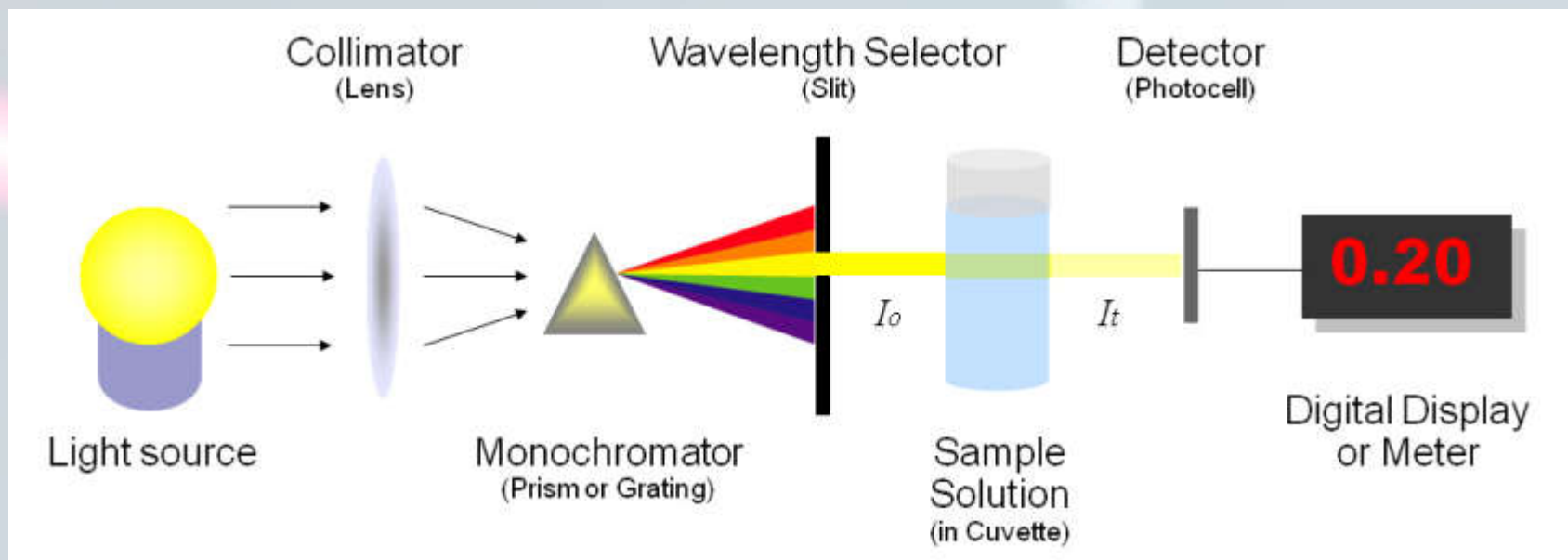
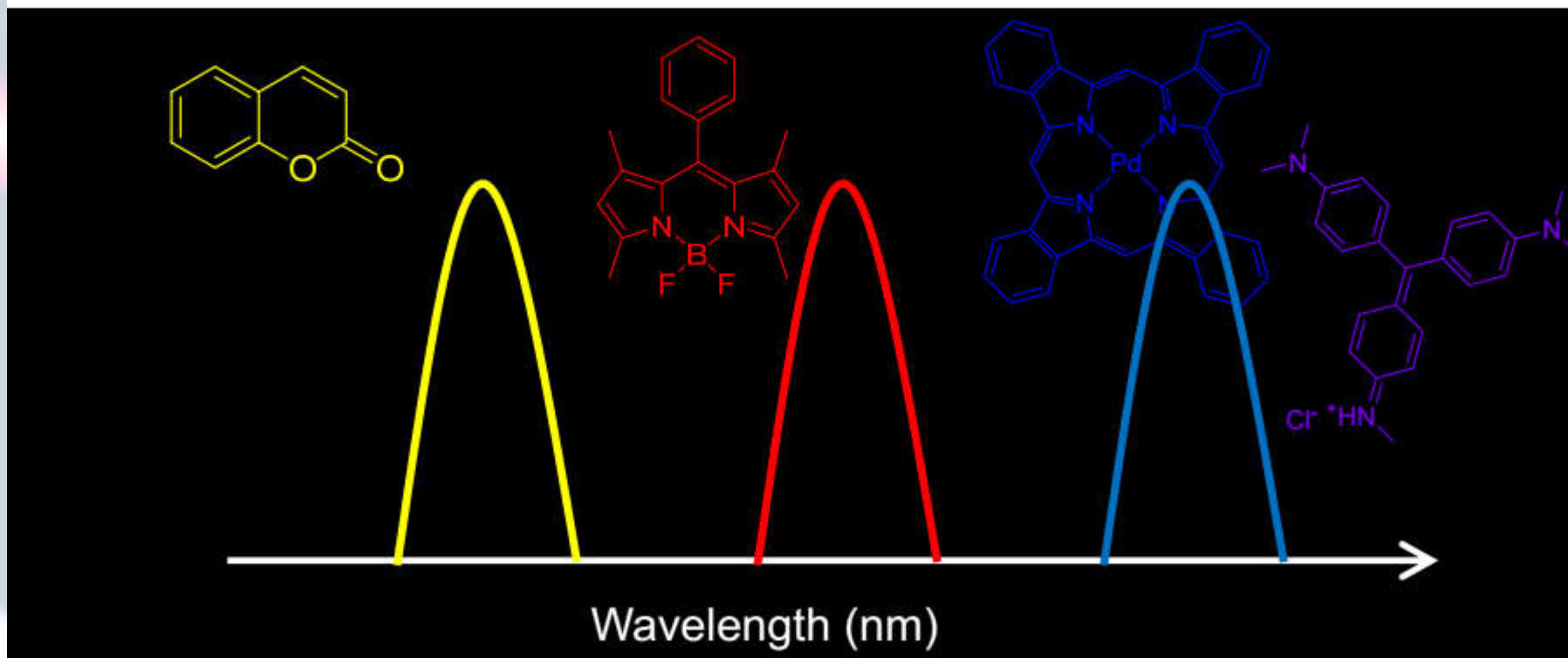
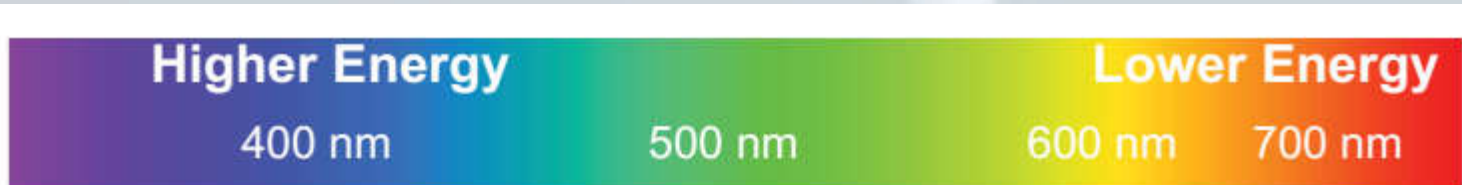


