M.Sc. Semester-IV

Core Course-9 (CC-9)

Synthetic Organic Chemistry

III. Photochemistry

2. Absorption and Luminescence Processes, Energy Transfer Through Photosensitization

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III Photochemistry 10 Hrs

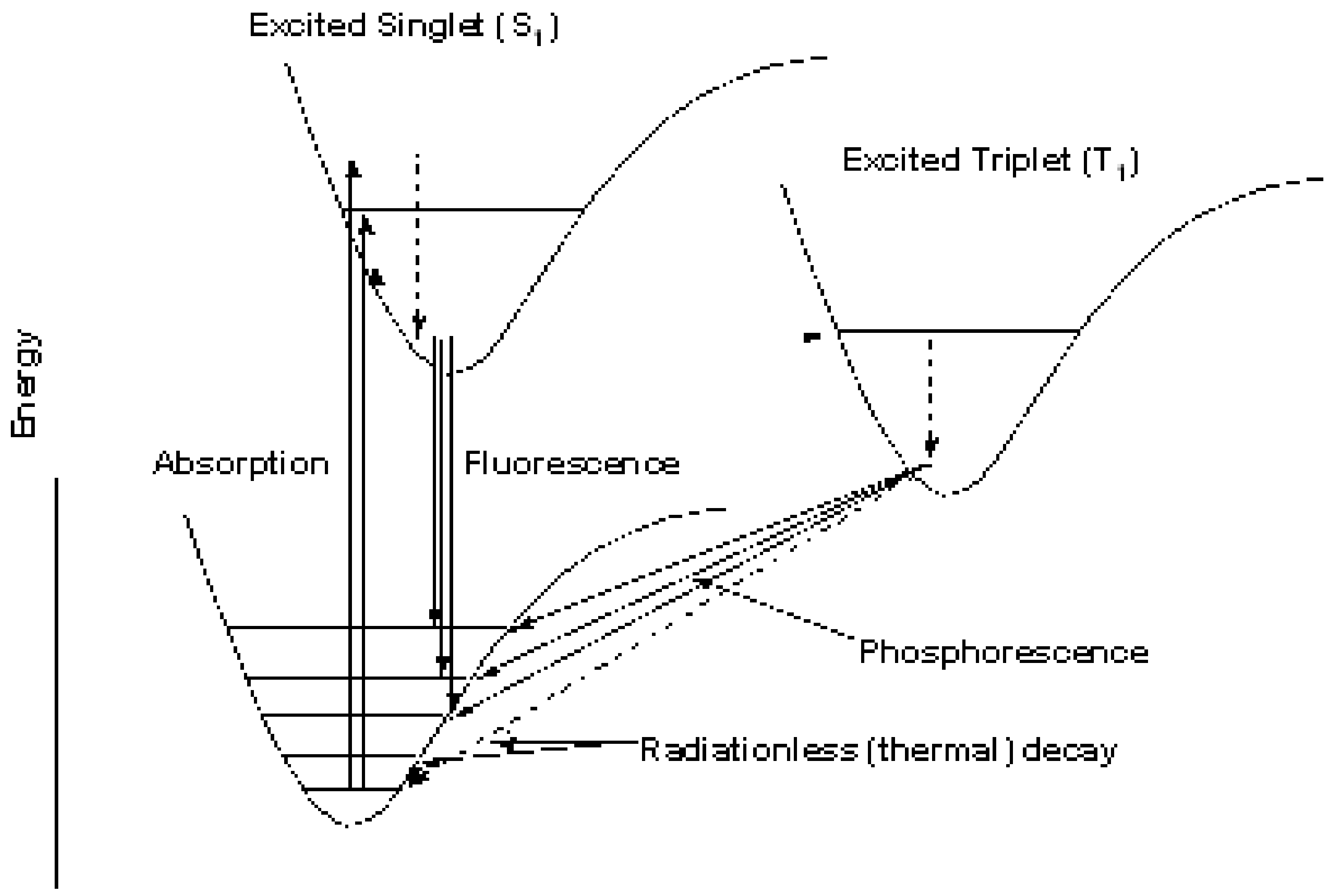
Thermal versus photochemical reactions, Electronic excitations: n–π* and π–π* transitions. Singlet and Triplet energy states: Comparison of energies, Lifetimes and Reactivity. Jablonski diagram, Allowed and forbidden transitions: Fluorescence, Phosphorescence and Internal conversion and Intersystem crossing.

