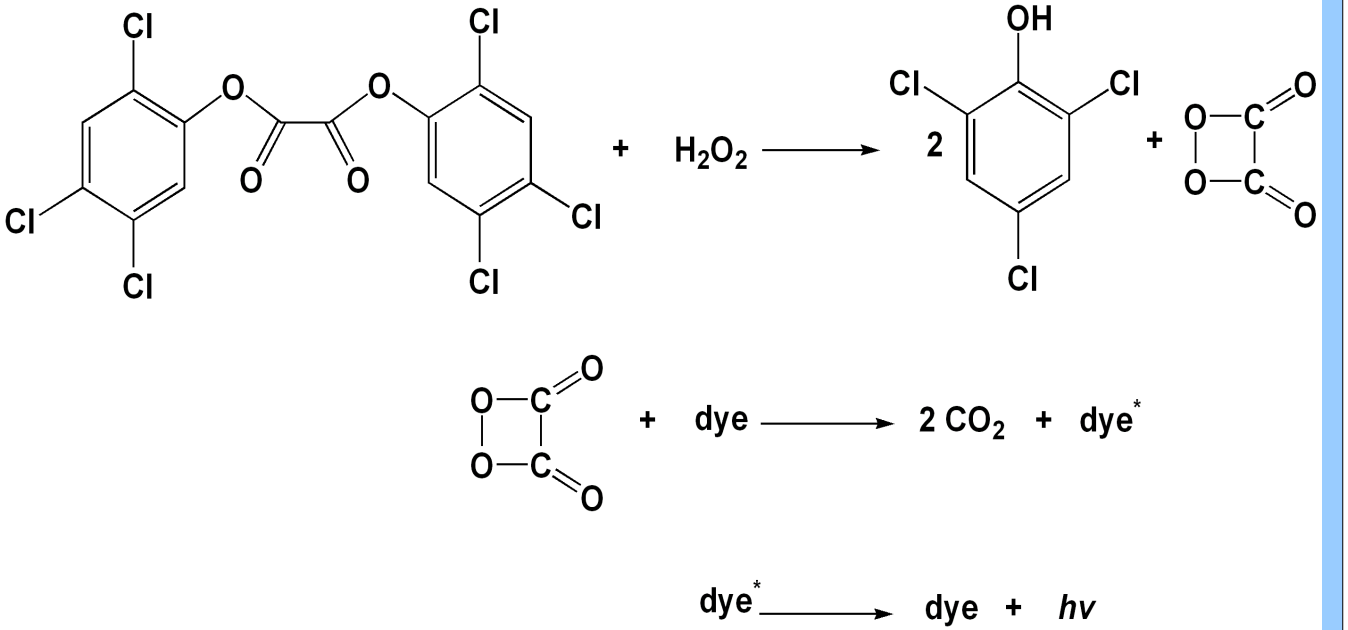
http://www.glowstickfactory.com/



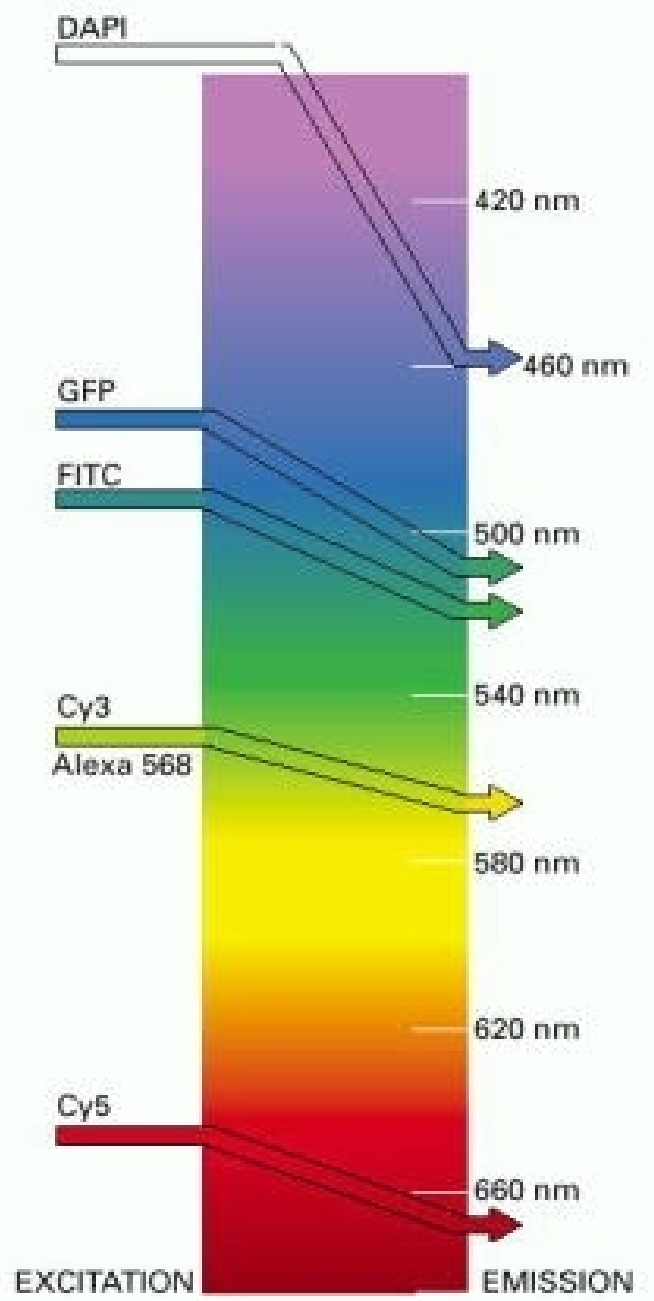
http://withfriendship.com/user/kalaikumar/visible-spectrum.php

The Chemiluminescent Process

In a chemiluminescent process,TCPO reacts with H_2O_2 to form 2 (2,4,6-tricholorphenol) and peroxyacid ester. The ester is very unstable and decomposes. Its decomposition releases energy that the fluorescent dye converts to a form of light through the following reaction pathway.



The sodium acetate (SA) enhances the reaction by keeping the solution in an alkaline condition and helping to remove the CO_2.

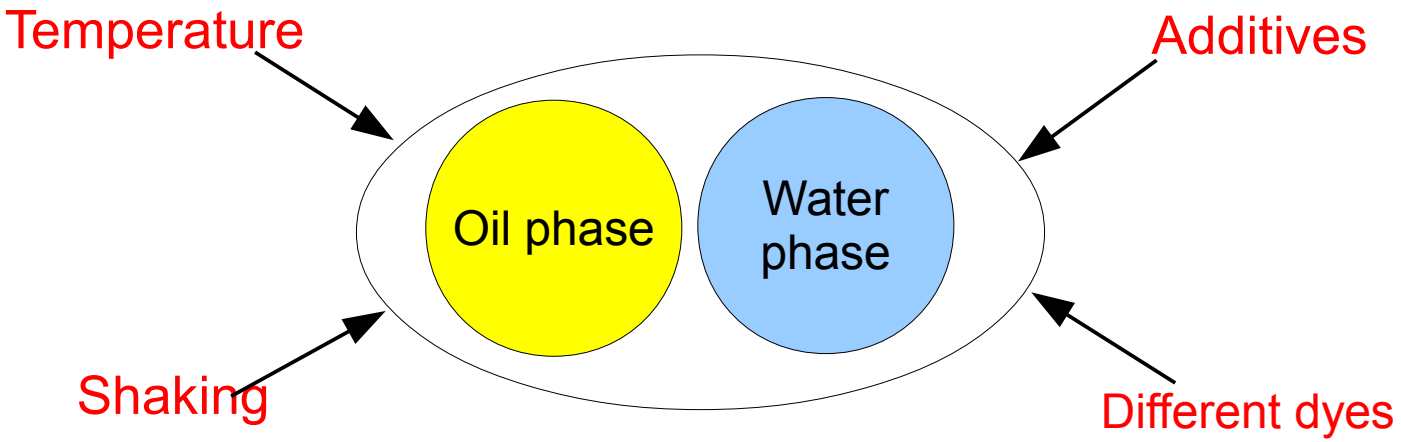


http://www.ncbi.nlm.nih.gov/books/NBK26880/figure/A1739/?report=objectonly

Hypotheses

- Adding sodium acetate makes the solution glow brighter.
- Shaking makes the solution glow brighter but shorter.
- Warmer temperatures makes the solution glow brighter but shorter.
- The dyes which emit purple colors will last shorter than dyes that emit red color.