Light Absorption: Spectrophotometer to Quantify





Charge-Transfer  Absorption (very rough approximation)

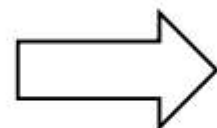
No Interactions



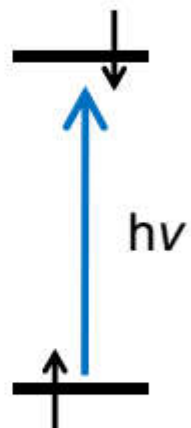
Donor



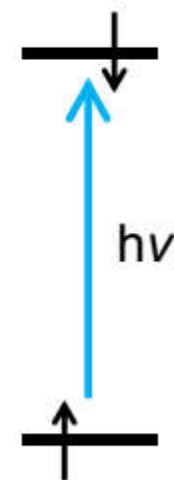
Acceptor



Their Own Absorption

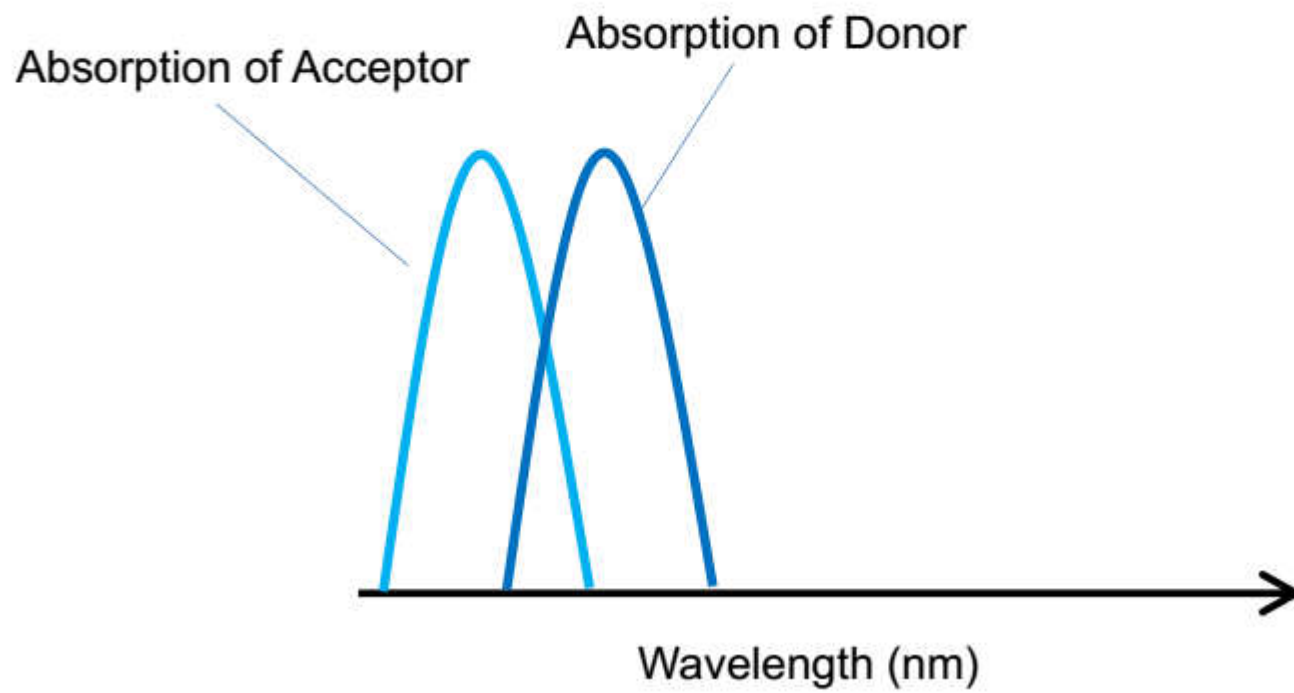


Donor



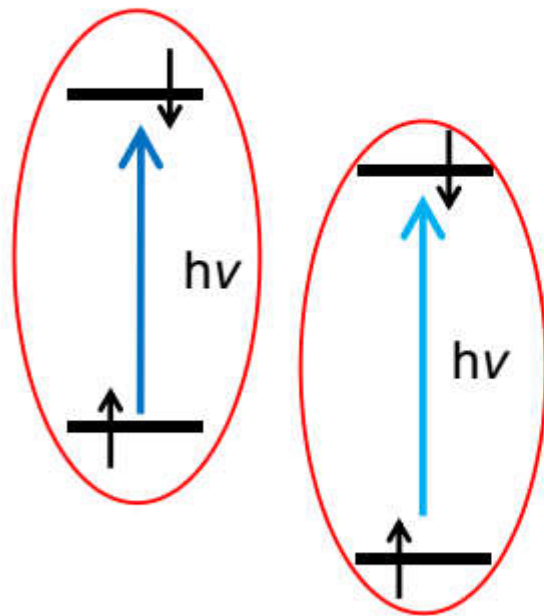
Acceptor

No Interactions of Donor and Acceptor



CT Absorption: Orbital View

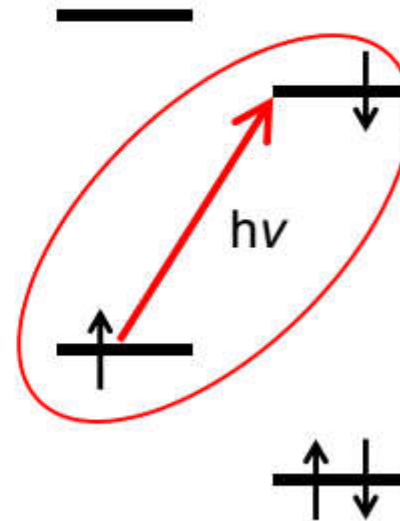
Normal (Local)



