TSRI
Oct 31, 2011

Chemiluminescence

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Luminescence and others

- *Luminescence* - a spontaneous emission of radiation from an electronically excited species (or from a vibrationally excited species) not in thermal equilibrium with its environment

- *Incandescence* - a spontaneous emission of radiation from a body in thermal equilibrium with its envoronment (independent of the body's composition!)

- *Radioactivity* - a spontaneous emission of "ionizing particles" from an atomic nucleous of an unstable atom (not limited to electromagnetic radiation!)

Luminescence: Types

- Photoluminescence (photoexcitation)
    - fluorescence (spin multiplicity retained, “allowed”)
    - phosphorescence (spin multiplicity changed, “forbidden”)
- Chemiluminescence (chemical reaction, Eilhard Wiedemann, 1888)
    - electrochemiluminescence (electrochemical reaction)
- Bioluminescence (living organisms)
- Electroluminescence (electric current)
    - cathodoluminescence (electron beam)
- Radioluminescence (ionizing radiation)
- Sonoluminescence (cavitation)
- Thermoluminescence (re-emission of absorbed radiation upon heating)
- Mechanoluminescence (mechanical action)
    - triboluminescence (breakage of chemical bonds)
    - fractoluminescence (crystal fracture)
    - piezoluminescence (deformation)
- Lyoluminescence (dissolution of irradiated solid)

Chemiluminescence: The Basics

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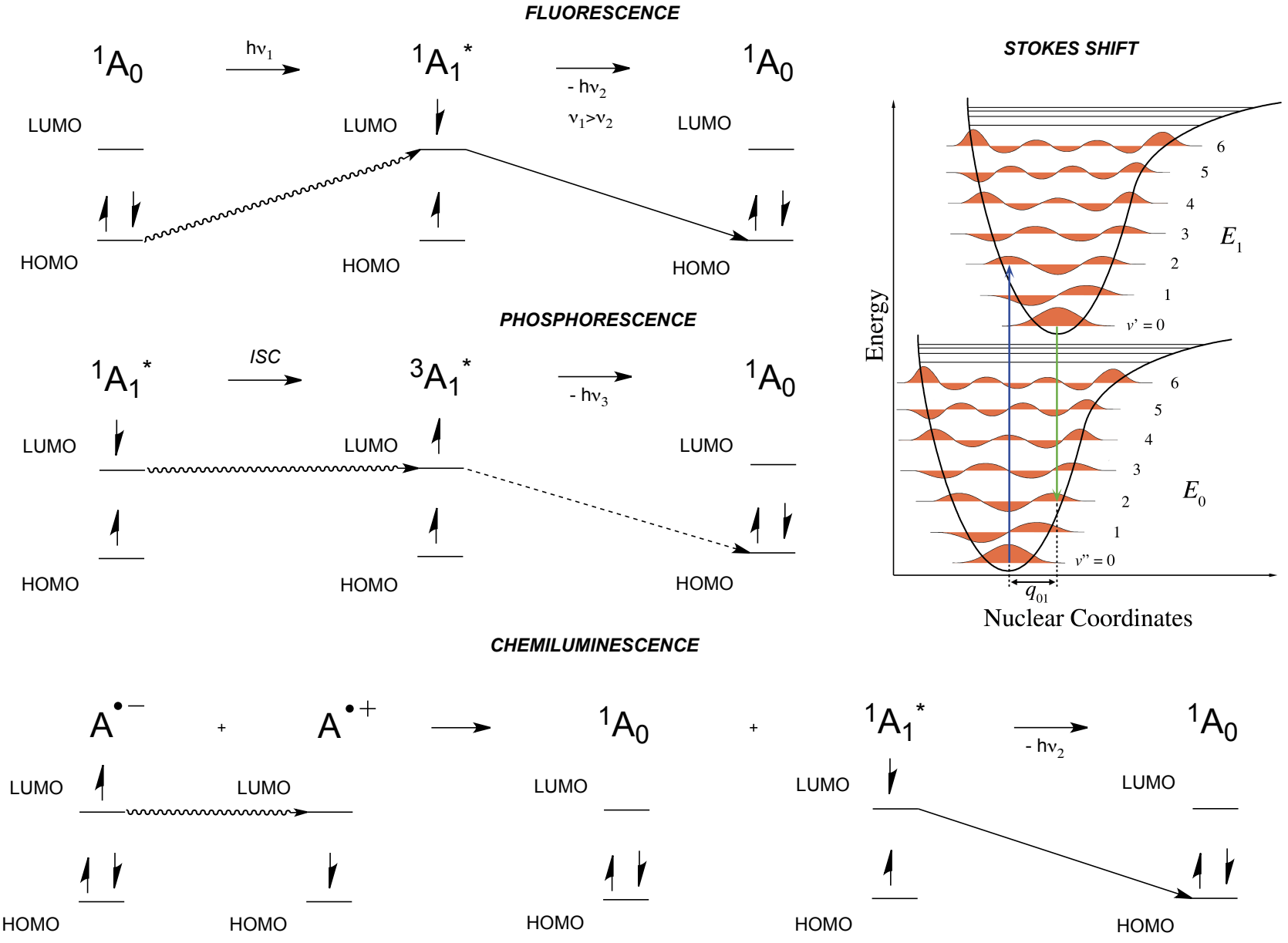

Chemiluminescence: Criteria

Criteria for a “successful” chemiluminescent reaction

- Sufficient excitation energy provided (by the chemical reaction)

  for red emission (λ = 600 nm) 47.6 kcal/mol
  for blue emission (λ = 450 nm) 63.5 kcal/mol
- Formation of products capable of forming an excited state

  multiple bonds, conjugation, aromatic systems
- Presence of an emitter (doesn’t have to be a product)

  multiple bonds, conjugation, aromatic systems
- Rapid kinetics (of the chemical reaction)

  rate is more important than high yield (ϕ_{CL})

  $\phi_{CL} = \phi_{rxn}$(rxn) × ϕ_f(fluor.) << 10% (typical)
- Reaction coordinate system must favor formation of an excited state over ground state of product(s)