Variables

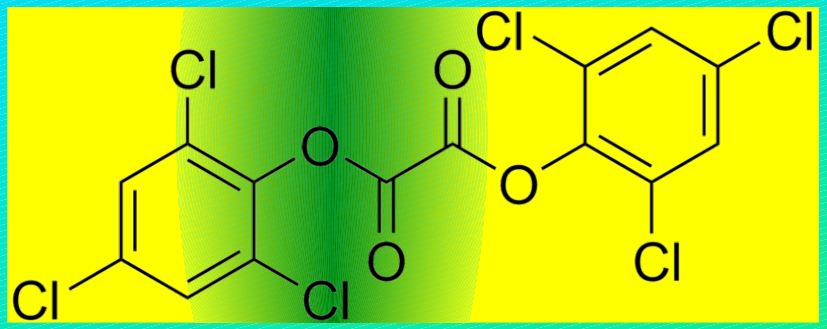


List of Materials

Illuminance meter – for light intensity measurement

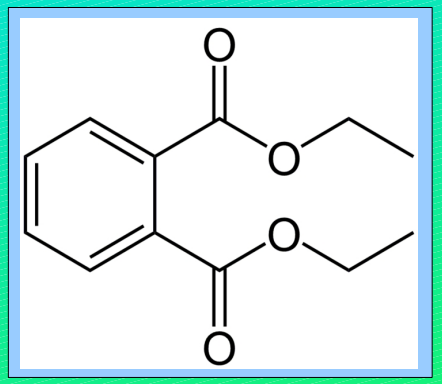
Chemicals and Their Structures

Name	State	Density (g/cm^3)	Solubility in water
Diethyl Phthalate	Liquid	1.12	1080 mg/L
Sodium Acetate	Solid	1.528	464 g/L
TCPO	Solid	1.698	0.01962 mg/L
Hydrogen Peroxide (30%)	Liquid	1.11	mixible



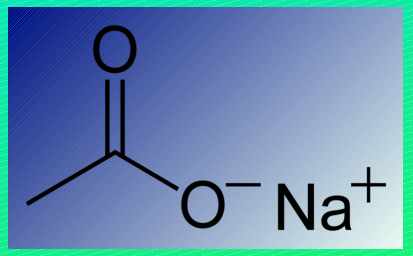
Bis-2,4,6-(trichlorophenyl)oxalate (TCPO)

$C_{14}H_4Cl_6O_4$



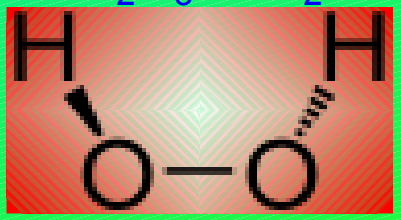
Diethyl phthalate (DEP)

$C_{12}H_{14}O_4$



Sodium acetate

$C_2H_3NaO_2$



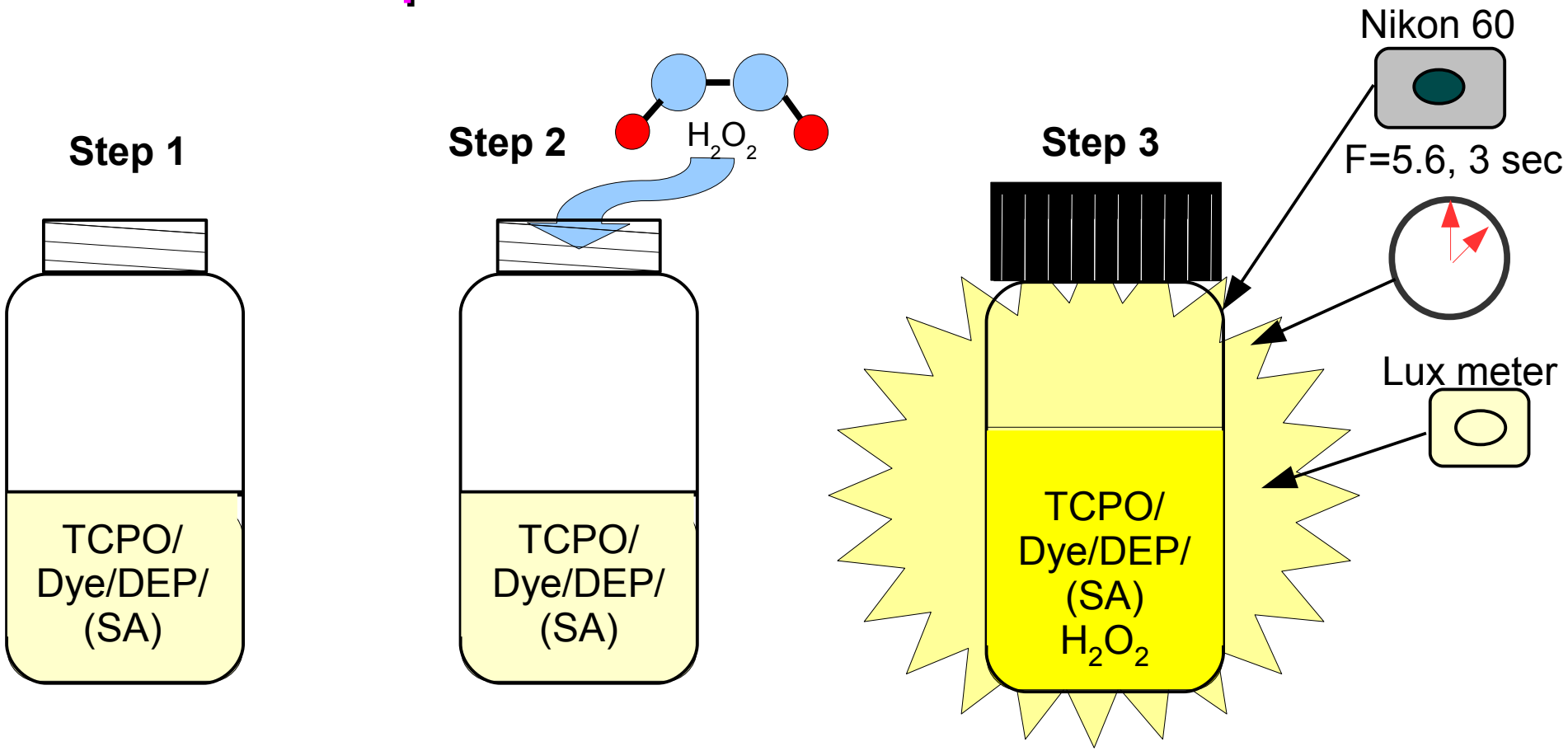
Hydrogen peroxide

H_2O_2

Fluorescent Dyes

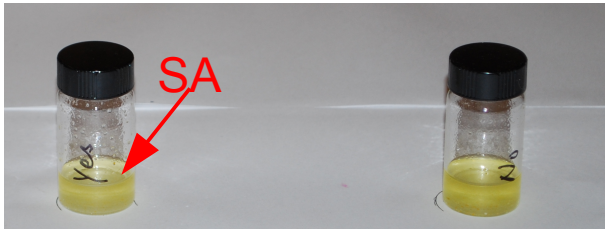
	Molecular Formula	Emission Color
Rhodamine B	$C_{28}H_{31}ClN_2O_3$	Red
Rhodamine 6G	$C_{28}H_{31}N_2O_3Cl$	Orange
Rubrene	$C_{42}H_{28}$	Yellow
9,10-bis(phenylethynyl) Anthracene (9,10 BPEA)	$C_{30}H_{18}$	Lime Green
Auramine	$C_{17}H_{21}N_3HCl$	Green
Coumarine 307	$C_{14}H_{17}NO_2$	Blue
Coumarine 460	$C_{14}H_{17}NO_2$	Purple – blue
Stilbene 3	$C_{14}H_{17}NO_2$	Purple

Experimental Procedures

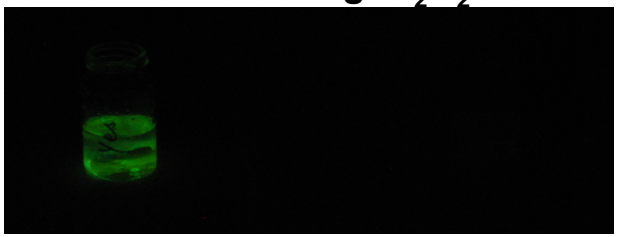


- Either shake or don't shake the solution
- Vary temperature to investigate its effects
- Measure the pH of solution if sodium acetate (SA) is added
- Repeat each experiment 3 times to ensure the reproducibility