Donor

Acceptor

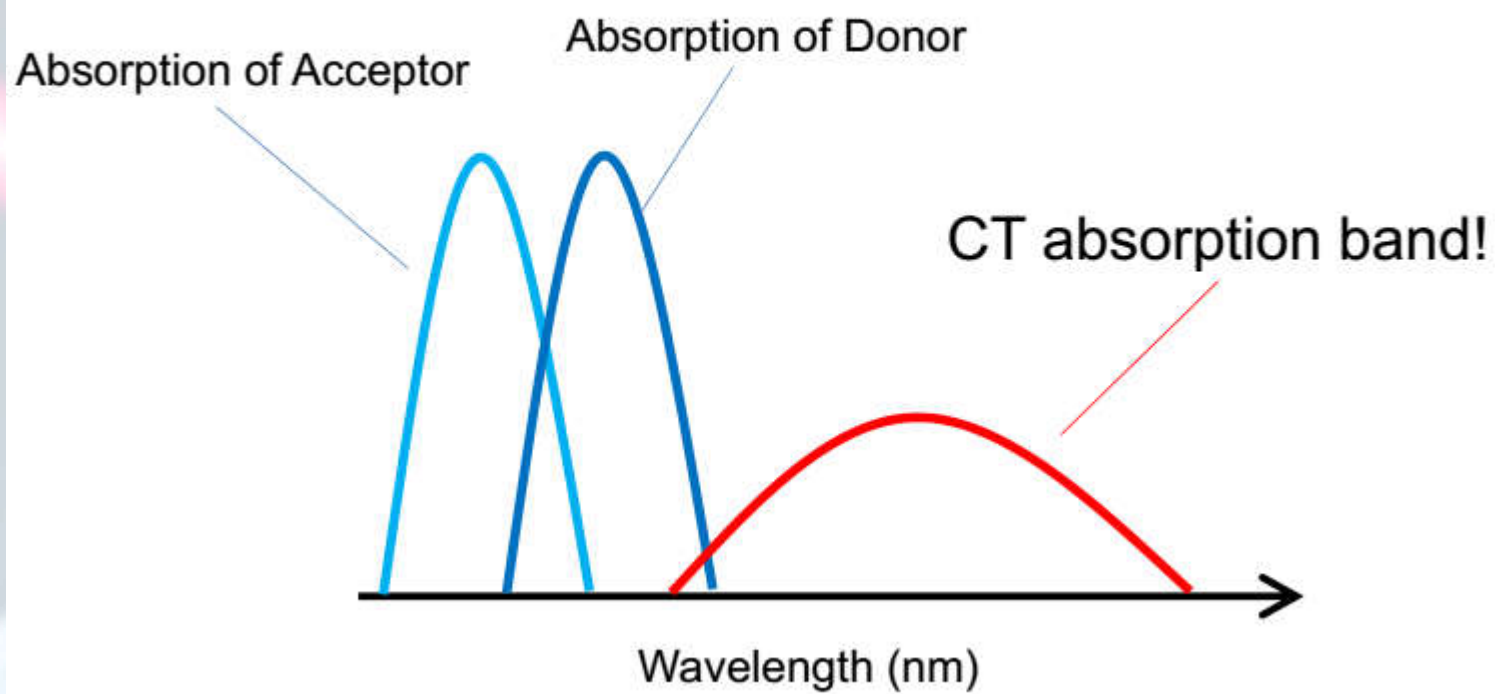
CT



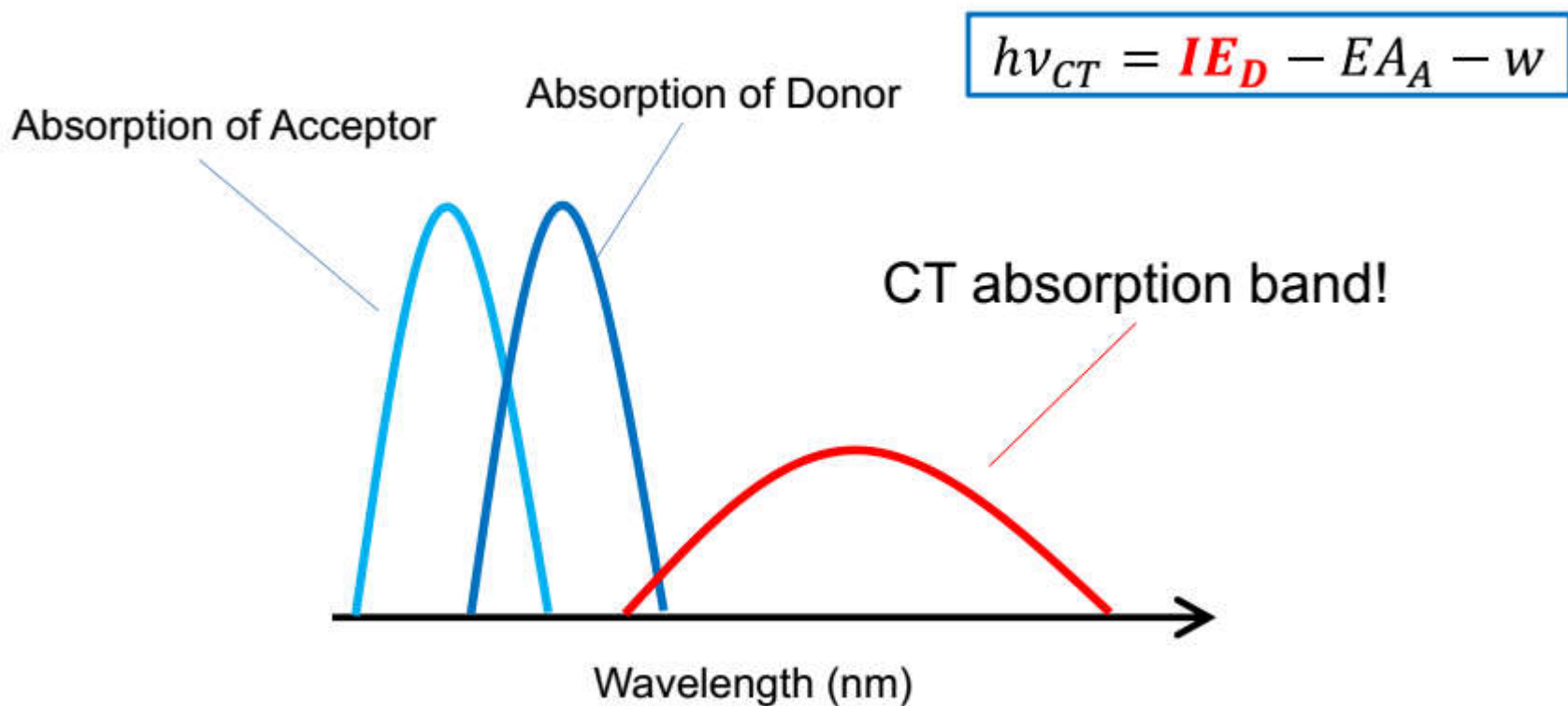
Donor

Acceptor

Charge-Transfer (CT) Absorption: New Absorption Band!



New Absorption Band Depends on Donor* = Color Change



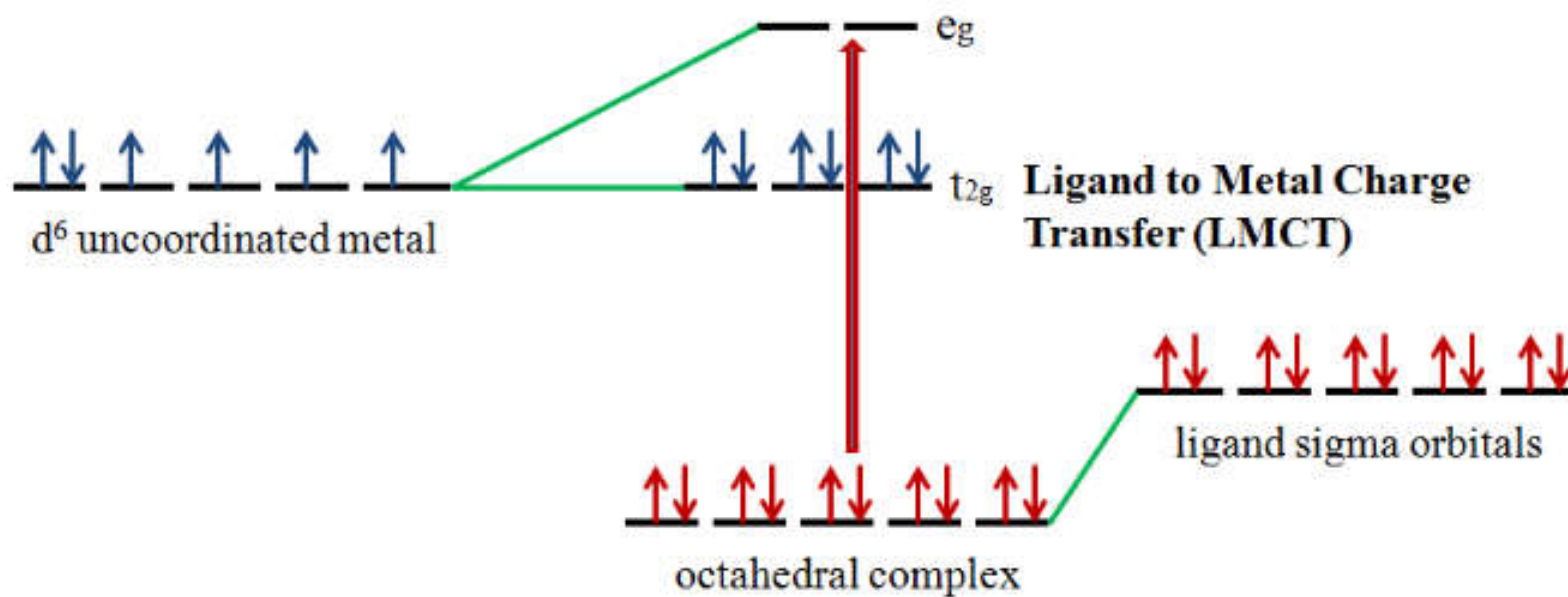
*Keeping the same acceptor.

