

**B.Sc. Semester-VI  
Group-A / DSE-4  
Organic Synthesis**



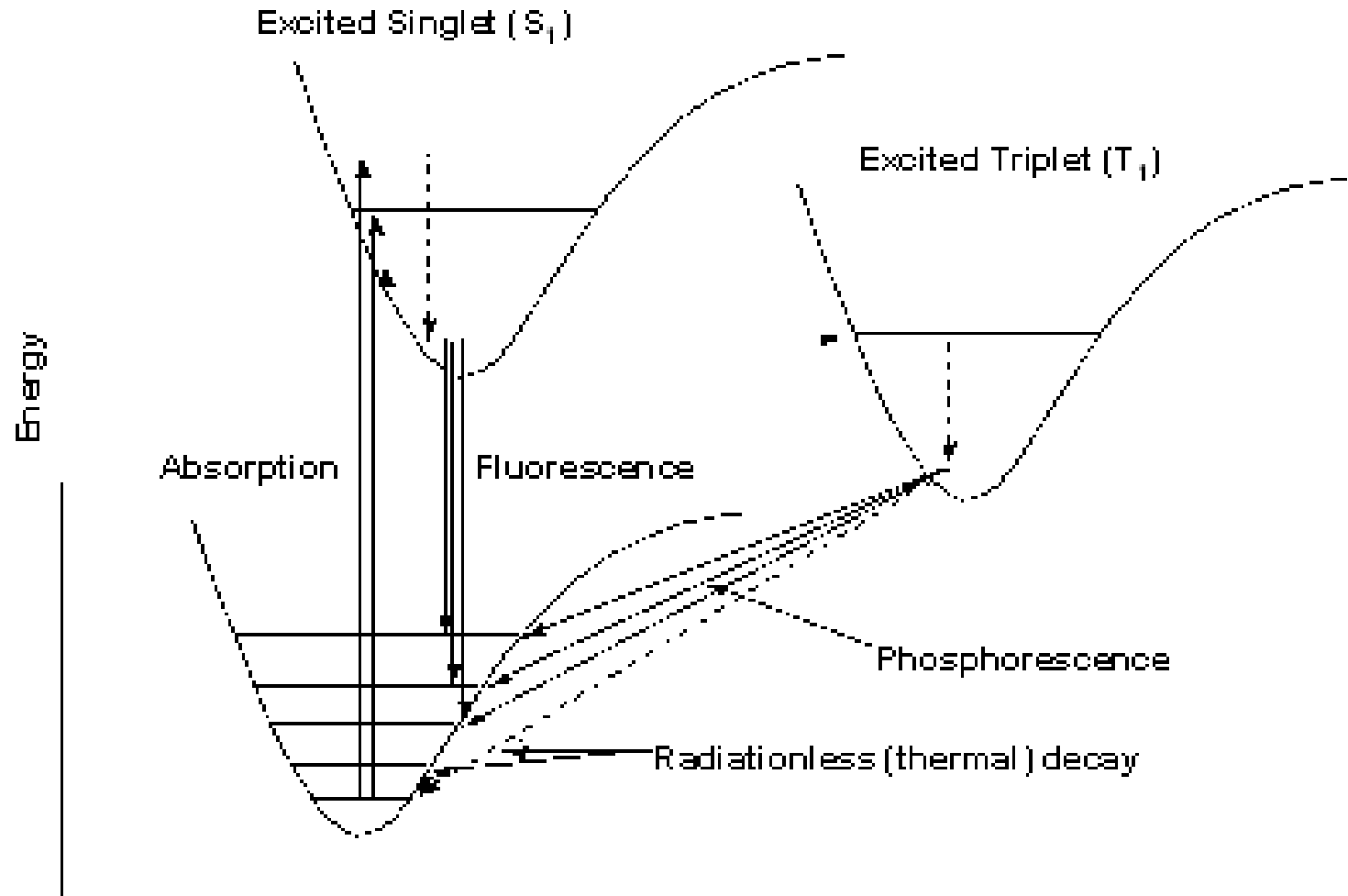
**III. Photochemistry**

**2. Absorption and Luminescence Processes, Energy  
Transfer Through Photosensitization**



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University Department of Chemistry  
Dr. Shyama Prasad Mukherjee University, Ranchi**