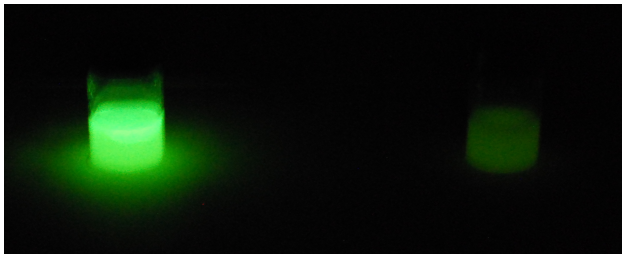
Effect of Sodium Acetate (SA) Addition



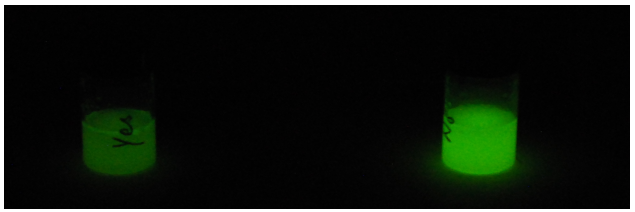
before adding H_2O_2



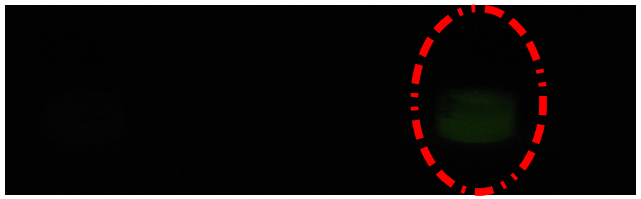
t = 0, after adding peroxide, no shaking



t = 1 min; after shaking

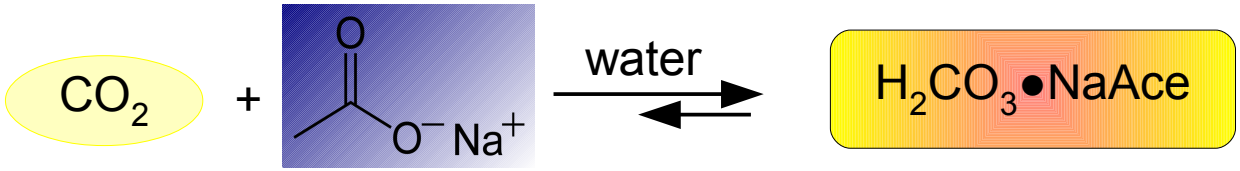


t = 5 min; keep shaking



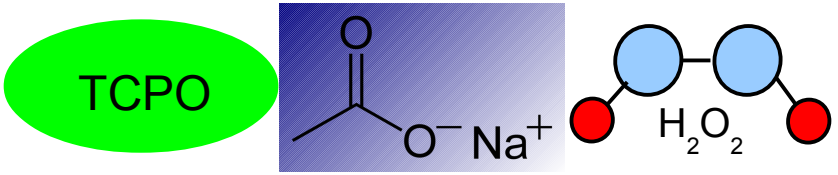
t = 20 min; keep shaking

1) Remove CO_2 to help reaction proceed (pH changes from 6.2 to 7.0)



Weak base

2) Helps TCPO and H_2O_2 to react



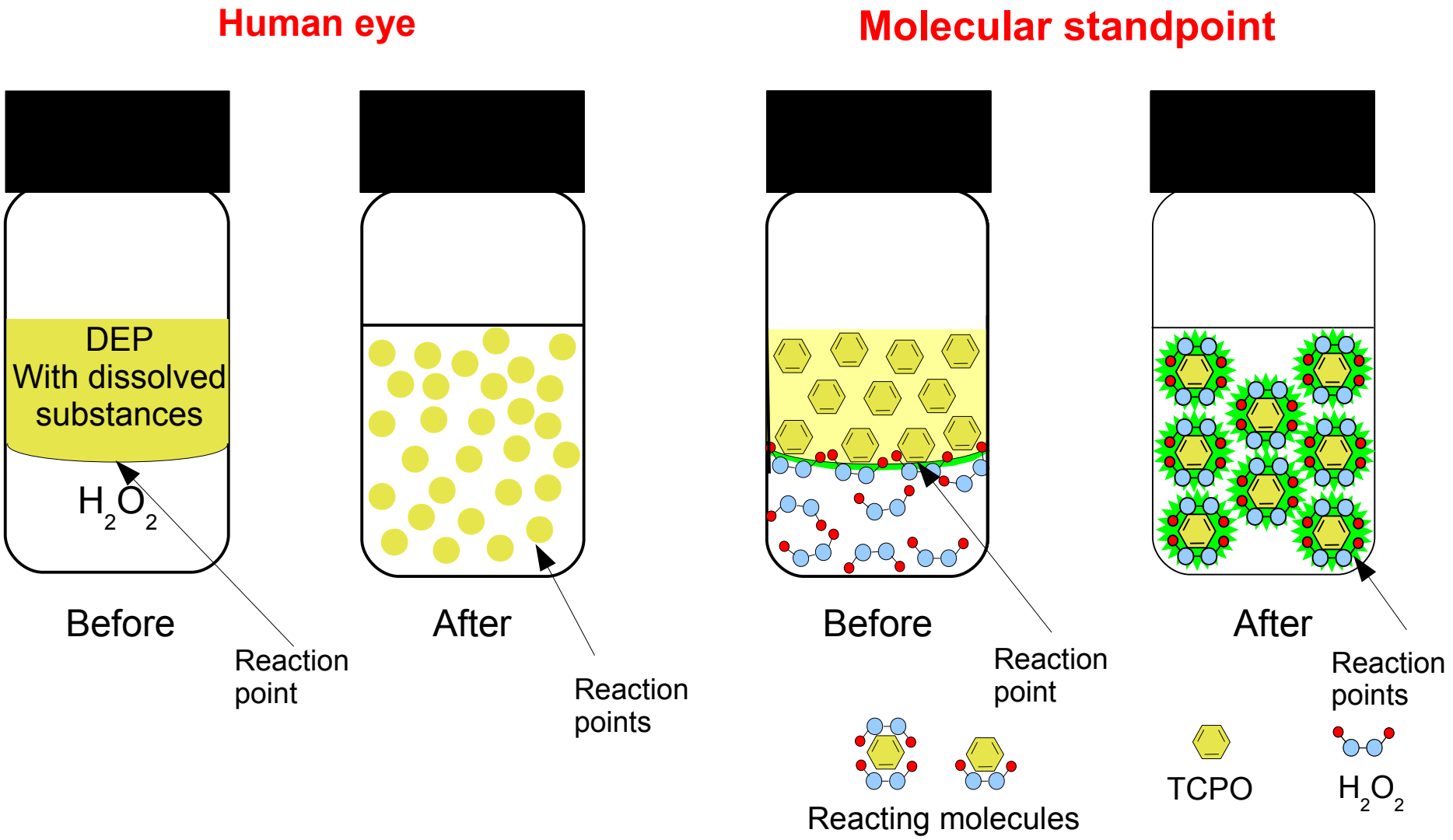
In DEP

In water

- **Accelerates the reaction**
  - **makes brighter**
  - **shortens glowing time**
- **What is shaking effect?**

Fluorescent dye: Auramine

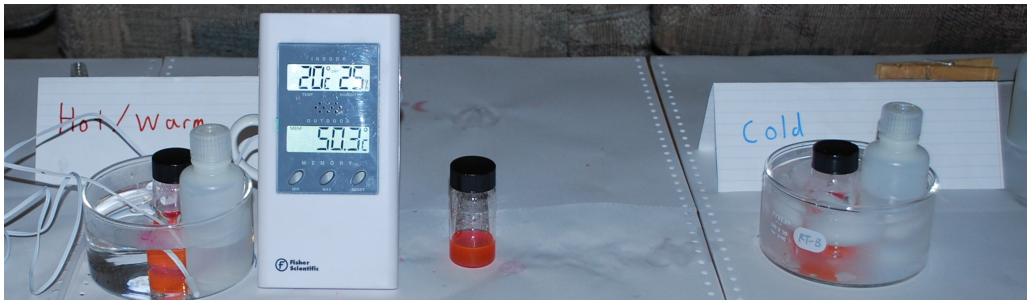
Shaking Effect



- **Increases the interface area between TCPO and H_2O_2 .**
- **Accelerates the reaction – glows brighter!**