Chemiluminescence: Excited State vs. Ground

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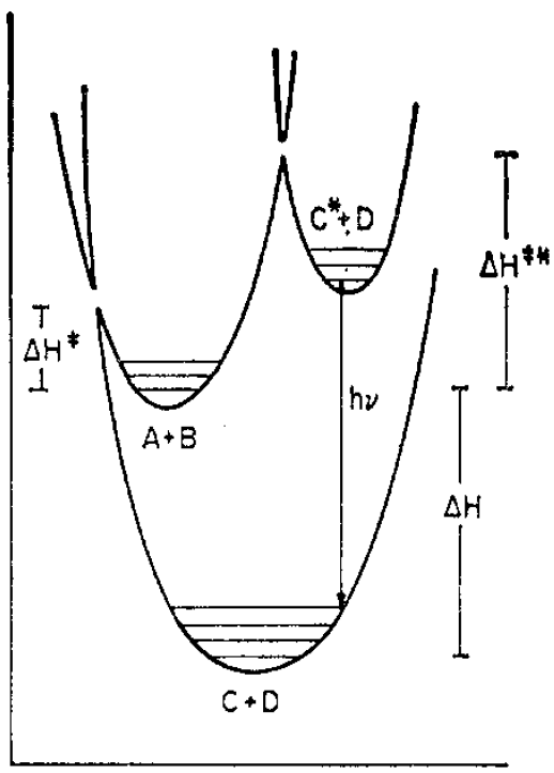
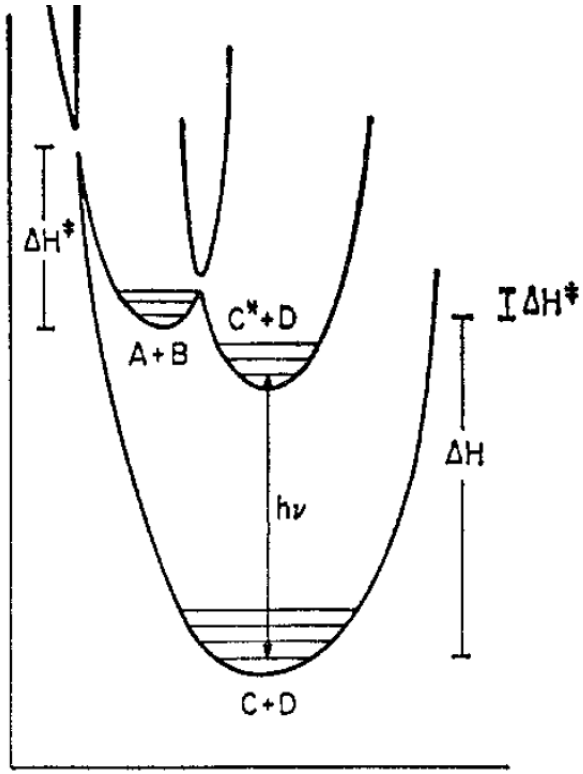
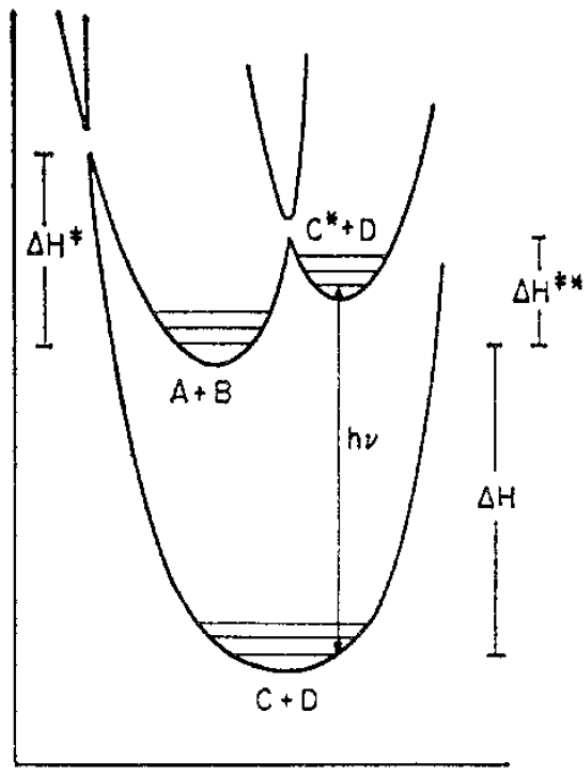


Non chemiluminescent reaction
(product is fluorescent)
$\Delta H^{\neq *} > \Delta H^{\neq}$



Chemiluminescent reaction
($h\nu < \Delta H$)
$\Delta H^{\neq *} < \Delta H^{\neq}$



Chemiluminescent reaction
($h\nu > \Delta H$)
$\Delta H^{\neq *} > \Delta H^{\neq}$

For highly exothermic reactions accompanied by small configurational changes production of an excited state of product(s) is more probable than ground

Electrochemiluminescence: Annihilation

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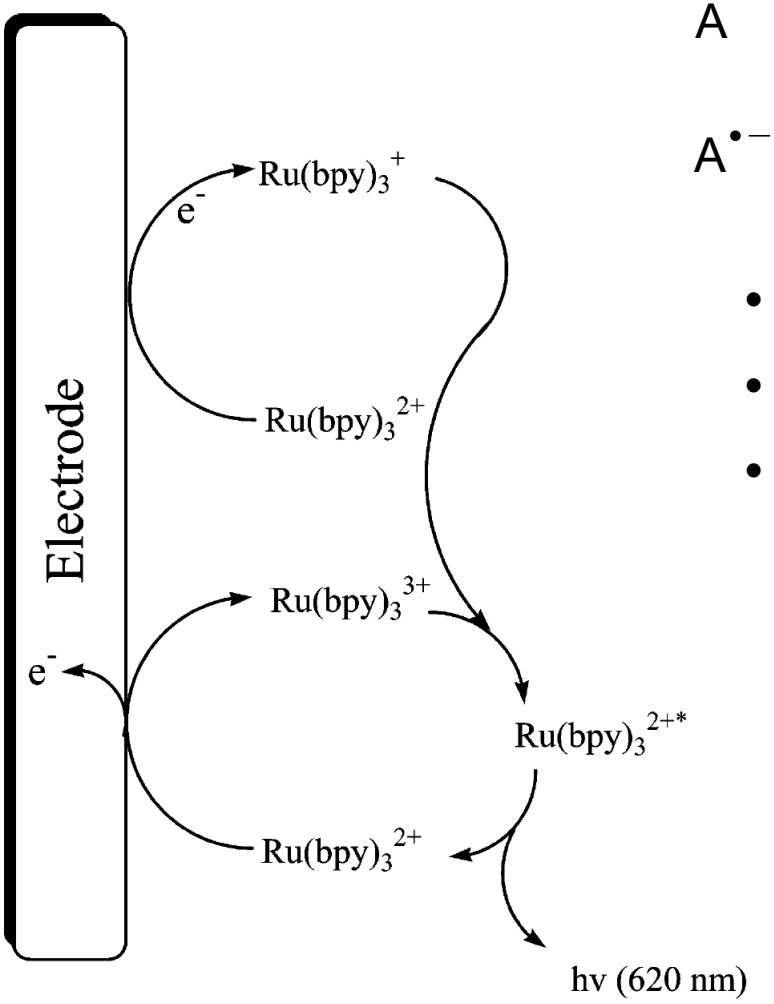
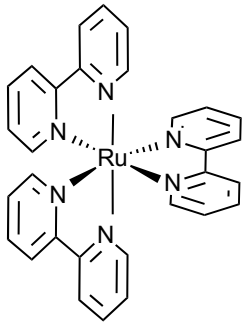