# Absorption and Luminescence Processes

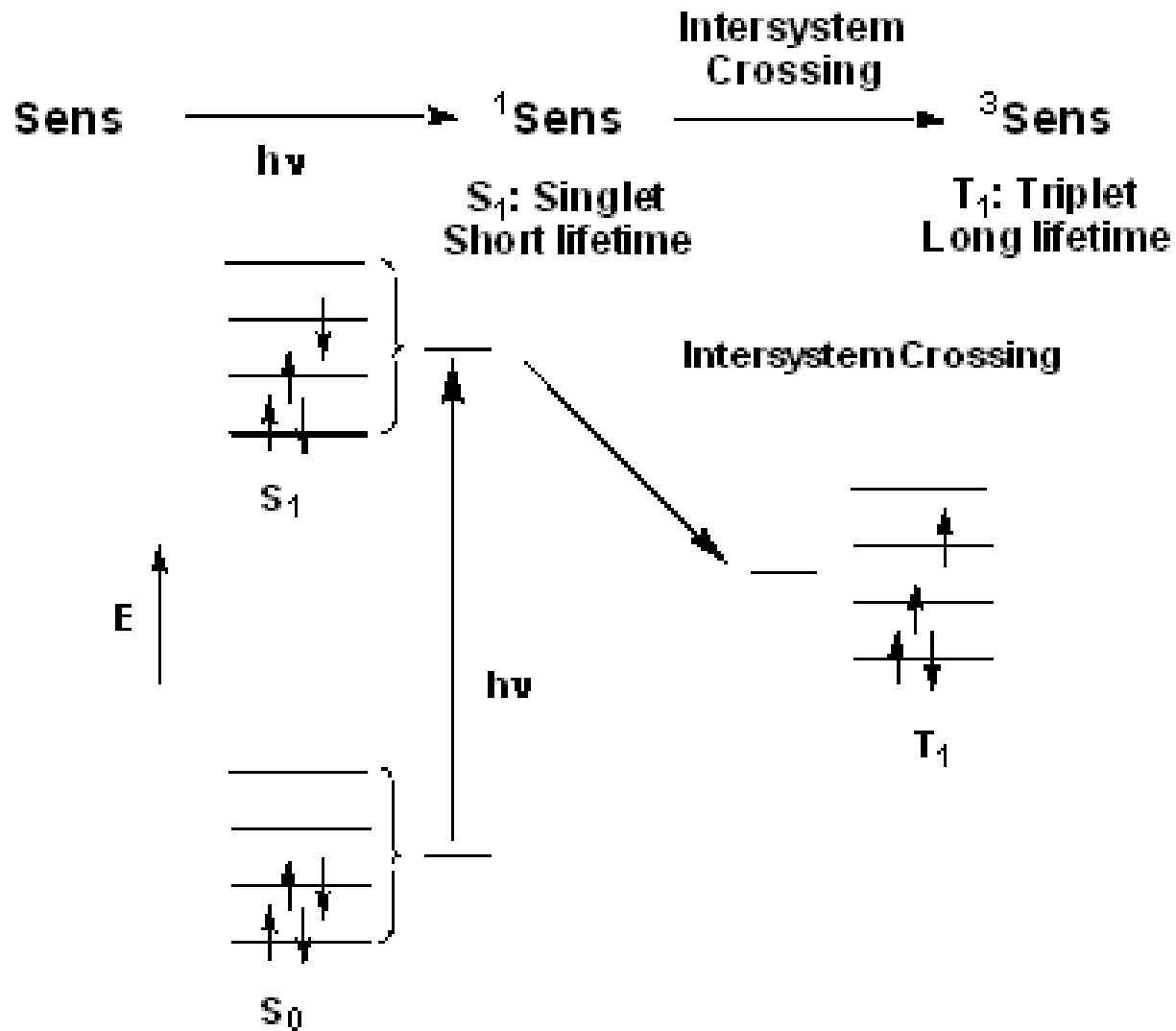


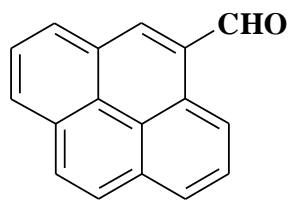
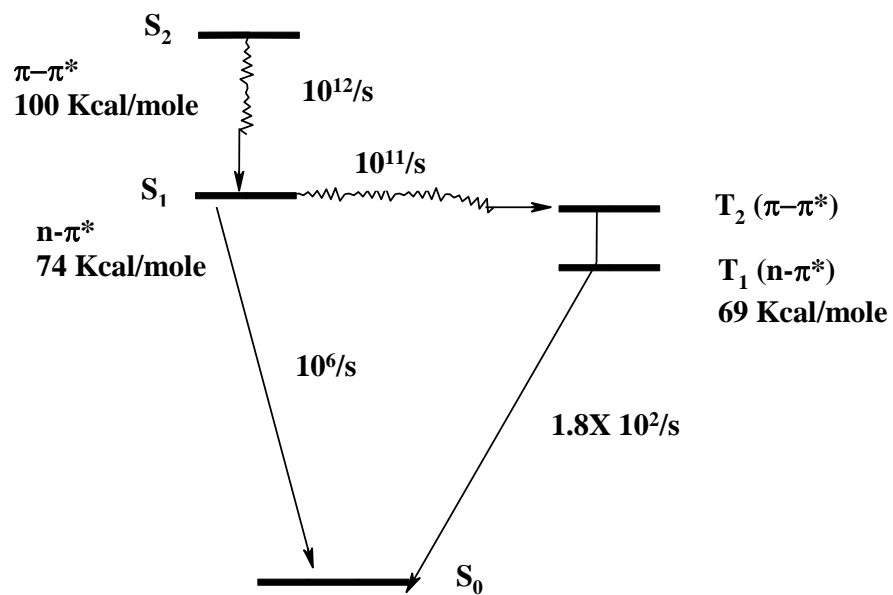
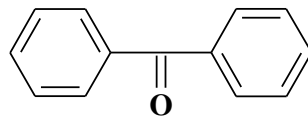
Fluorescence: Spin allowed, fast ( $10^{-8}$ - $10^{-10}$  sec)

Phosphorescence: Spin forbidden, slow ( $10^{-6}$ - $10^2$  sec)