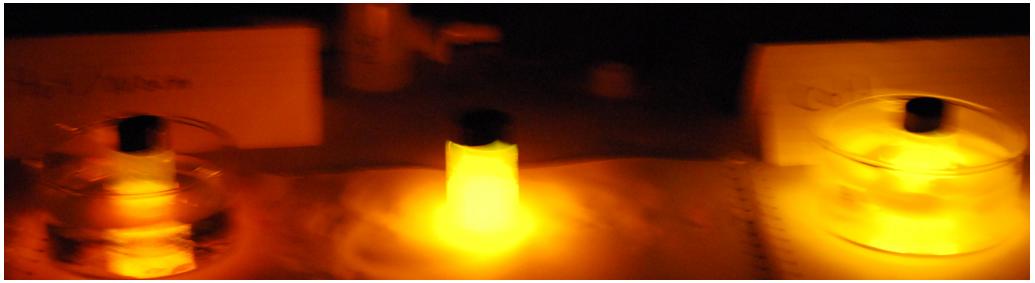
Fluorescent dye: Auramine

Temperature Effect

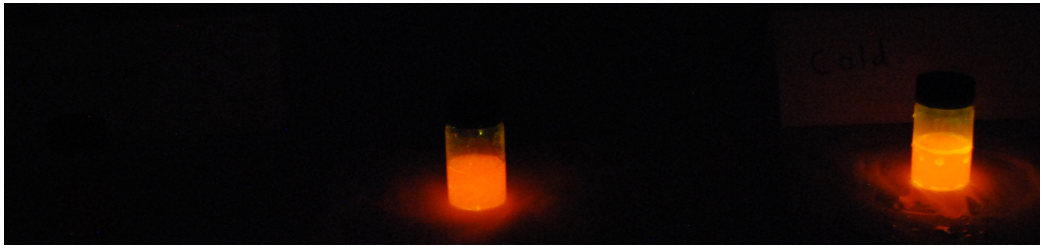


before adding peroxide

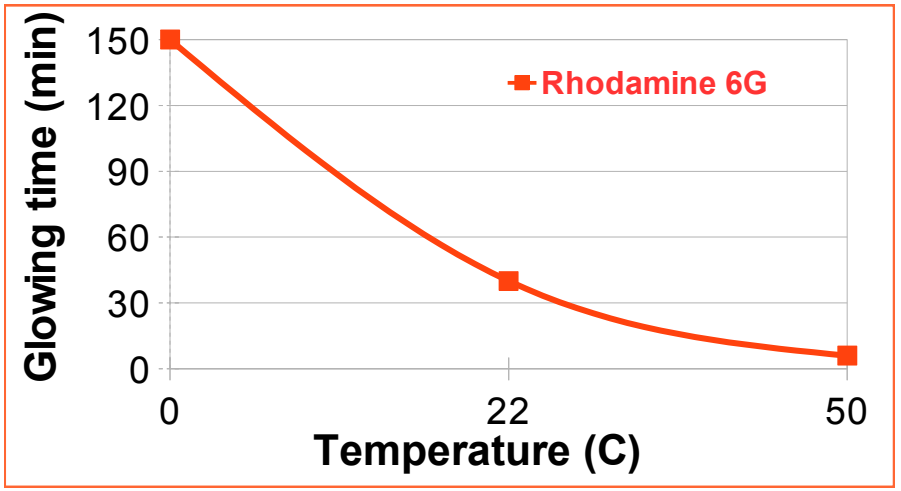
t = 0, after adding peroxide, no shaking

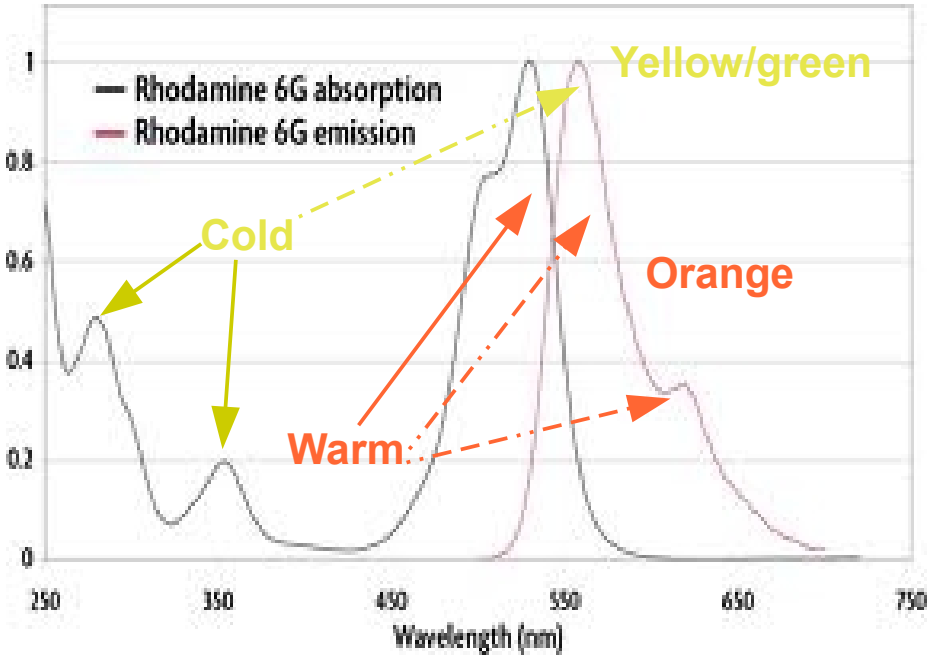


t = 5 min; after shaking



t = 6 min, "Hot" one stops to glow





- Accelerates the reaction – brighter.
- Shortens the glowing time – dies quickly.
- Possibility of a complicated reaction.

Fluorescent dye: Rhodamine 6G

http://www.activemotif.com/catalog/617/fluorescent-secondary-antibodies

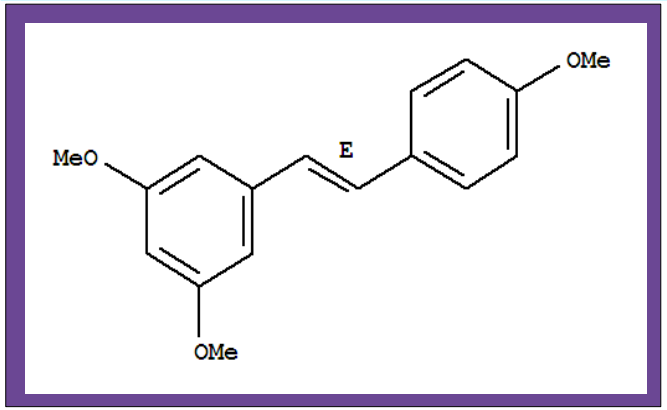
Dyes with Different Excitation and Emission Energies[1,2,3]

Dye	Excitation Wavelength (nm)	Emission Wavelength (nm)
Stilbene 3 (1)	293	~440
Coumarine 460 (2)	242, 378	~450
Coumarine 307 (3)	390	~470
Auramine (4)	390	~500
9,10-Bis(phenylethynyl) anthracene (5)	223, 310, 434, 450	~560
Rubrene (6)	~526	~590-600
Rhodamine 6G (7)	248, 530	~630
Rhodamine B (8)	250, 543	~640

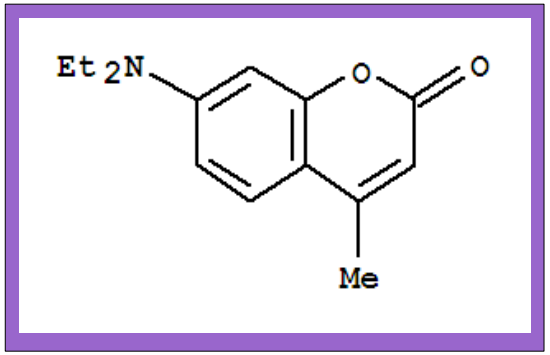
- Can they all glow in TCPO/H_2O_2 reaction?
- What their glowing colors in diethyl phthalate (DEP)?
- How long do they glow?
- How bright are they?

[1]:http://www.nature.com/nmat/journal/v9/n11/fig_tab/nmat2872_F4.html;
[2]:http://iopscience.iop.org/1367-2630/11/1/015001/fulltext/ (Rubrene in cyclohexane)
[3]:http://omlc.ogi.edu/spectra/PhotochemCAD

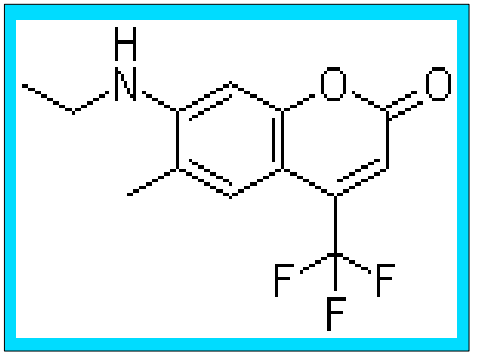
Molecular Structures of Fluorescent Dyes - I