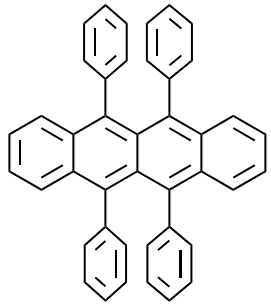
$$A + e^- \longrightarrow A^{\bullet -} \qquad B - e^- \longrightarrow B^{\bullet +}$$

$$A^{\bullet -} + B^{\bullet +} \longrightarrow A(B) + B(A)^* \longrightarrow B(A) + h\nu$$

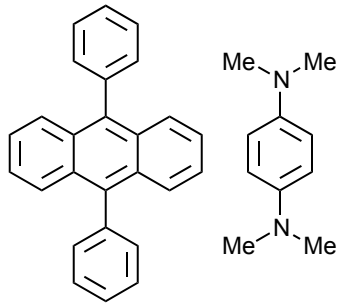
- Necessity for potential alternation
- Stability of $A^{\bullet -}$ and $B^{\bullet +}$ generated
- Sufficient potential window of solvent



$Ru(bpy)_3$



Rubrene



DPA/TMPD system

Early examples of electroluminescence were based almost exclusively on annihilation

Electrochemiluminescence: Co-Reactants

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"Oxidative-Reductive" scenario

$$\text{(Luminophore)} - e^- \longrightarrow \text{(Luminophore)}^+$$

$$\text{(Co-reactant)} - e^- \longrightarrow [\text{(Co-reactant)}^+] \longrightarrow \text{(Reductant)}^-$$

$$\text{(Luminophore)}^+ \xrightarrow{\text{(Reductant)}^-} \text{(Luminophore)}^* \xrightarrow[-\ h\nu]{} \text{(Luminophore)}$$

"Reductive-Oxidative" scenario

$$\text{(Luminophore)} + e^- \longrightarrow \text{(Luminophore)}^-$$

$$\text{(Co-reactant)} + e^- \longrightarrow [\text{(Co-reactant)}^-] \longrightarrow \text{(Oxidant)}^+$$

$$\text{(Luminophore)}^- \xrightarrow{\text{(Oxidant)}^+} \text{(Luminophore)}^* \xrightarrow[-\ h\nu]{} \text{(Luminophore)}$$

Electrochemiluminescence: Co-Reactants

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"Oxidative-Reductive" scenario

Ru/Oxalate system

$$Ru(bpy)_3^{2+} - e \rightarrow Ru(bpy)_3^{3+}$$

$$Ru(bpy)_3^{3+} + C_2O_4^{2-} \rightarrow Ru(bpy)_3^{2+} + C_2O_4^{\bullet -}$$

$$C_2O_4^{\bullet -} \rightarrow CO_2^{\bullet -} + CO_2$$

$$Ru(bpy)_3^{3+} + CO_2^{\bullet -} \rightarrow Ru(bpy)_3^{2+*} + CO_2$$

$$Ru(bpy)_3^{2+} + CO_2^{\bullet -} \rightarrow Ru(bpy)_3^{+} + CO_2$$

$$Ru(bpy)_3^{3+} + Ru(bpy)_3^{+} \rightarrow Ru(bpy)_3^{2+*} + Ru(bpy)_3^{2+}$$

$$Ru(bpy)_3^{2+*} \rightarrow Ru(bpy)_3^{2+} + h\nu$$

"Reductive-Oxidative" scenario

Ru/Persulfate system

$$S_2O_8^{2-} + e \rightarrow S_2O_8^{\bullet 3-}$$

$$Ru(bpy)_3^{2+} + e \rightarrow Ru(bpy)_3^{+}$$

$$Ru(bpy)_3^{+} + S_2O_8^{2-} \rightarrow Ru(bpy)_3^{2+} + S_2O_8^{\bullet 3-}$$

$$S_2O_8^{\bullet 3-} \rightarrow SO_4^{2-} + SO_4^{\bullet -}$$

$$Ru(bpy)_3^{+} + SO_4^{\bullet -} \rightarrow Ru(bpy)_3^{2+*} + SO_4^{2-}$$

$$Ru(bpy)_3^{2+} + SO_4^{\bullet -} \rightarrow Ru(bpy)_3^{3+} + SO_4^{2-}$$

$$Ru(bpy)_3^{3+} + Ru(bpy)_3^{+} \rightarrow Ru(bpy)_3^{2+*} + Ru(bpy)_3^{2+}$$

Typical inorganic luminophores include complexes of Ru, Re, Pt, Os, Mo, Ir, Eu

Typical co-reactants include oxalate, persulfate, tripropylamine, substituted biphenyls

Co-Reactant ECL: Ruthenium-Tripropylamine system

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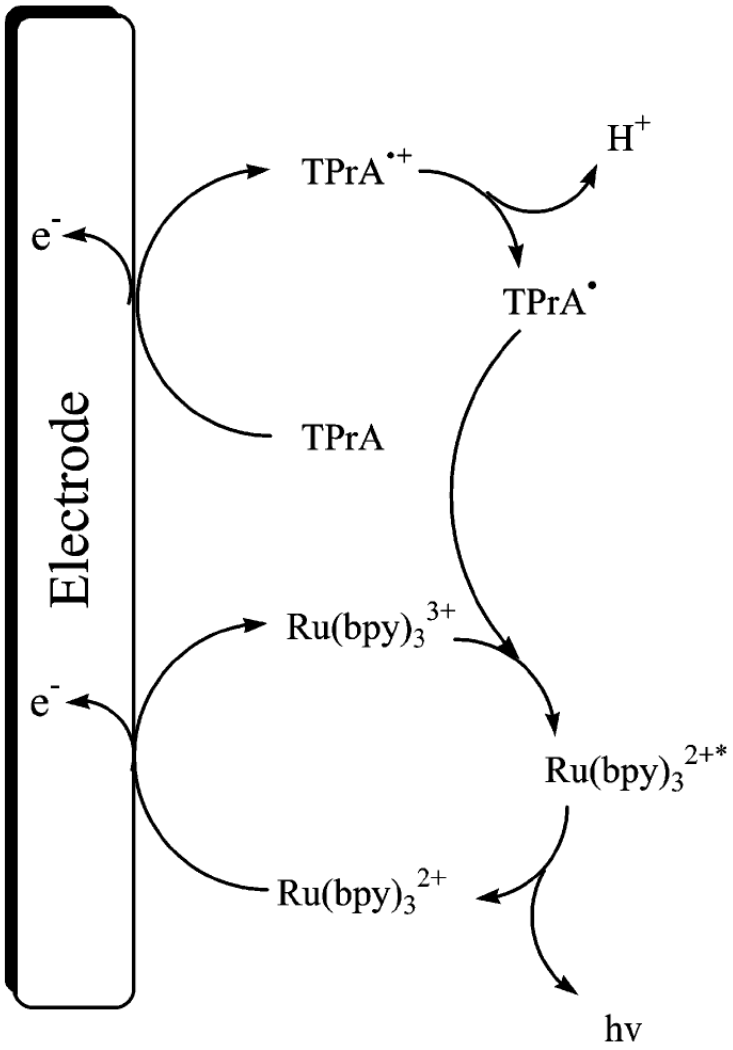