Photochemical reactions of saturated ketones : Norrish Type I and Norrish Type II reaction, Photoreduction of ketone, Photoaddition reactions, Paterno Buchi reaction. Photochemistry of simple olefins : Cis-trans isomerization, Di-pi methane rearrangement. Photooxidation : Formation of peroxy compounds, oxidative couplings : Barton reaction. Photo rearrangements : Photo-Fries rearrangement and Photo rearrangement of 2,5-Cyclohexadienones.

Coverage:

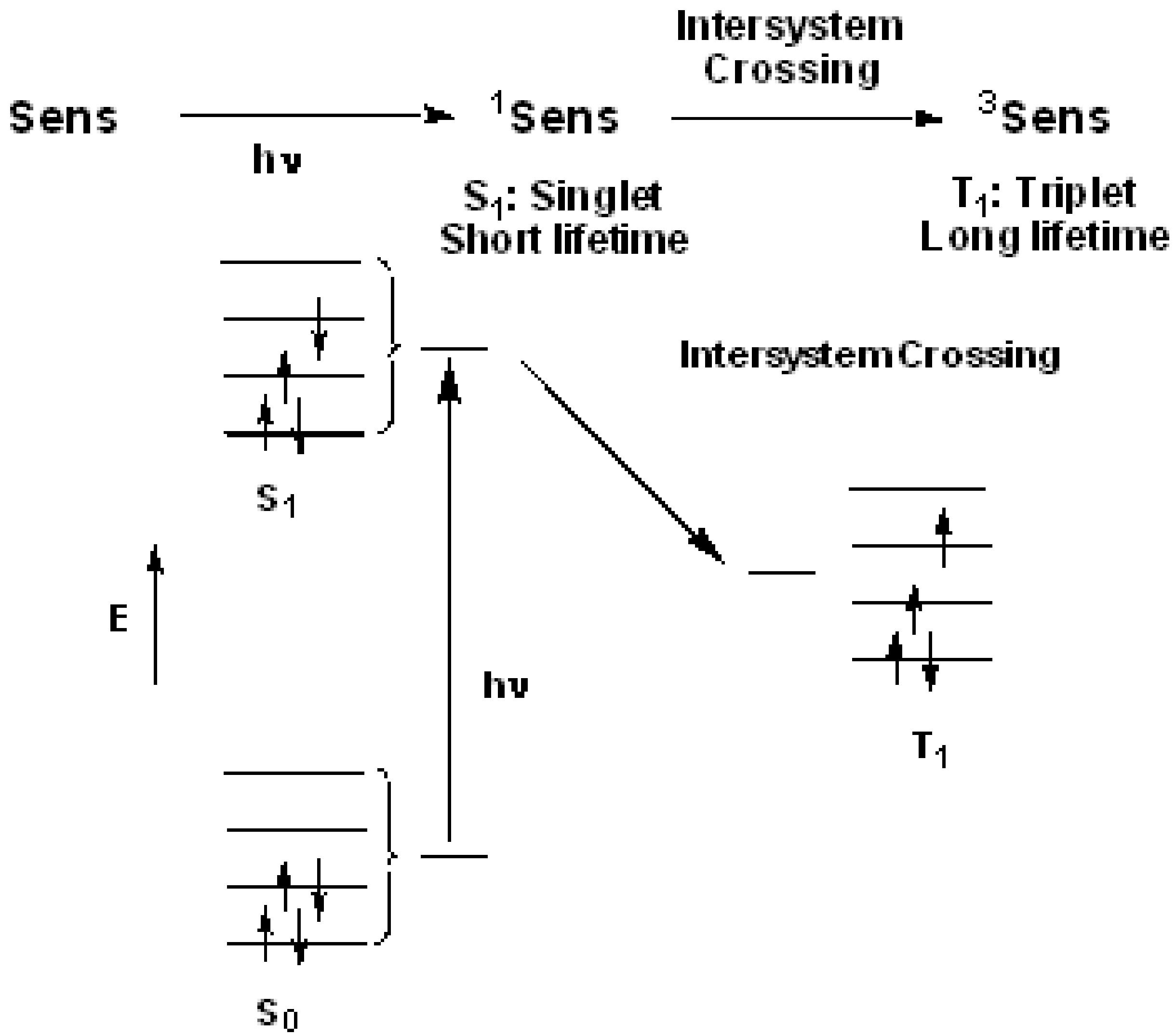
1. Absorption and Luminescence Processes
2. State Diagram
3. Jablonski Diagram for Naphthalene
4. Energy Transfer Through Photosensitization
5. Sensitizer, Criteria of an Ideal Sensitizer