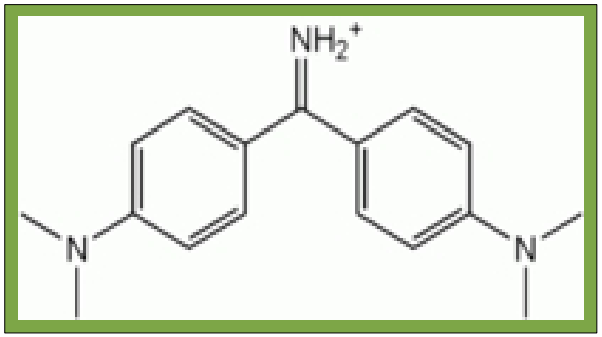
Stilbene 3 (1)
$C_{14}H_{11}O_3Me_3$



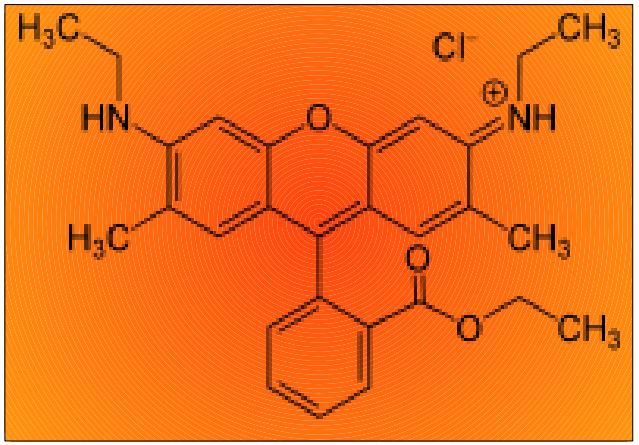
Coumarin 406 (2)
$C_{14}H_{17}NO_2$



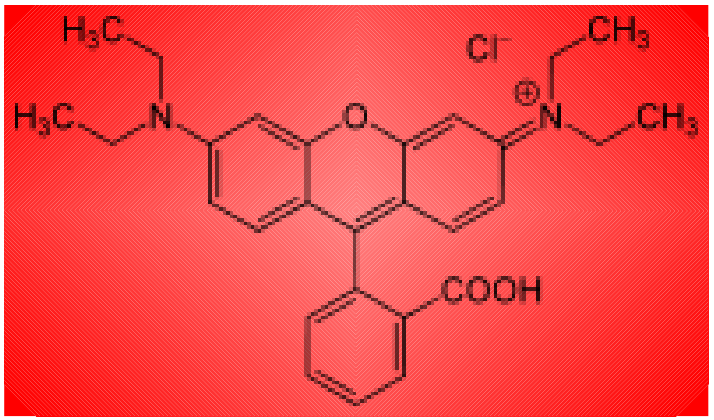
Coumarin 307 (3)
$C_{13}H_{12}F_3NO_2$



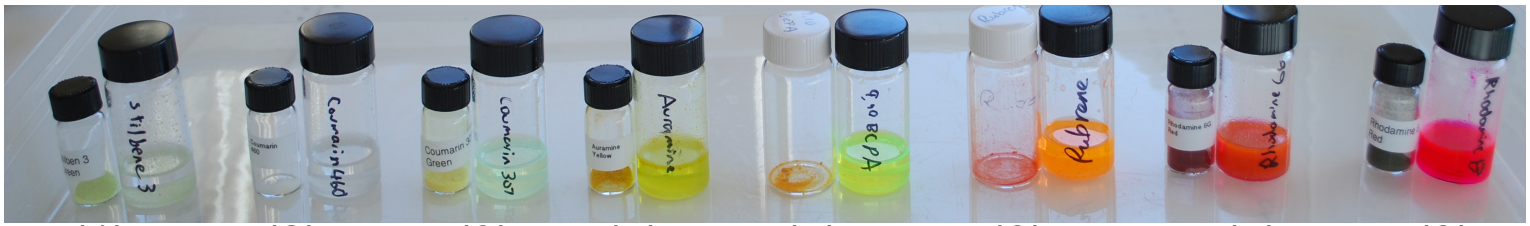
Auramine (4)
$C_{17}H_{21}N_3HCl$



Rhodamine 6G (7)
$C_{28}H_{31}N_2O_3Cl$



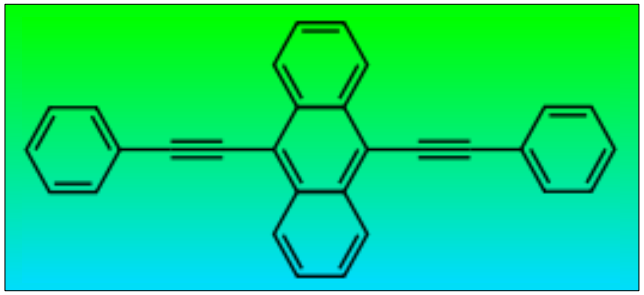
Rhodamine B (8)
$C_{28}H_{31}N_2O_3Cl$



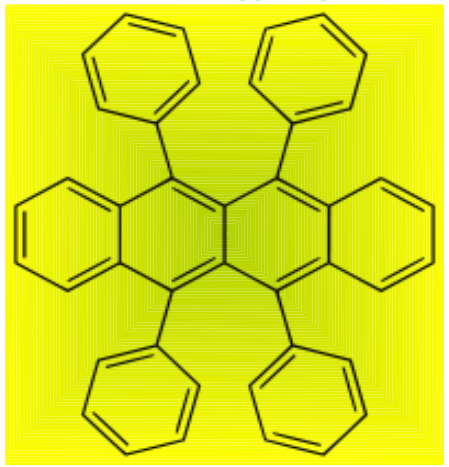
(1) (2) (3) (4) (5) (6) (7) (8)

Http://www.wikipedia.org

Molecular Structures of Fluorescent Dyes - II

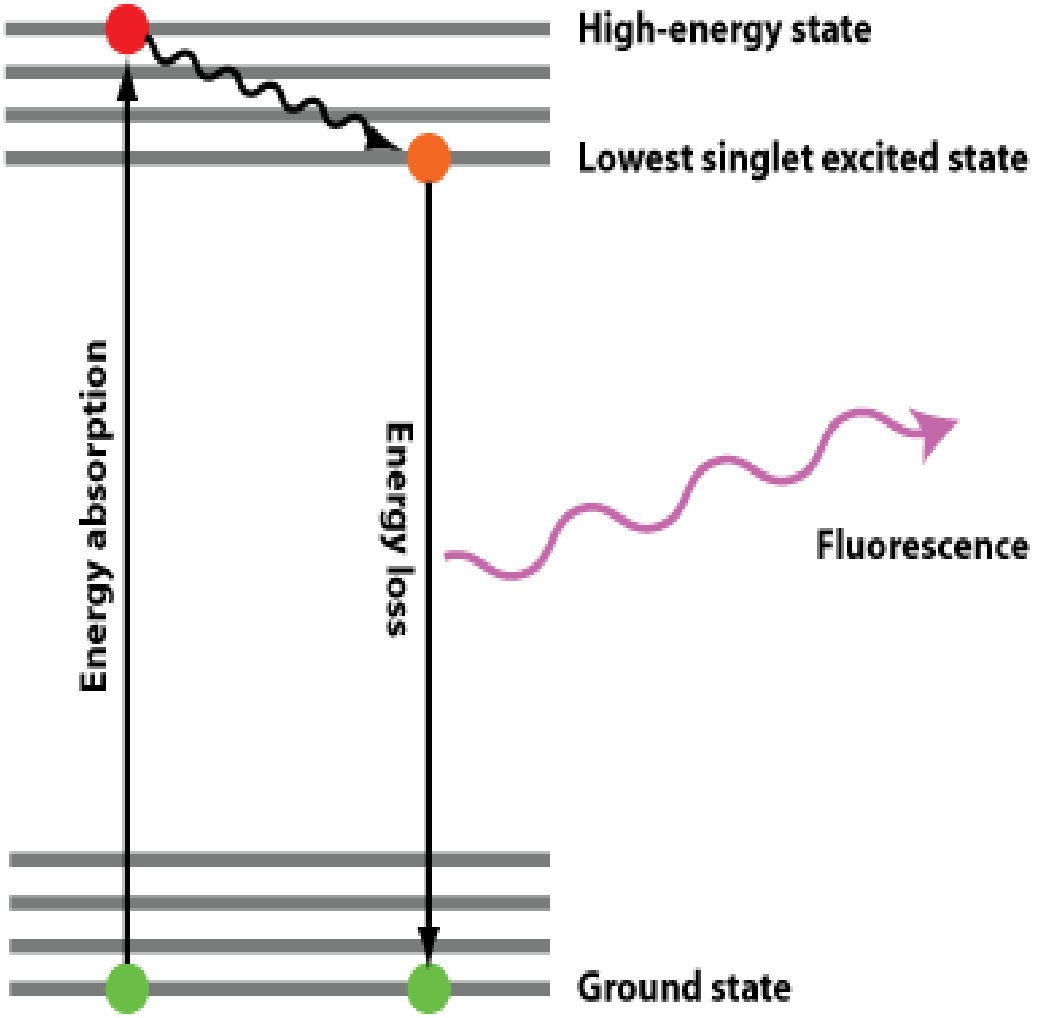


9,10-Bis(phenylethynyl)anthracene
9,10-BPEA (5)
$C_{30}H_{18}$



Rubrene (6)
$C_{42}H_{28}$

Jablonski diagram

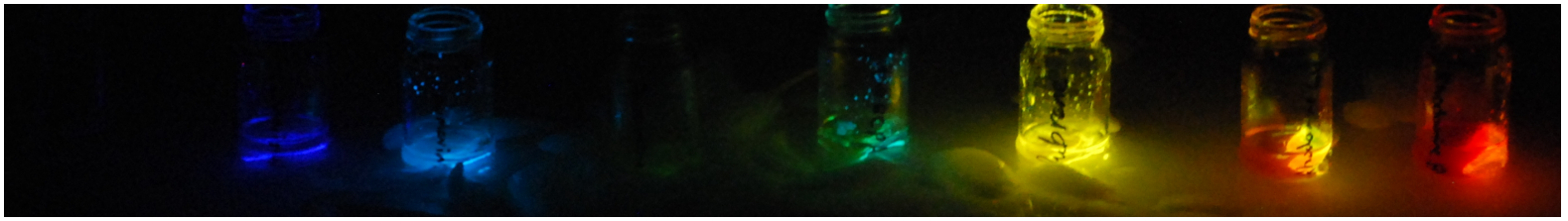


Http://www.wikipedia.org

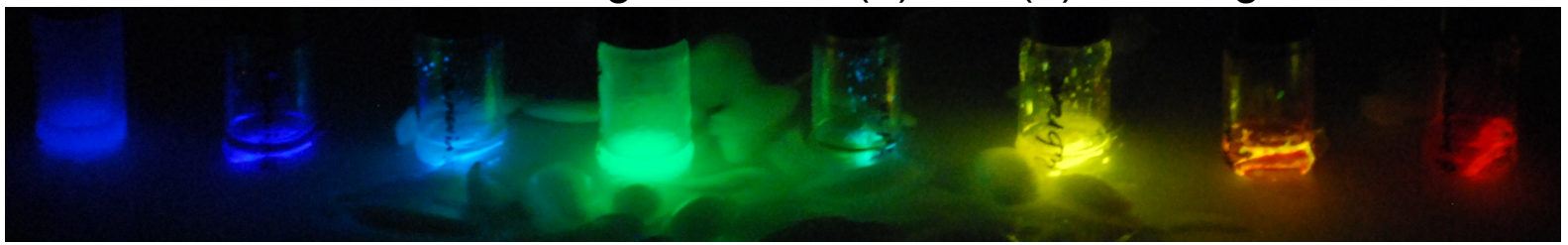
Http://www.google.com/imghp

http://www.bioimaging.dk/index.php?id=79

(1) (2) (3) (4) (5) (6) (7) (8)