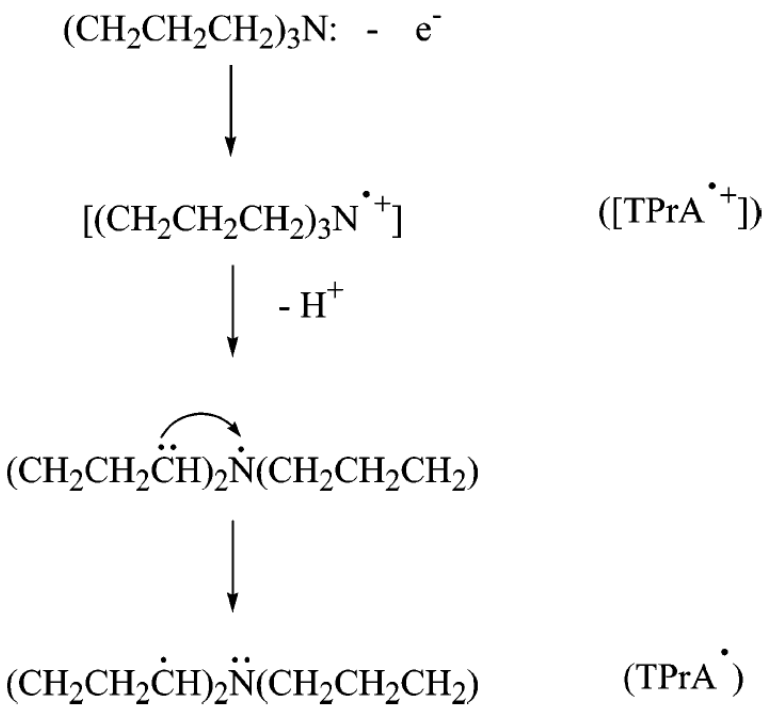

Co-Reactant ECL: Ruthenium-Tripropylamine system

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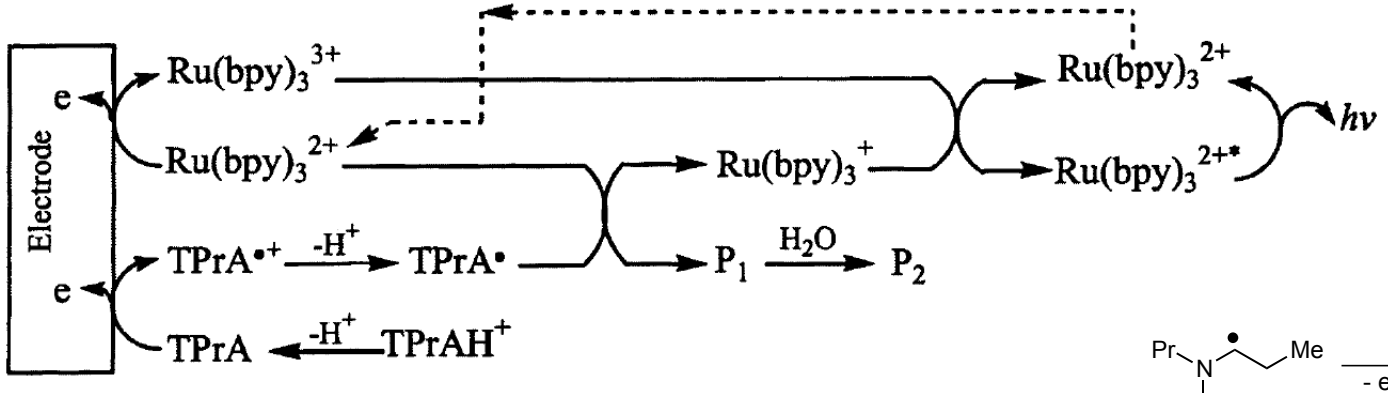