Absorption and Luminescence Processes



Fluorescence: Spin allowed, fast (10^{-8} - 10^{-10} sec)
Phosphorescence: Spin forbidden, slow (10^{-4} - 10^{2} sec)
Radiationless deactivation competes

State Diagram



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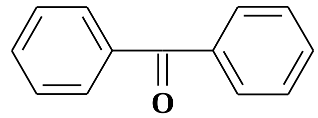
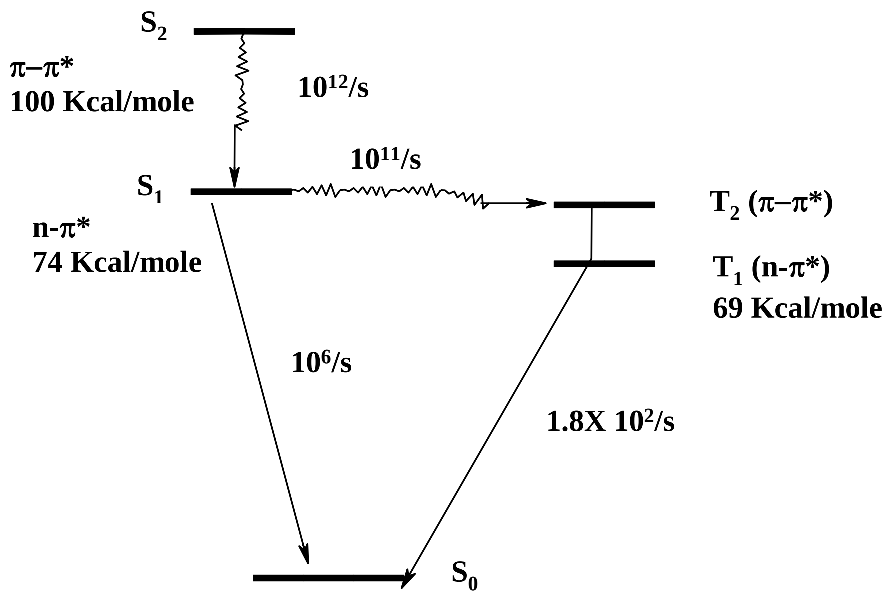
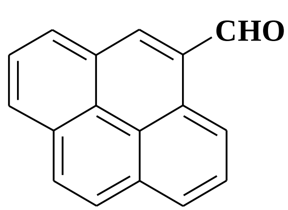
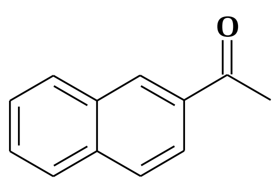