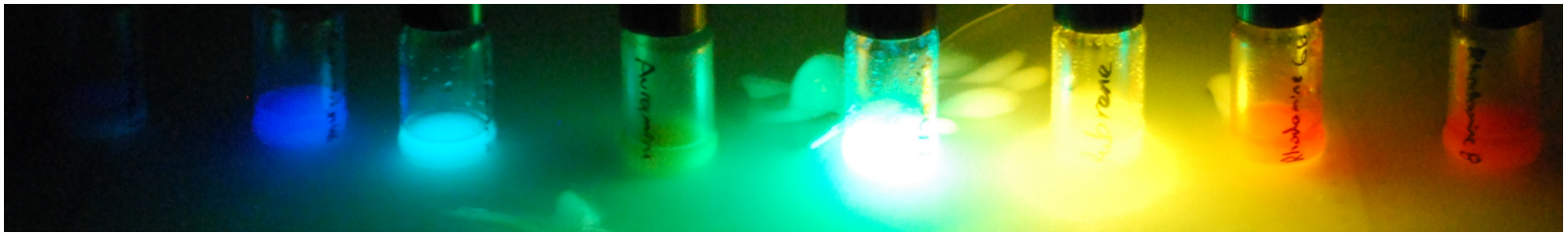


T = 0, without shaking, Solutions(1) and (4) do not glow.

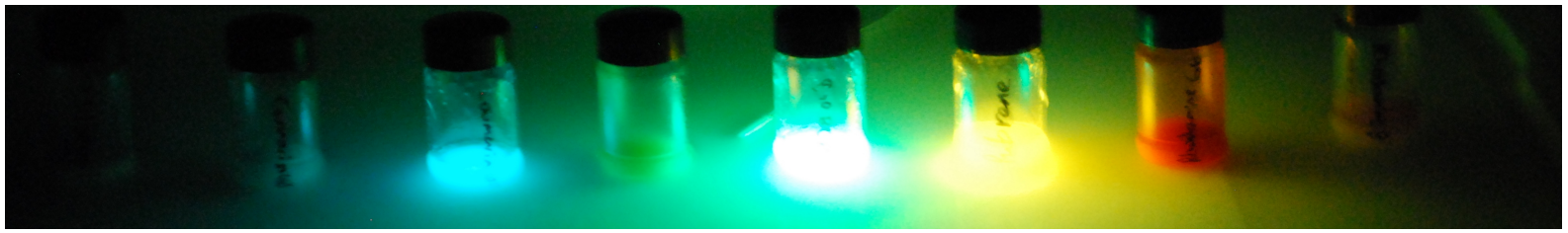


t = 3 min, only shook Solutions (1) and (4) to make them glow.

t = 10 min, shook all of the solutions, Solutions (1) and (4) start to dim.



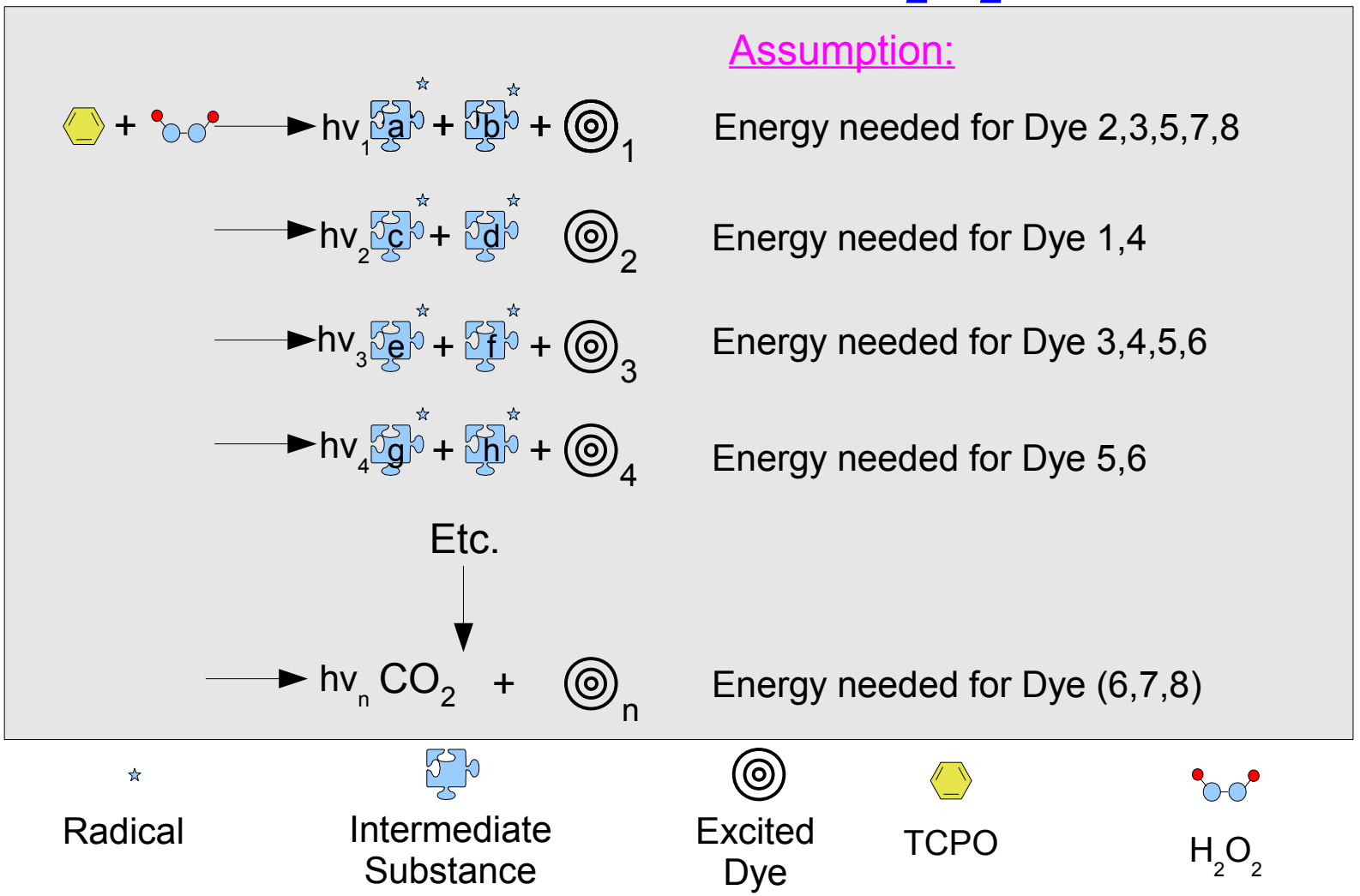
t = 30 min, Stilbene 3 - Solutions (1) and (4) are very dim.



t = 90 min, Courmine 460 - Solution (2) stops glowing.

Question: Why do all dyes glow?

Possible Steps of a TCPO/H_2O_2 Reaction?