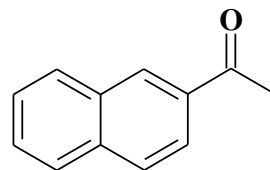
Radiationless deactivation competes

# State Diagram

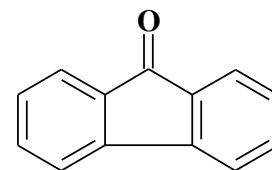




pyrene aldehyde



2-acetonaphthone



fluorenone

lowest triplet state is π-π\*

## Jablonski Diagram for Naphthalene

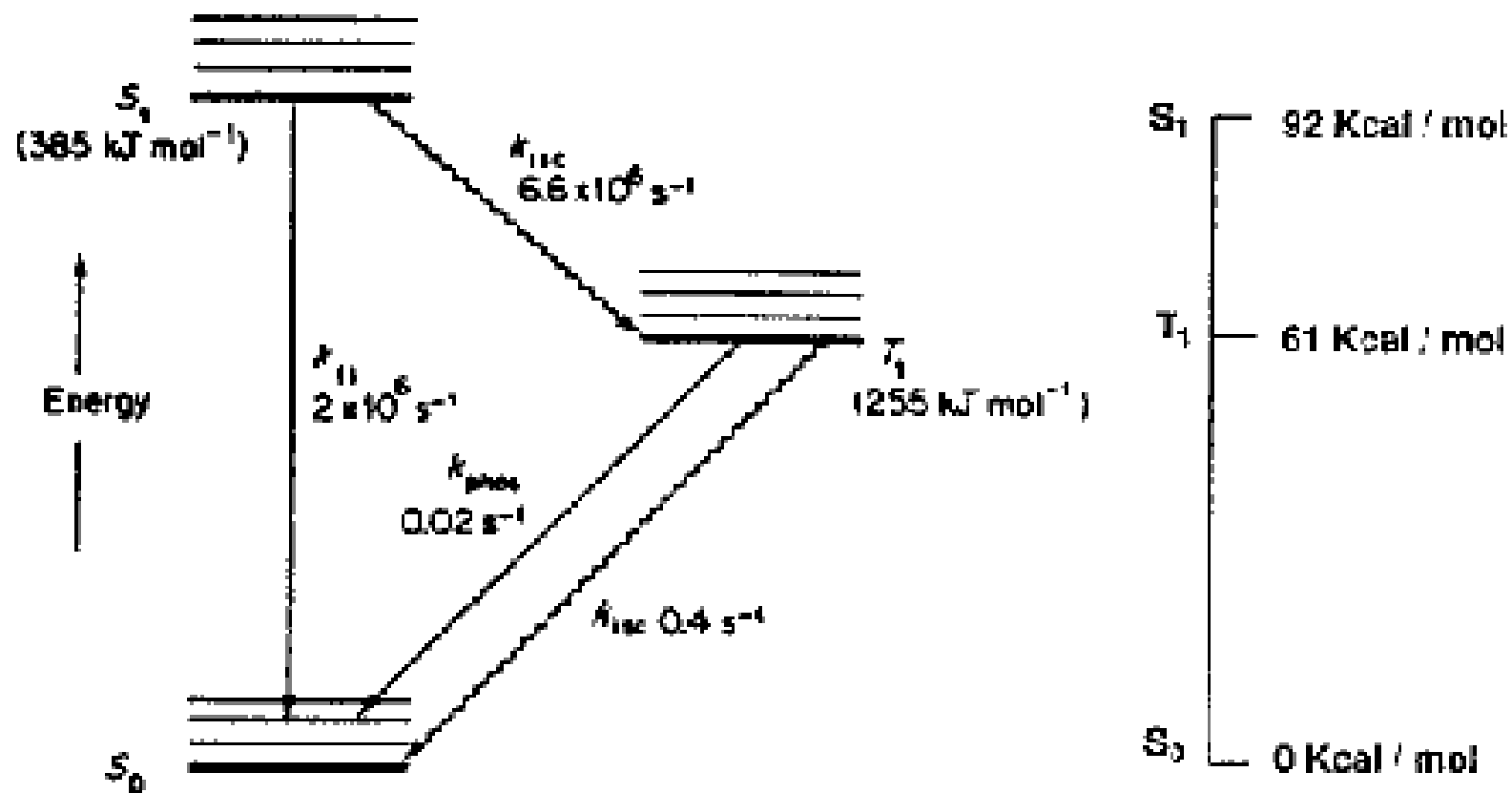
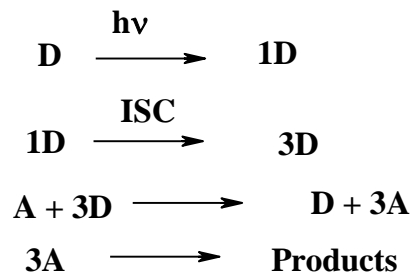