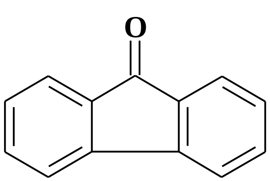




pyrene aldehyde



2-acetonaphthone



fluorenone

lowest triplet state is π–π*

Jablonski Diagram for Naphthalene

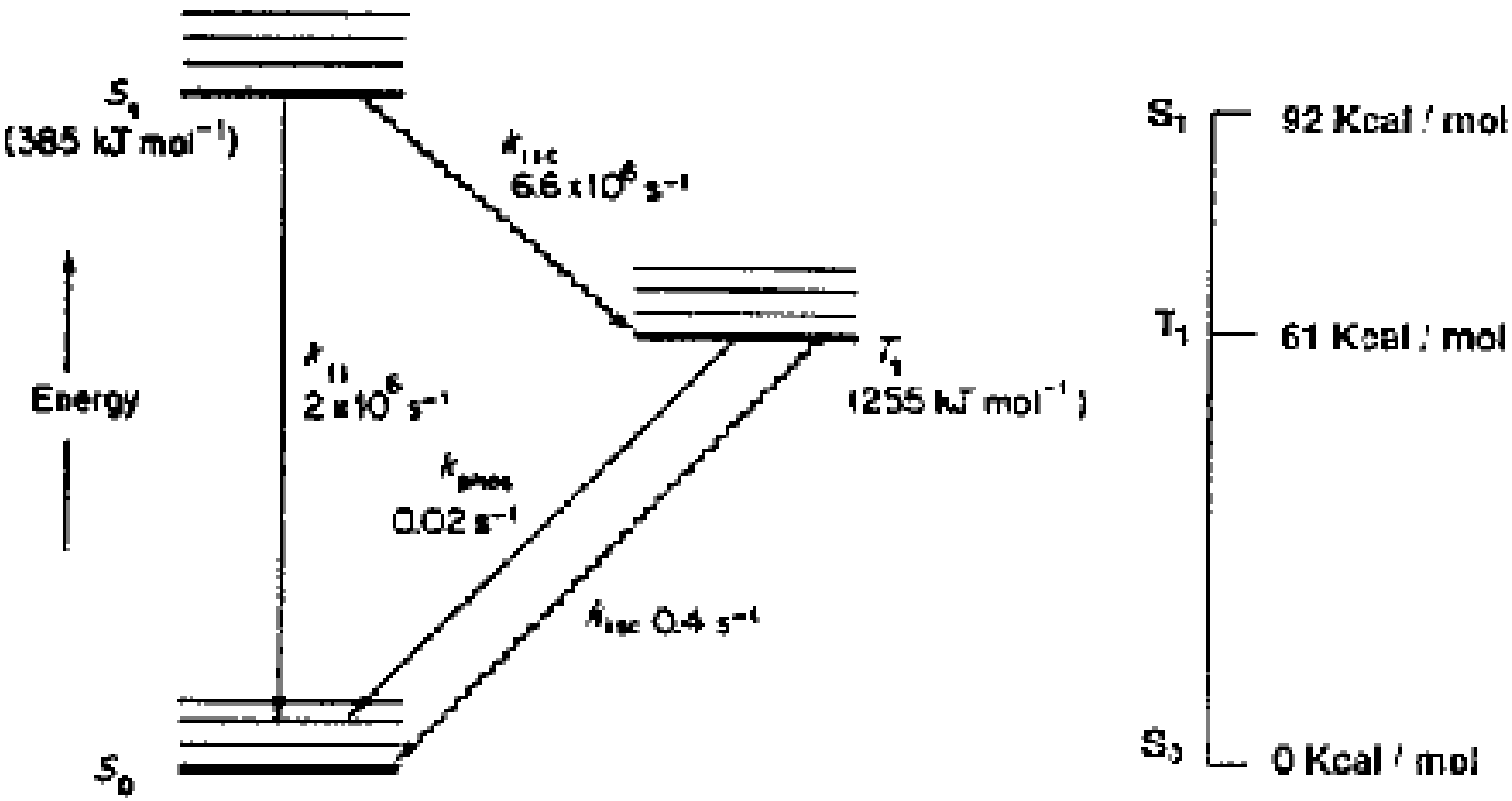


Figure 1.13 A Jablonski diagram for naphthalene, showing selected rate constants.