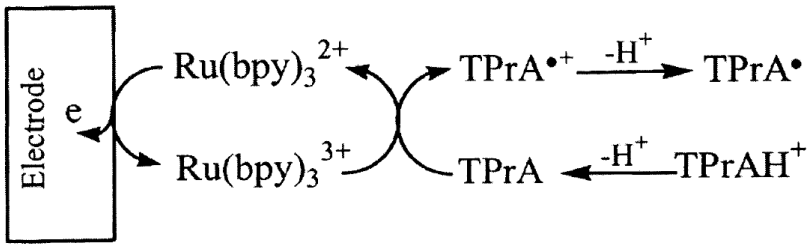

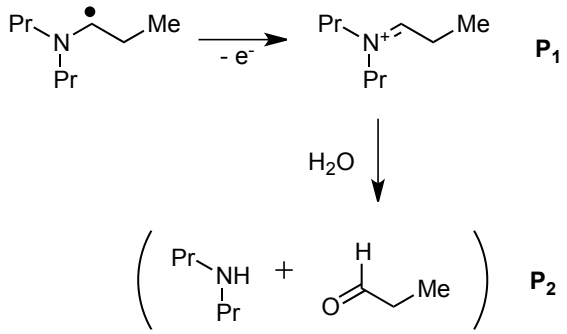

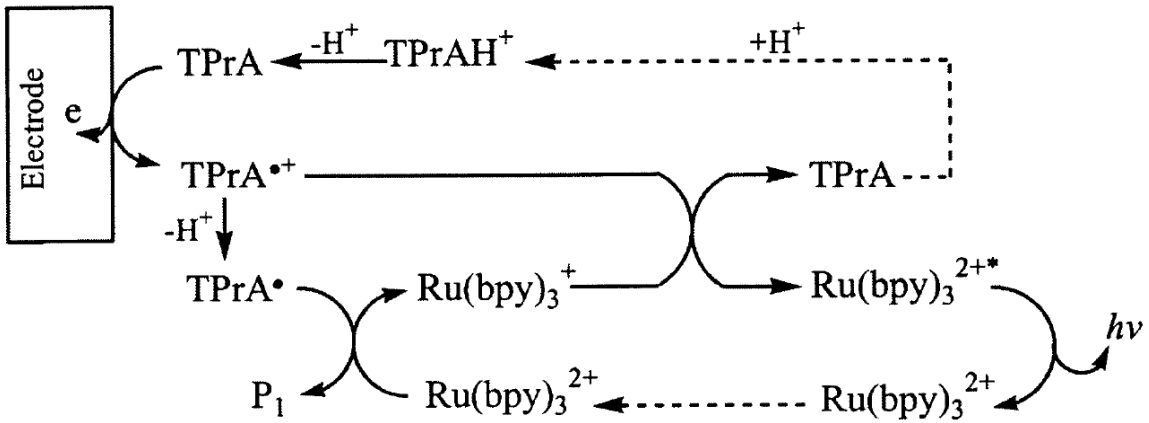

Ru(bpy)/TPrA remains to be the most widely utilized system in applied ECL

Chemiluminescence: Organic Peroxides

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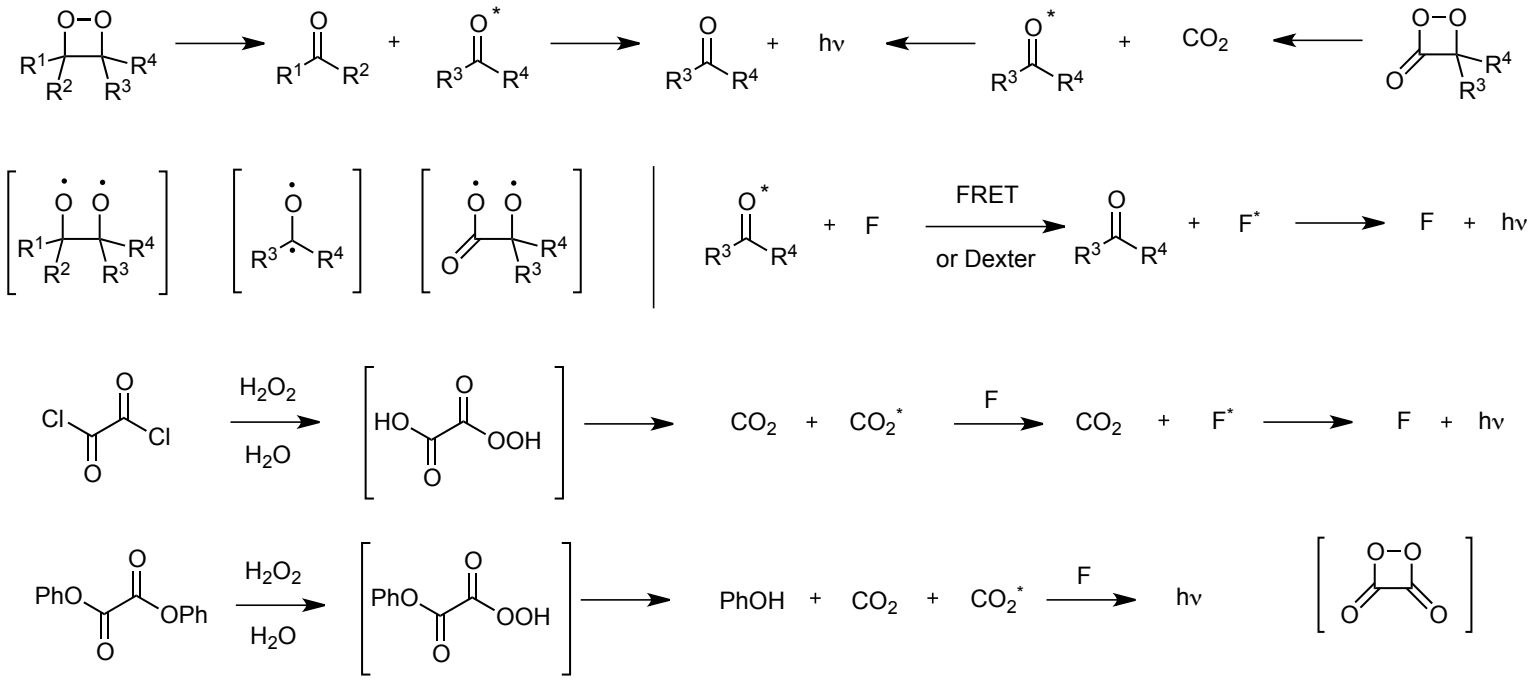

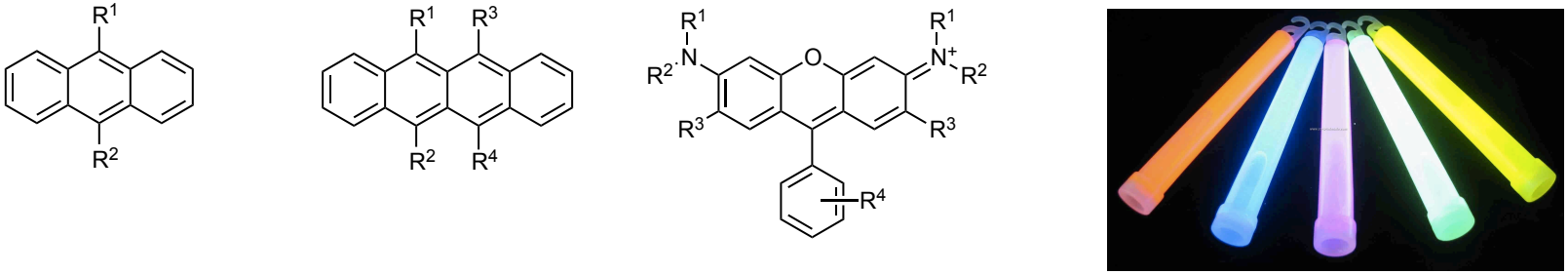

Lots of fluorescent dyes – lots of colors

Chemiluminescence: Luminol

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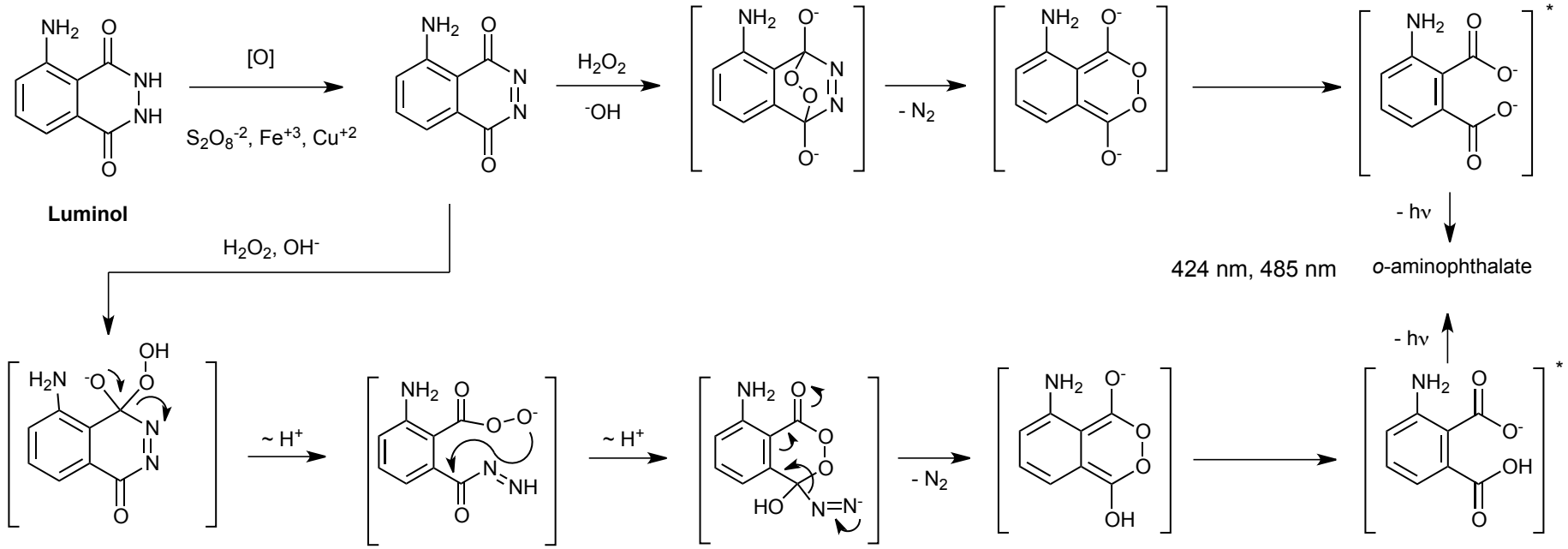