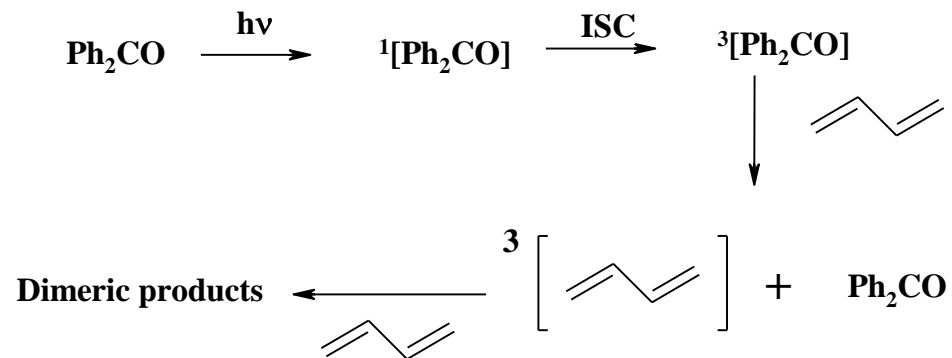
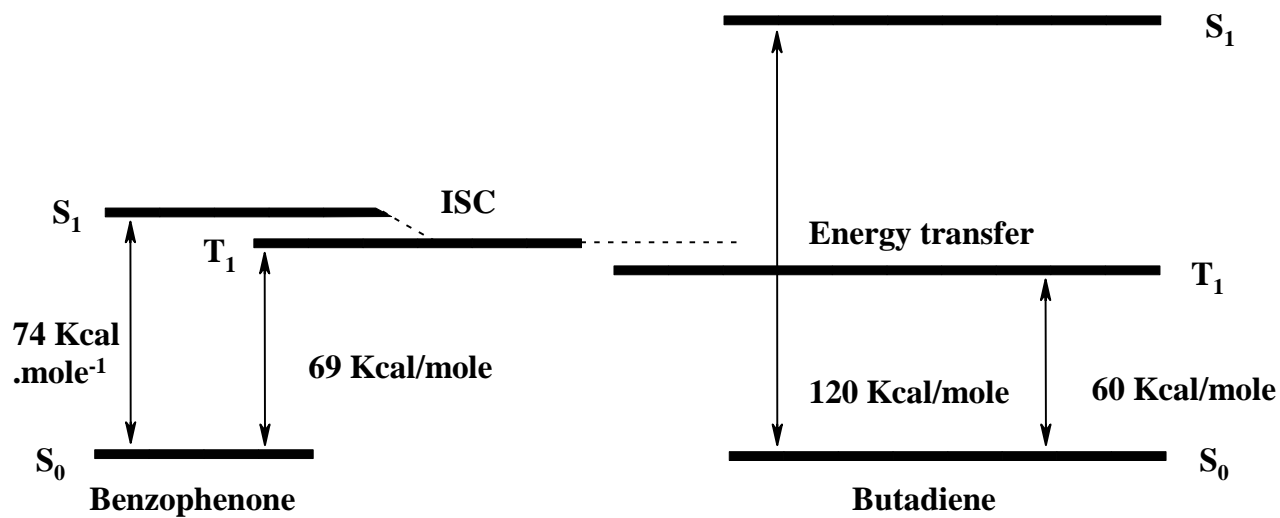
Figure 1.13 A Jablonski diagram for naphthalene, showing selected rate constants.