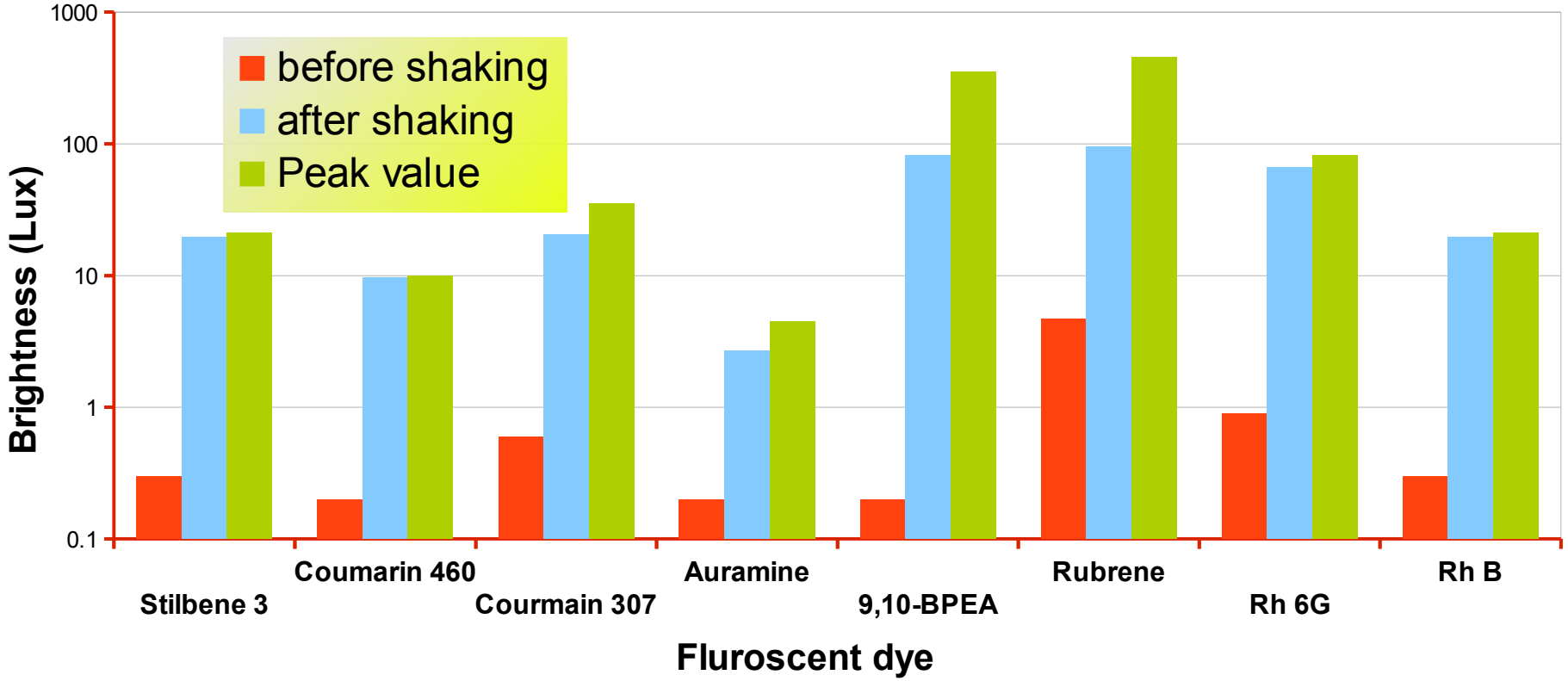
- **Many steps are needed to reach the final state.**
- **Each step generates different wave lengths of energies potentially absorbed by dyes depending on their excitation energy.**
- **Dyes then emit lights of corresponding wave length (colors).**
- **Glowing strength depends on the excitation energy, availability of electrons in the fluorescent dyes, and the efficiency of the dyes.**

Glowing Color in Diethyl Phthalate

Dye	Color of Glow	Estimated wavelength (nm)
Stilbene 3(1)	Violet/blue	~430-450
Coumarin 460 (2)	Navy Blue	~450-460
Coumarin 307 (3)	Turquoise Blue	~480-500
Auramine (4)	Green	~530-540
9,10-Bis(phenylethynyl)anthracene (9,10-BPEA) (5)	Turquoise Green	~500, -550
Rubrene (6)	Bright Yellow	~590-600
Rhodamine 6G (7)	Green, Orange	~540, ~630
Rhodamine B (8)	Red	~640-660

- The colors of those dyes are very similar to the reported colors
- Some dyes emit different colors depending on the energy level at which the electrons are excited.

Brightness of the Glow

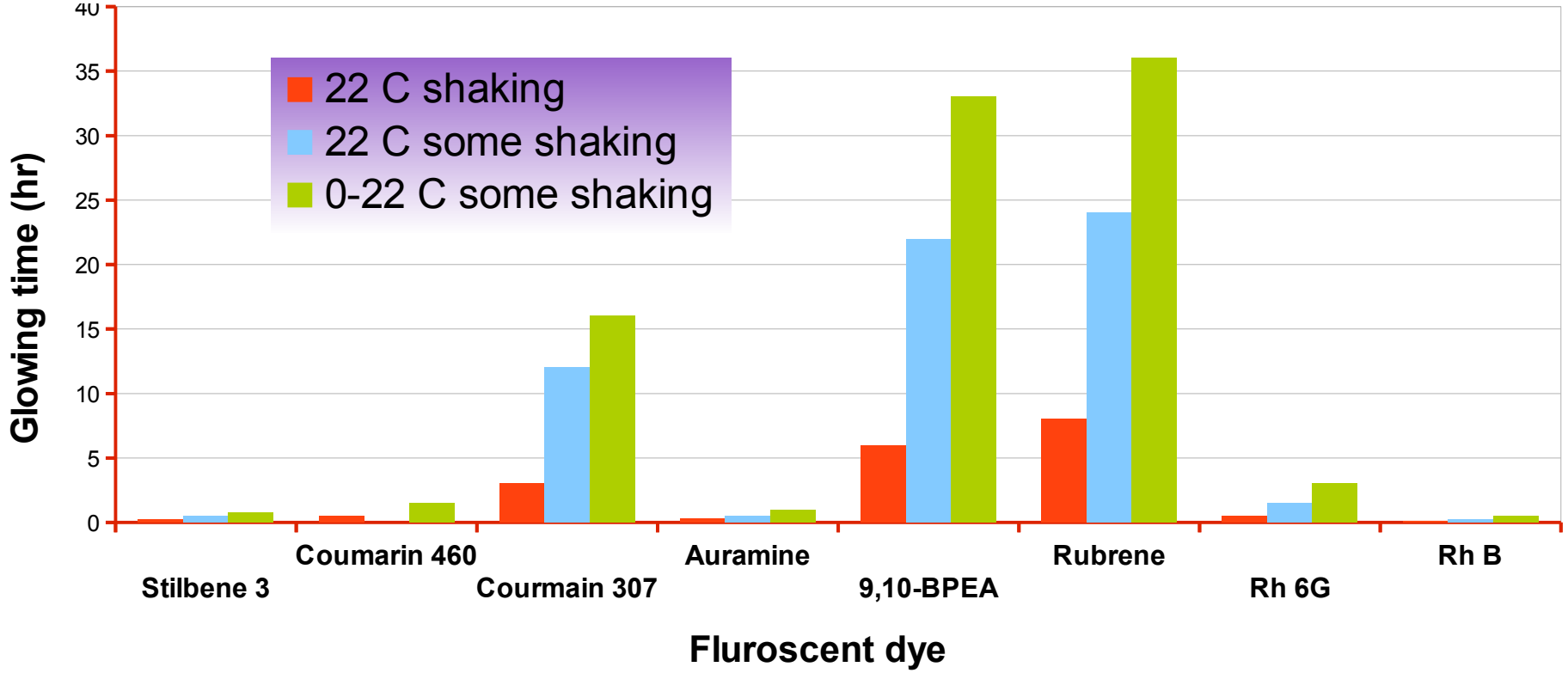


- Without shaking, with the exception of Rubrene and Rh 6G, all other dyes are barely visible
- After shaking, Rubrene and 9,10-BPEA are the brightest dyes whereas Auramine does not glow much and quickly stops glowing.

Lux is a SI unit of illumination measuring the luminous flux per unit of area. One Lux is equal to one lumen per square meter.

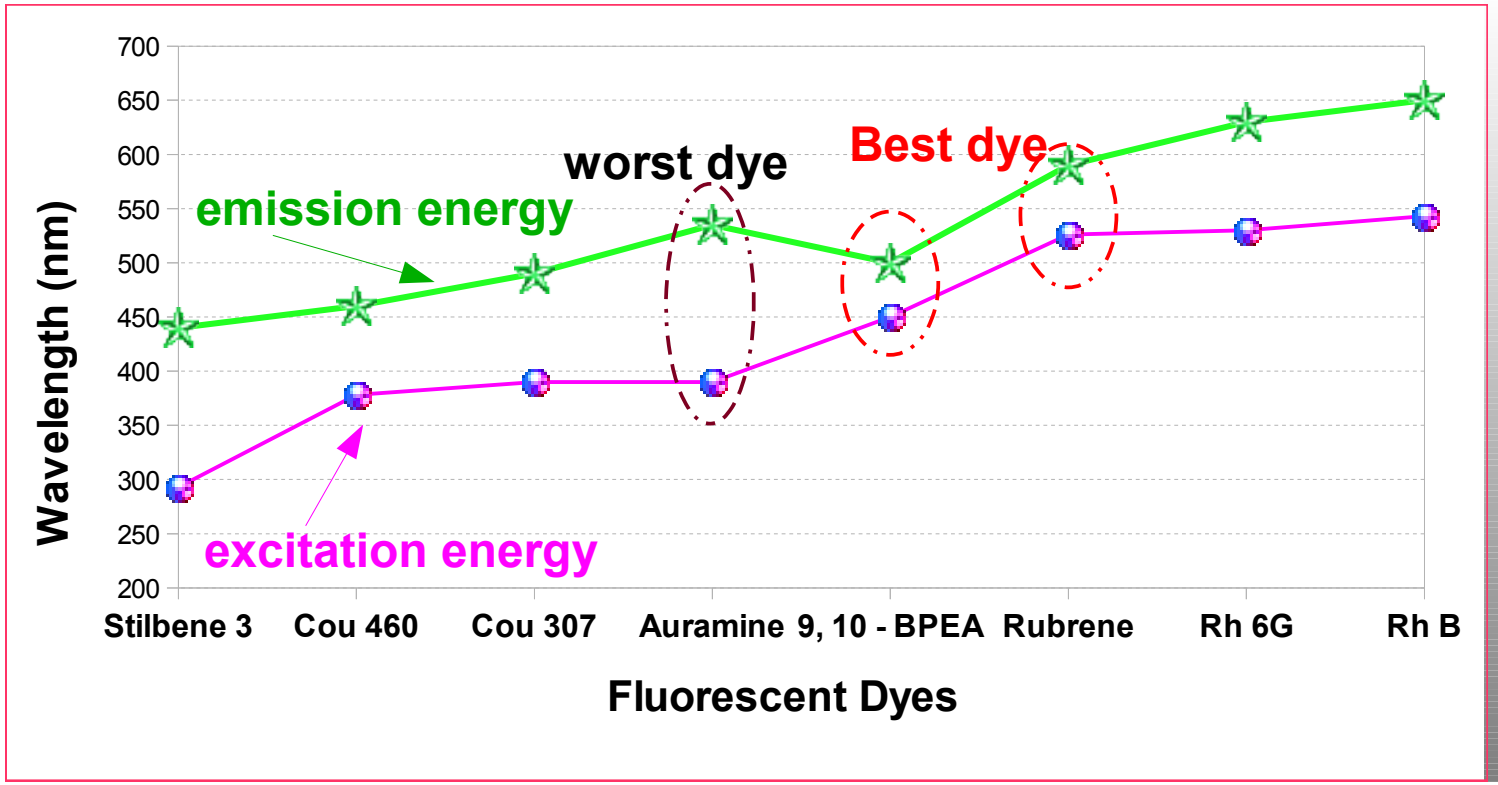
Full moon on a clear night: 0.27 lux
Office light: 320 – 500 lux
Full daylight: 10,000-25,000 lux
Direct sunlight: 32,000-130,000 lux