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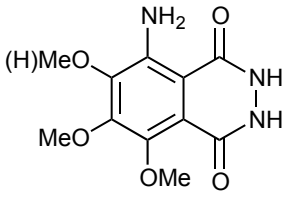

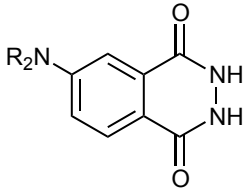

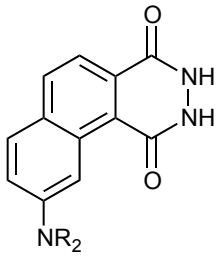

R = Me, Et, *n*-Pr

R,R = $-(CH_2)_4-$

Chemiluminescence: Lucigenin and Other Acridines

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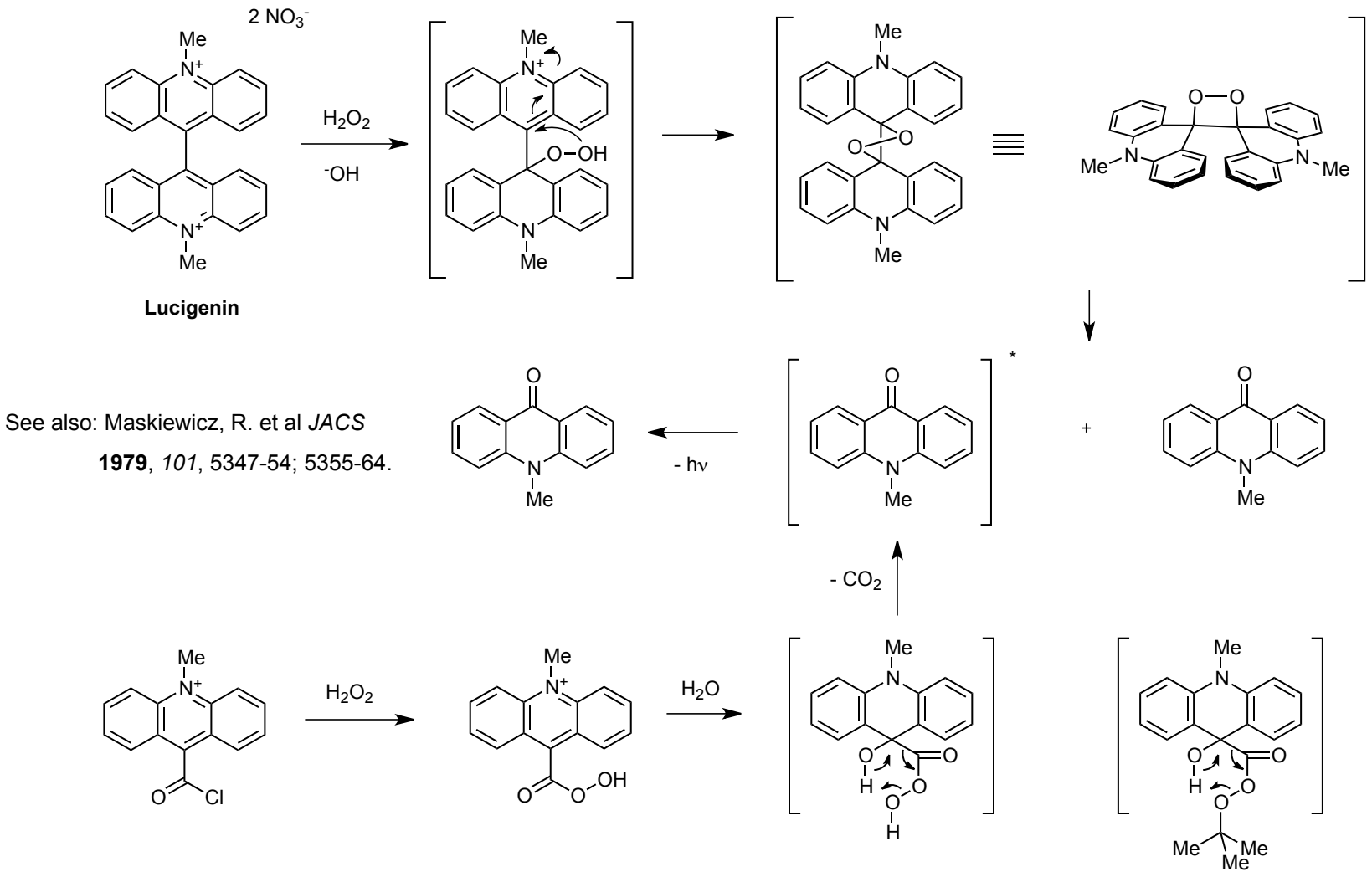