$$1 \text{ kcal} = 4.18 \text{ kJ}$$

# Energy transfer through photosensitization

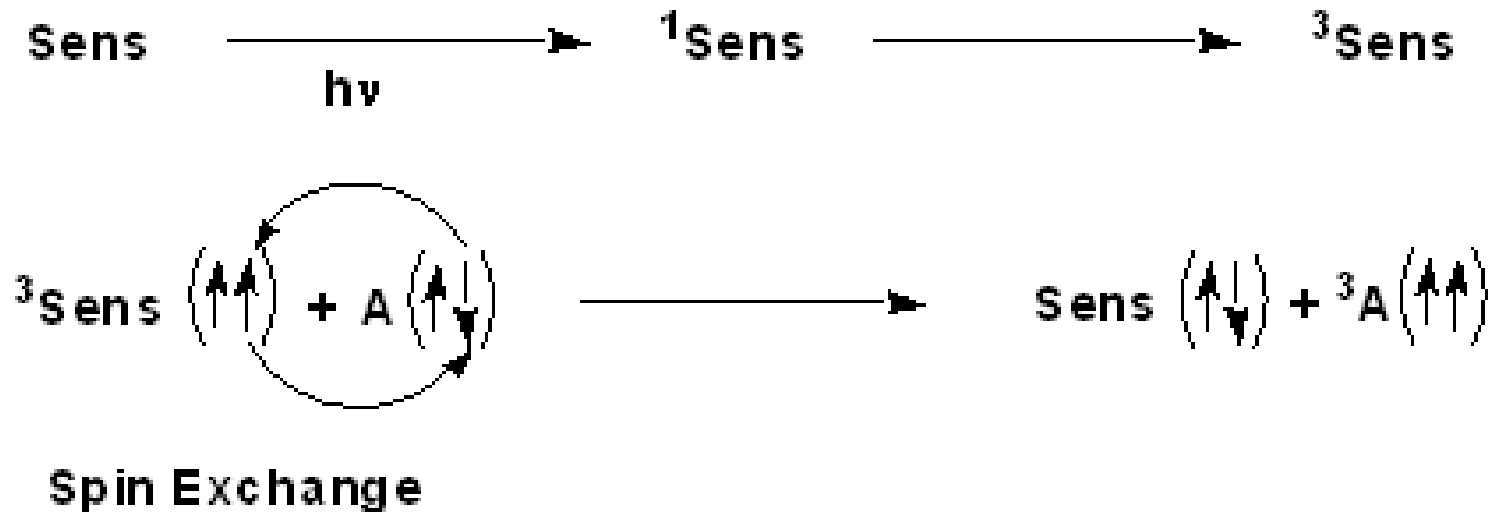


**D = Donor**  
**A = Acceptor**  
**1 = Singlet**  
**3 = Triplet**

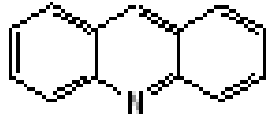


# Energy Transfer

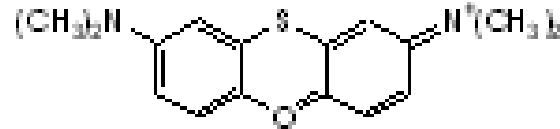
Most common mechanism of Energy Transfer is triplet-triplet; mechanism involves a collision, electron exchange.