1 kcal = 4.18 kJ

Energy transfer through photosensitization

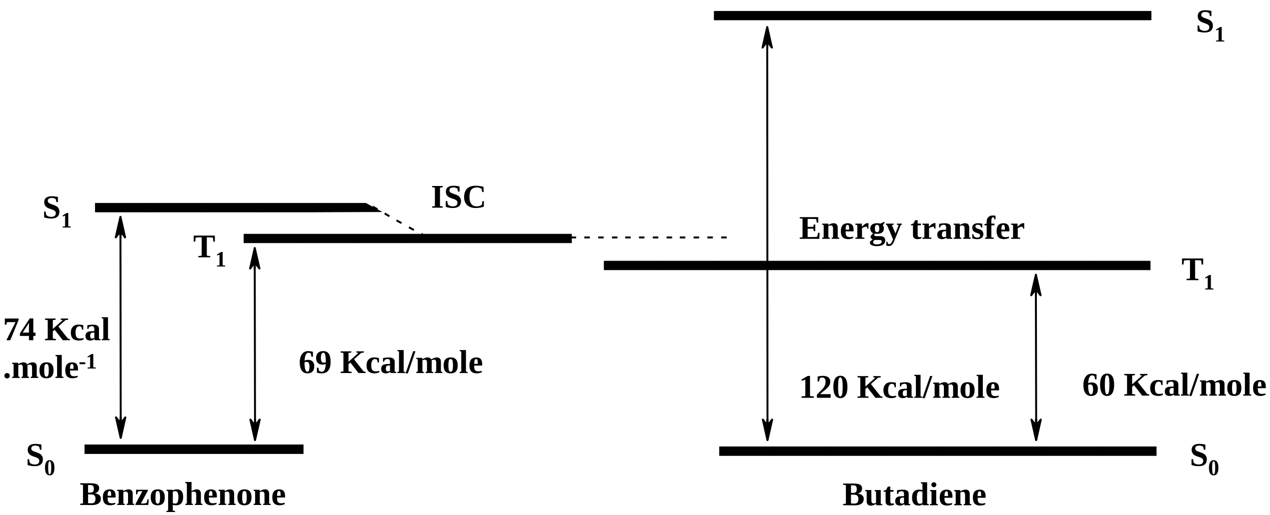
$D \xrightarrow{h\nu} 1D$

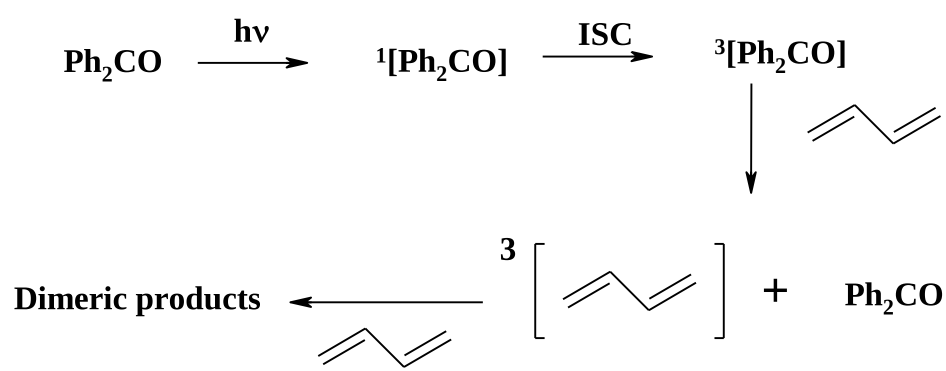
$1D \xrightarrow{ISC} 3D$

$A + 3D \longrightarrow D + 3A$

$3A \longrightarrow$ Products

D = Donor
A = Acceptor
1 = Singlet
3 = Triplet





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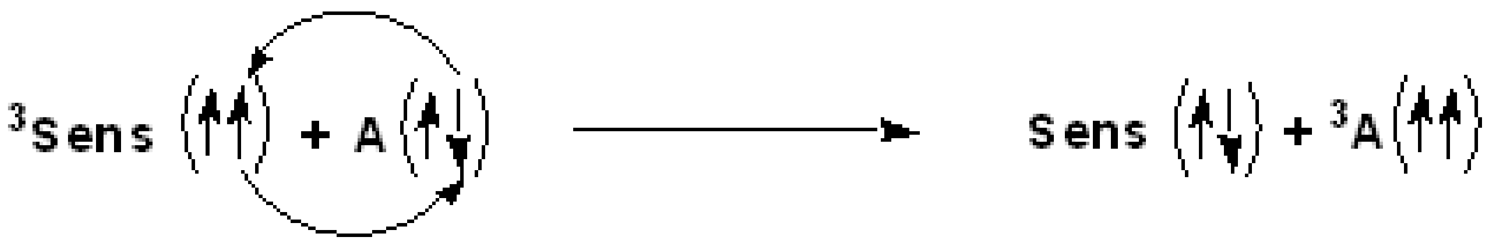
Energy Transfer

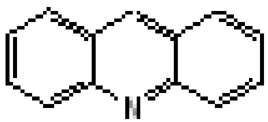
Most common mechanism of Energy Transfer is triplet-triplet; mechanism involves a collision, electron exchange.

$$\text{Sens} \xrightarrow[h\nu]{} {}^{1}\text{Sens} \longrightarrow {}^{3}\text{Sens}$$