Chemiluminescence: Singlet Dioxygen

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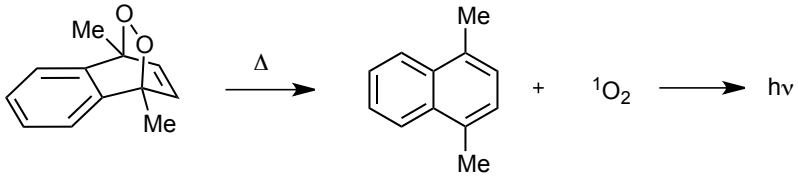
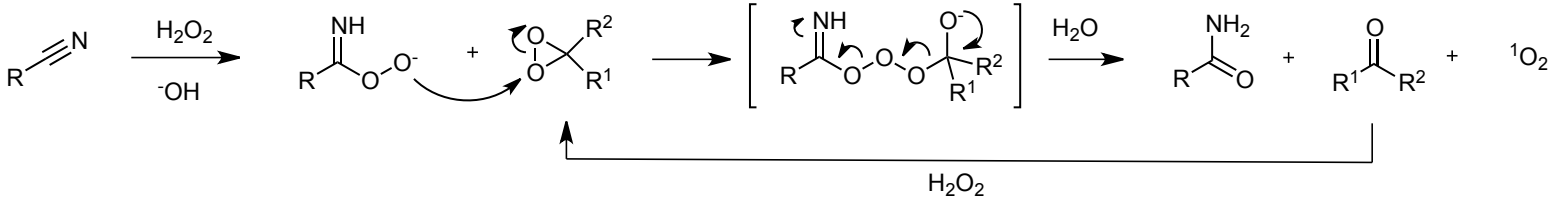
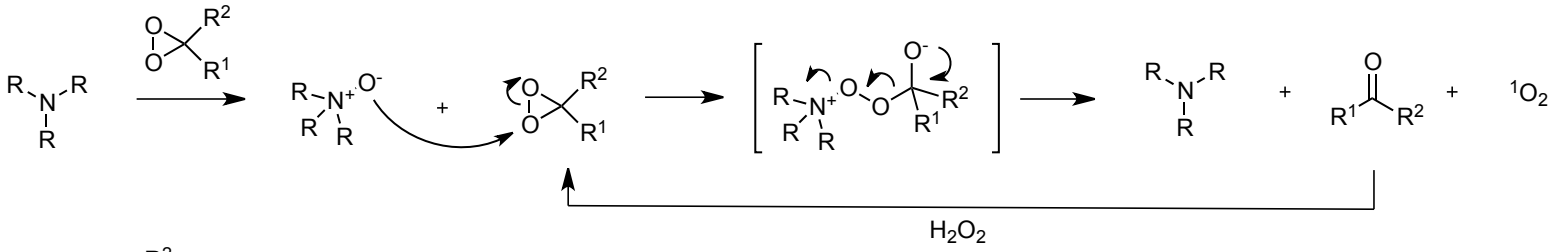
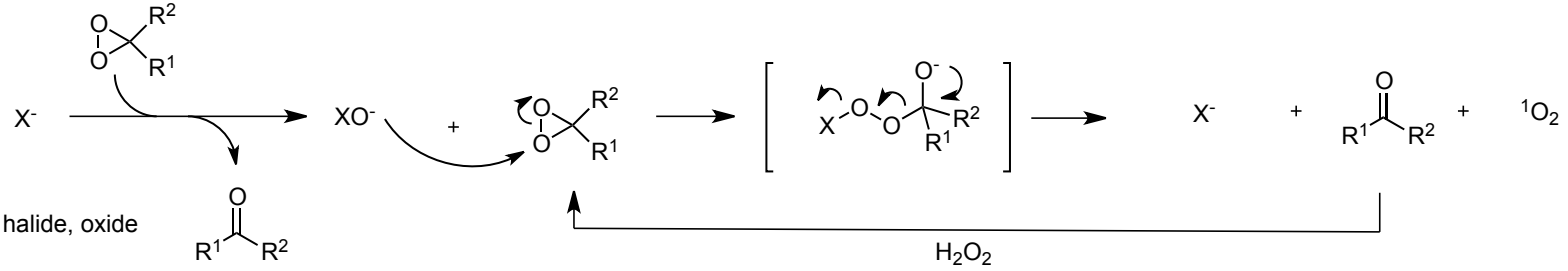


ΔE = 22.5 kcal/mol, emission at 1270 nm







Chemiluminescence: Bioluminescence

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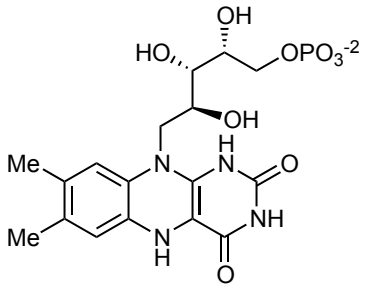
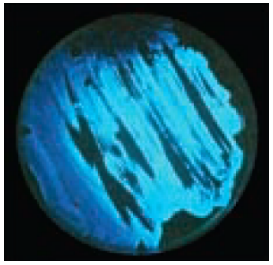
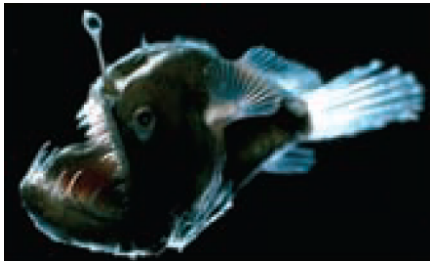
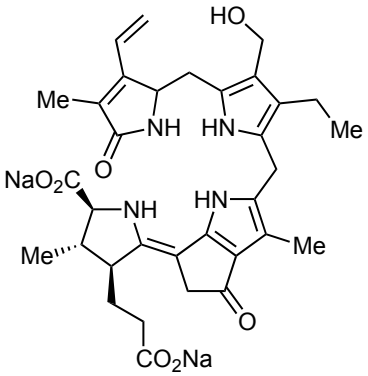


Bacterial luciferin



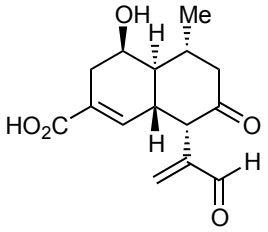


Found in marine bacteria, squid, and deep sea fish

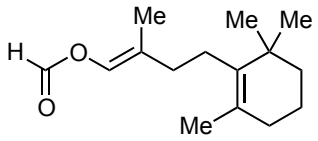


Dinoflagellate luciferin

Found in dinoflagellates and krill



Panal



Latia luciferin

From freshwater snail

Latia neritoides

Found in fungus

Panellus stipticus

Very often luciferins are acquired via food chain or symbiosis

Chemiluminescence: Bioluminescence

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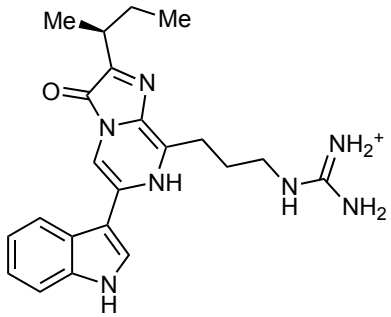
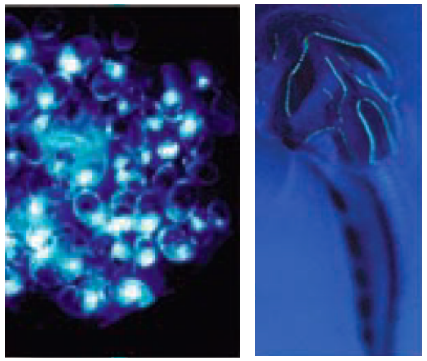
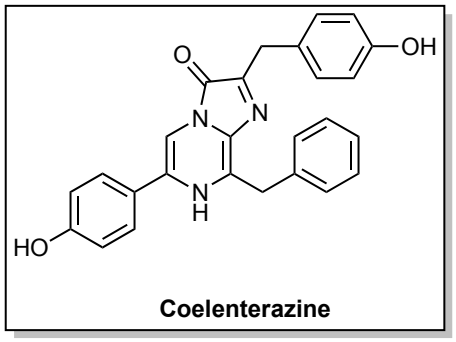


Cypridina-type luciferin (vargulin)