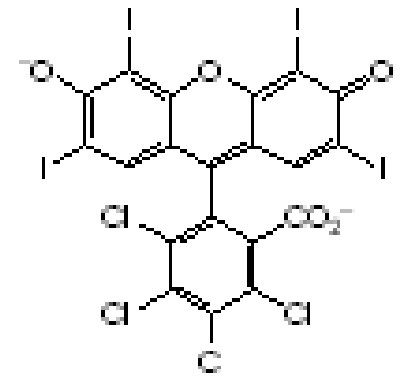
## Some Sensitizers



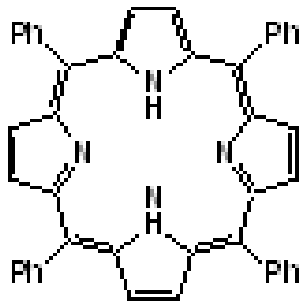
**Acridine**



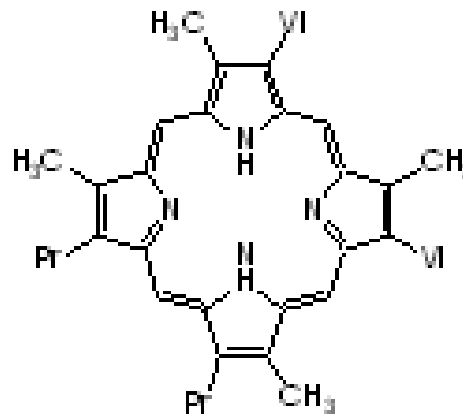
**Methylene Blue**



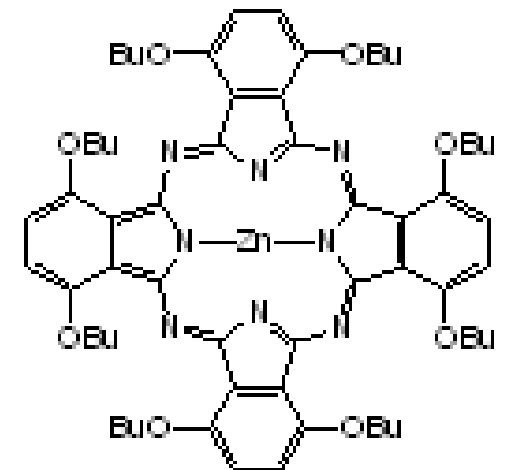
**Rose Bengal**



**Tetraphenylporphyrine**



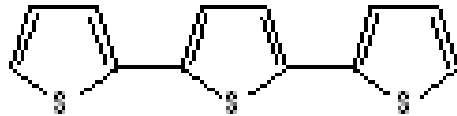
**A Protoporphyrin**



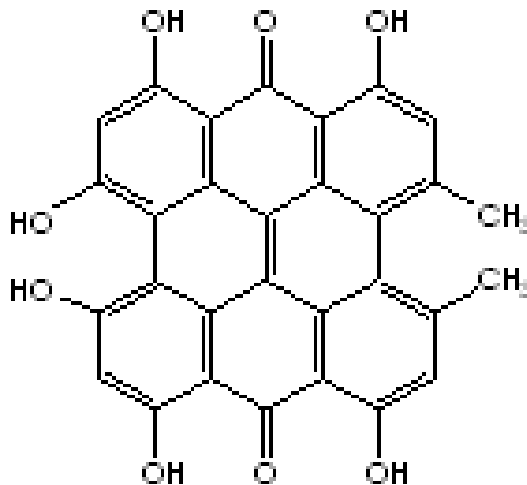
**A Phthalocyanine**



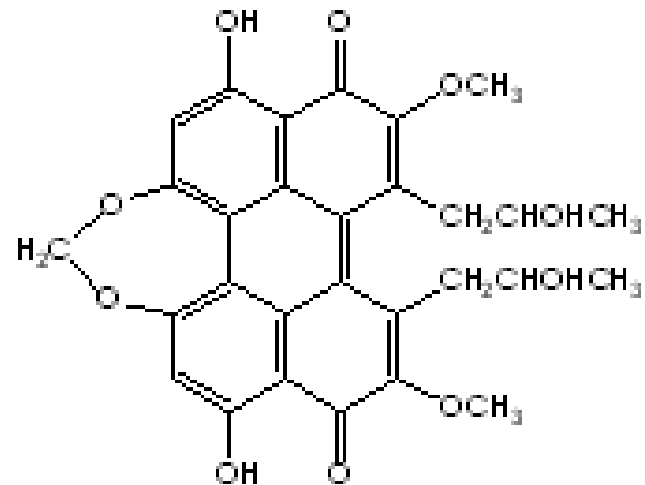
## Some Biological Sensitizers



**$\alpha$ -Terthienyl** - a photodynamic insecticide from marigolds



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



**Cercosporin** - a photodynamic mold toxin

## 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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