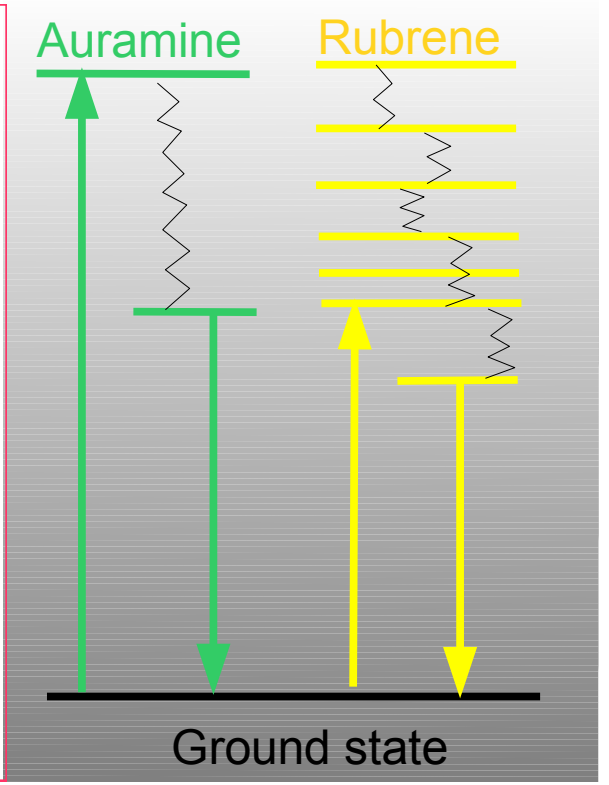
Effect of Expt. Conditions on Glowing Time



- The reaction can last more than 36 hours at cooler temperature with modestly shaking.
- Both 9,10 – BPEA and Rubrene last the longest because their electrons can be excited at different energies, and these dyes have more available electrons to be excited.
- Coumarin 307 also lasts >16 hours. However, in order to glow after one hour, it requires vigorous shakes. Shaking allows H_2O_2 and TCPO to contact and react.

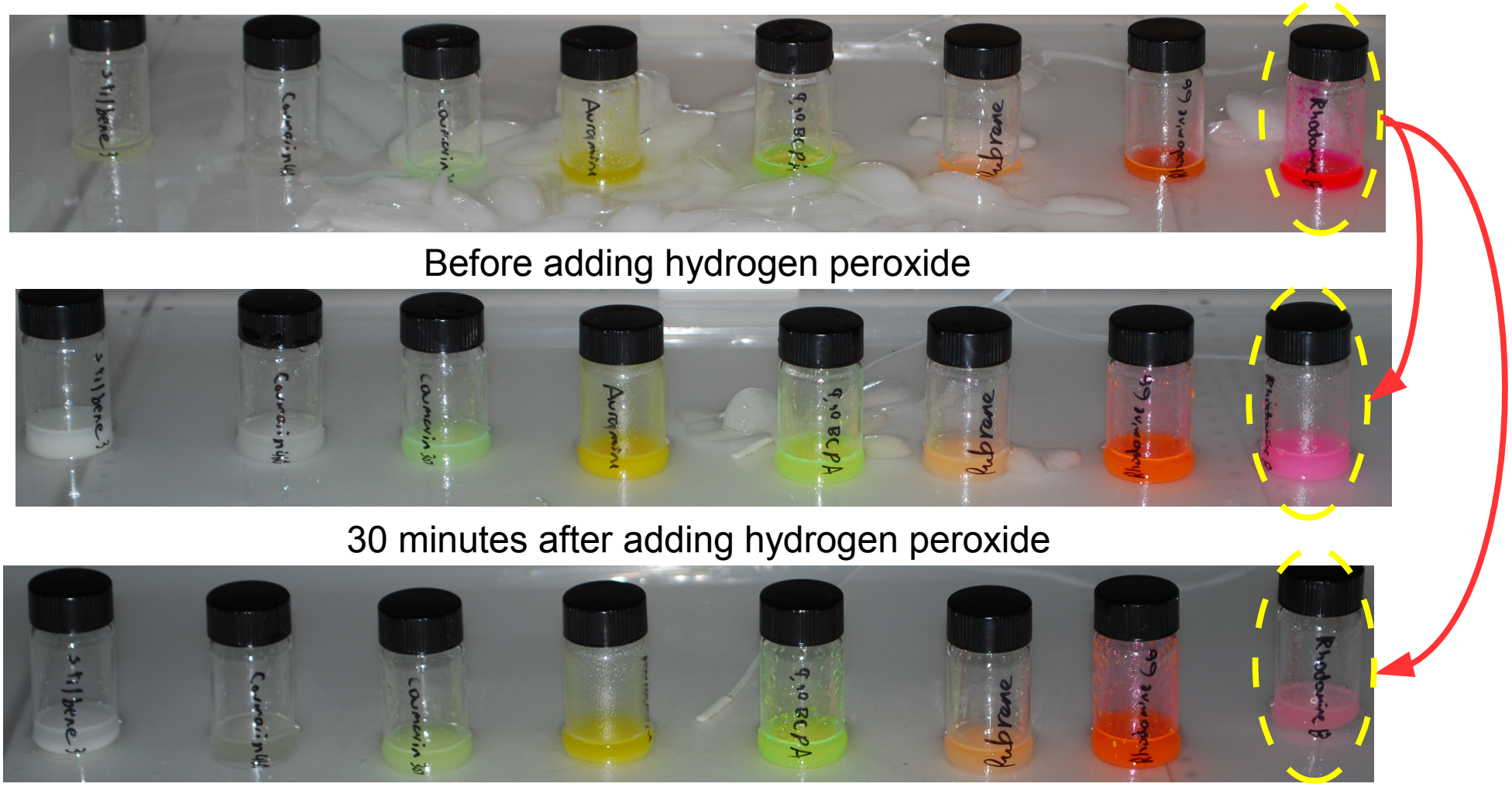
Brightness vs Dye Efficiency





- The dyes with smaller differences between excitation and emission energies have higher efficiencies, so they have more electrons available to be excited.
- The conjugated molecules, like Rubrene and 9,10-BPEA, have lower excitation energies, so their electrons are easily excited. They have the brightest glow!

Before and After Reaction



Before adding hydrogen peroxide

30 minutes after adding hydrogen peroxide

160 minutes after adding hydrogen peroxide

- Rhodamine B may be destroyed by hydrogen peroxide; becoming a substance which can no longer convert energy into light. Therefore, it stops glowing after a short time (<30 mins).

Conclusions

- Many factors - adding sodium acetate, increasing temperature, and shaking, accelerate the reaction rate and make dyes to glow brighter but shorten the glowing time.
- The molecular structures of fluorescent dyes determine the glow color and glow brightness.
- The purple dyes do not necessarily glow shorter than the red dyes; the combination of the excitation energy and the reaction time determines the glow time.
- The reaction between TCPO and hydrogen peroxide is more complicated than it is reported. There are some intermediate steps before reaching the final state – making many dyes glow!
- By using right combination of chemicals, organic solvents, additives, and fluorescent dyes, the brighter and longer glowing solution can be obtained.
- Chemiluminescent reactions are widely used in chemistry,biology, medical, and entertaining industries.

Acknowledgments

Thank to my parents for discussion, inspiration, encouragement, and help on the experiments. Thank LANL to donate the fluorescent dyes, and some accessories (safety glasses, gloves, and glass vials) so that I am able to conduct my experiments. I also thank a private company for providing some of the chemicals.

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