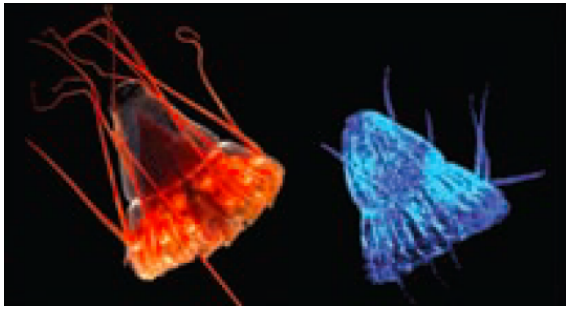
Found in osctracods, fish

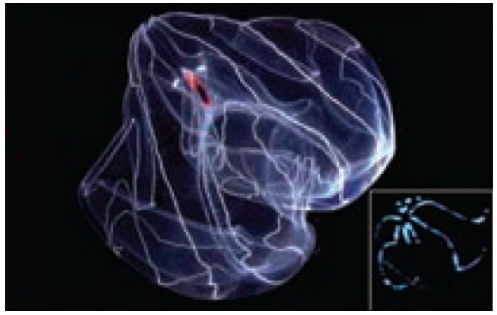
The most popular luciferin

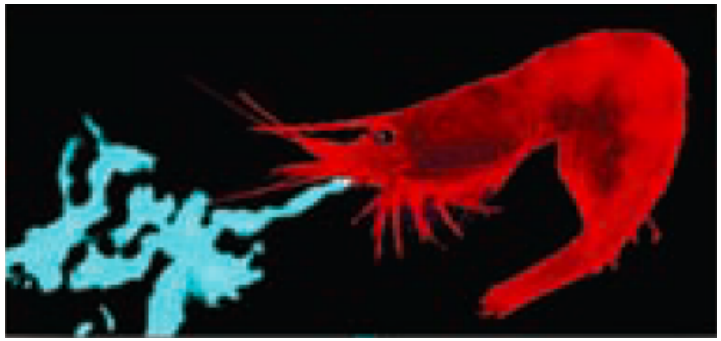


Coelenterazine

Found all over the ocean…







Chemiluminescence: Firefly Luciferin

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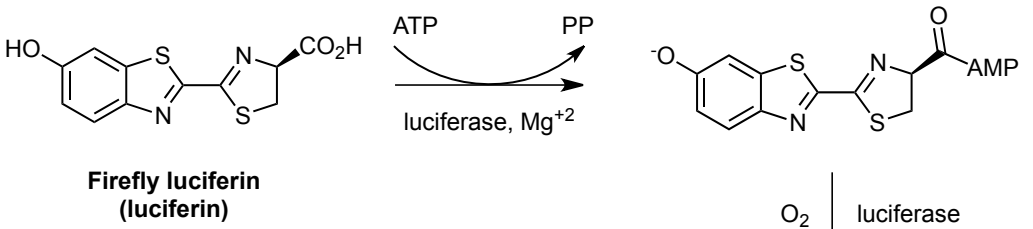
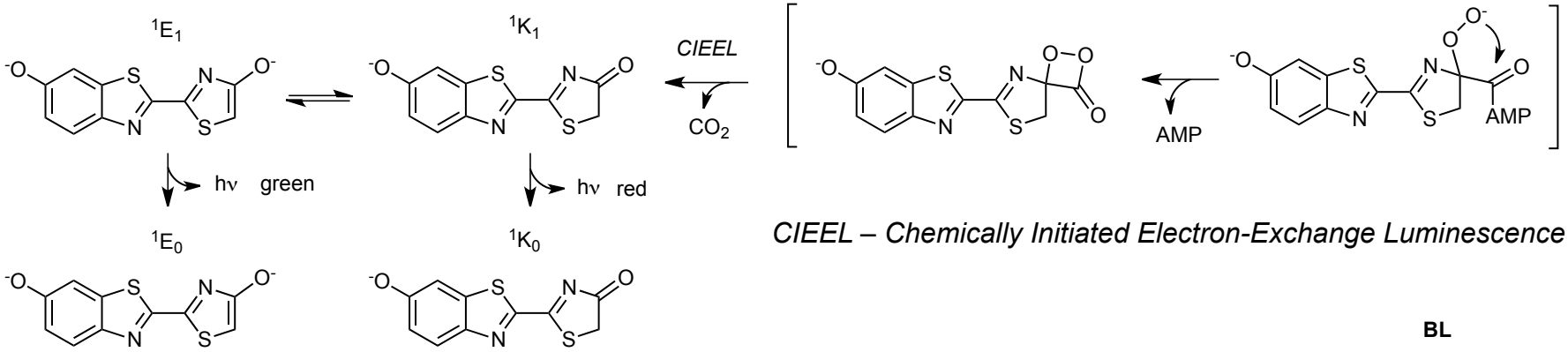
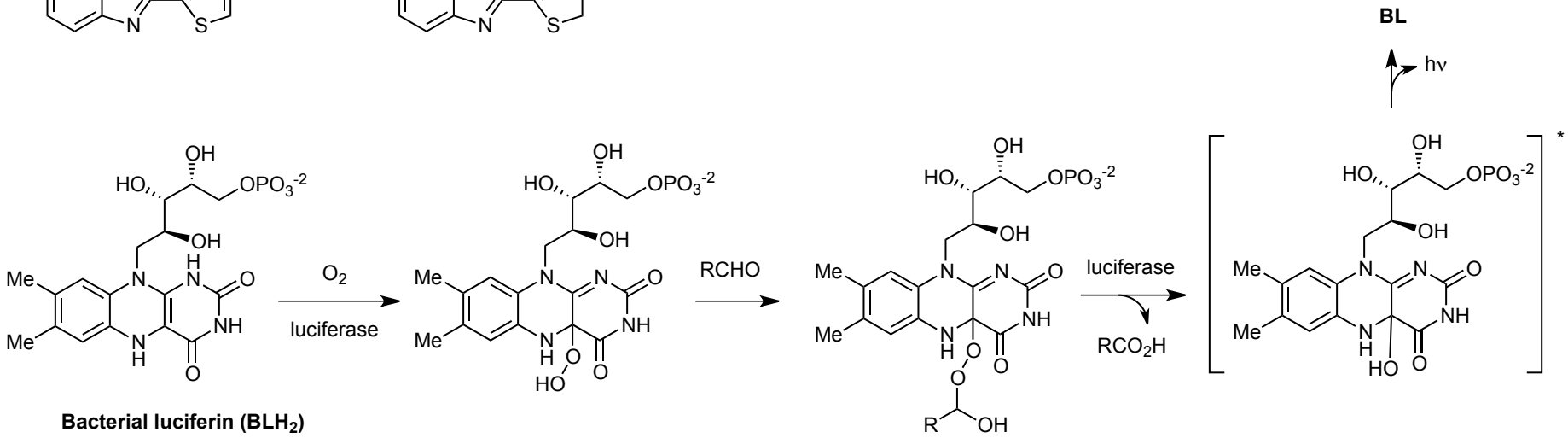
Photinus pyralis





CIEEL – Chemically Initiated Electron-Exchange Luminescence



Chemiluminescence: Applications

- Analysis
    - gas and liquid analysis (organic and inorganic analytes): water analysis, air analysis, etc.
    - bioassays :immunoassays, nucleic acid assays, blotting (Western, Southern, Northern), reporter gene-based assays, luciferase assay, BRET, etc.
    - *in vivo* imaging
- Lighting
    - will chemiluminescence replace LEDs?
- Entertainment
    - glow sticks, toys, etc.

Chemiluminescence: Resources

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