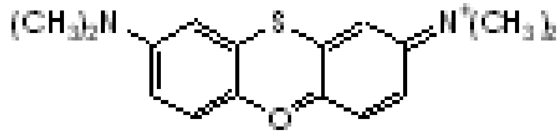


Spin Exchange

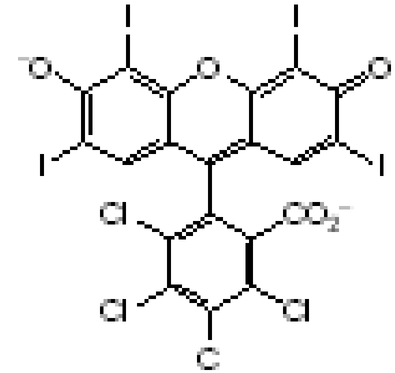
Some Sensitizers



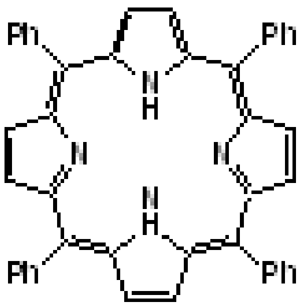
Acridine



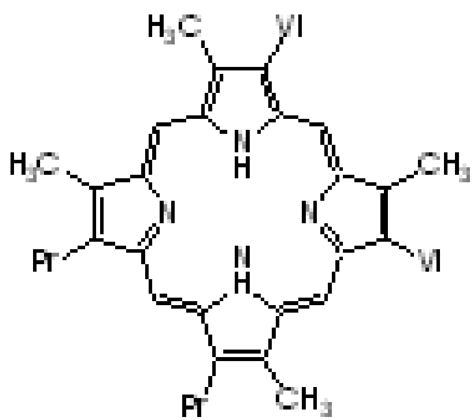
Methylene Blue



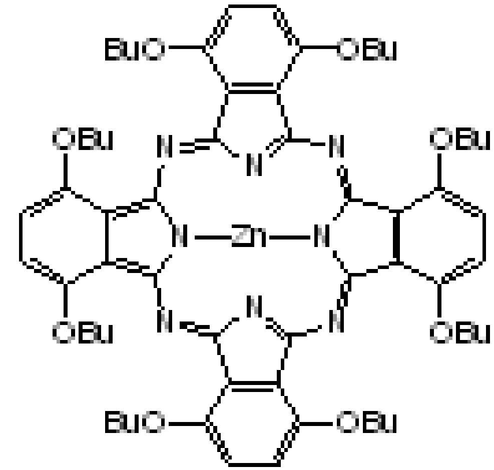
Rose Bengal



Tetraphenylporphine



A Protoporphyrin



A Phthalocyanine

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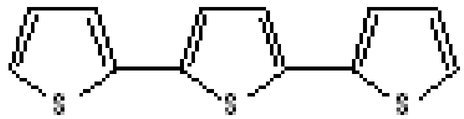
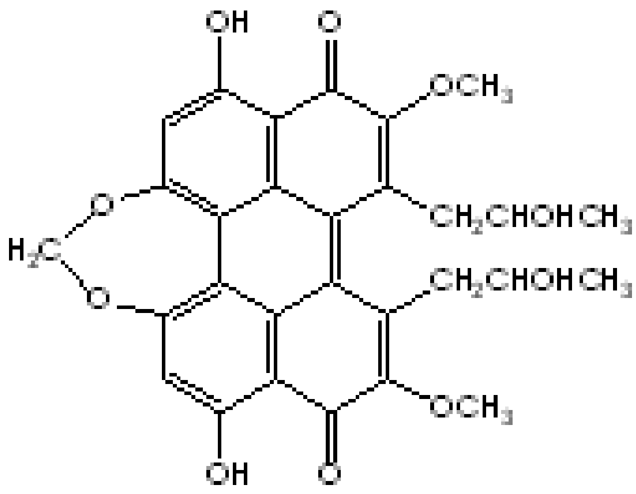
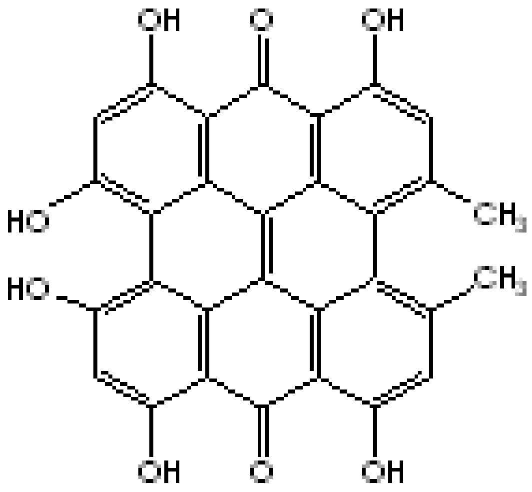
Some Biological Sensitizers



α-Terthienyl - a photodynamic insecticide from marigolds



Cercosporin - a photodynamic mold toxin

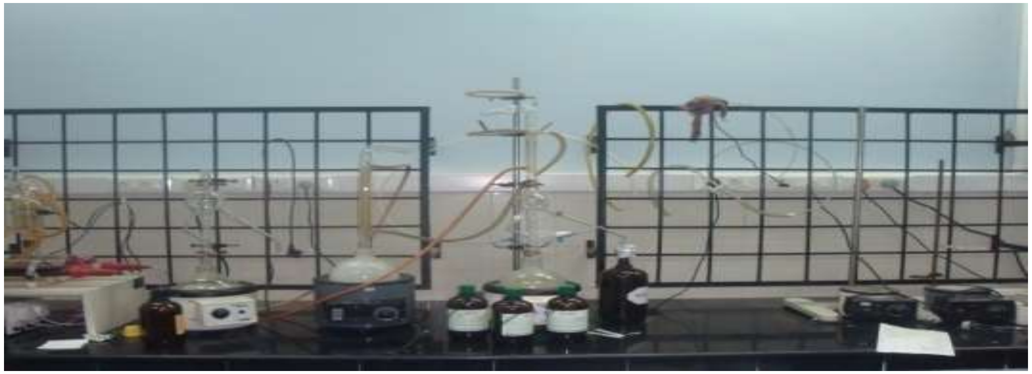


Hypericin - photodynamic principle from St. John's wort - livestock damage. Under investigation for antitumor, antiHIV activity

Criteria of an ideal sensitizer

- It must be excited by the irradiation to be used, small singlet triplet splitting. High ISC yield.
- It must be present in sufficient concentration to absorb more strongly than the other reactants under the condition.
- It must be able to transfer energy to the desired reactant, low chemical reactivity in Triplet state.

Thank You



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