What is CT Absorption Band?

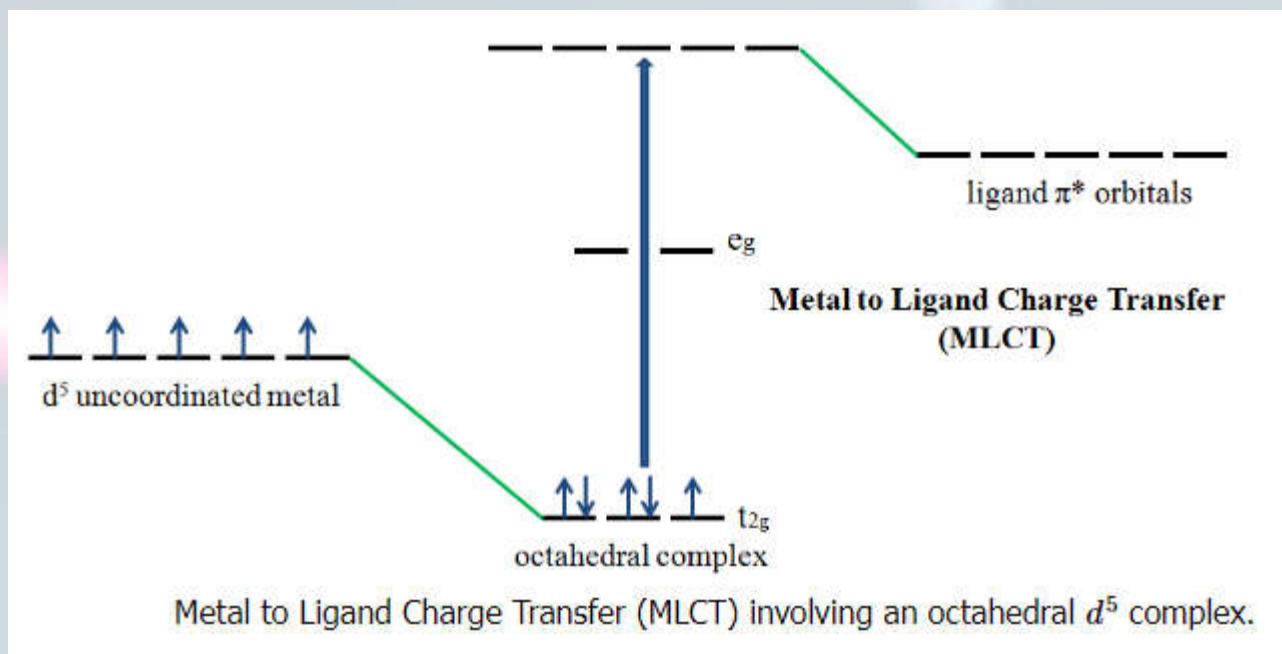
The charge transfer bands in the absorption spectra of these complexes involve the transfer of electrons between the metal and ligand. In particular, Metal to ligand charge transfer (MLCT or CTTL) bands involve the transfer of an electron from a filled or partly filled metal d orbital to a ligand π^* -type orbital.

Ligand to Metal and Metal to Ligand Charge Transfer Bands

Ligands possess σ , σ^* , π , π^* , and nonbonding (n) molecular orbitals. If the ligand molecular orbitals are full, charge transfer may occur from the ligand molecular orbitals to the empty or partially filled metal d-orbitals. The absorptions that arise from this process are called ligand-to-metal charge-transfer (LMCT) bands. LMCT transitions result in intense bands. Forbidden d-d transitions may also take place giving rise to weak absorptions. Ligand to metal charge transfer results in the reduction of the metal.

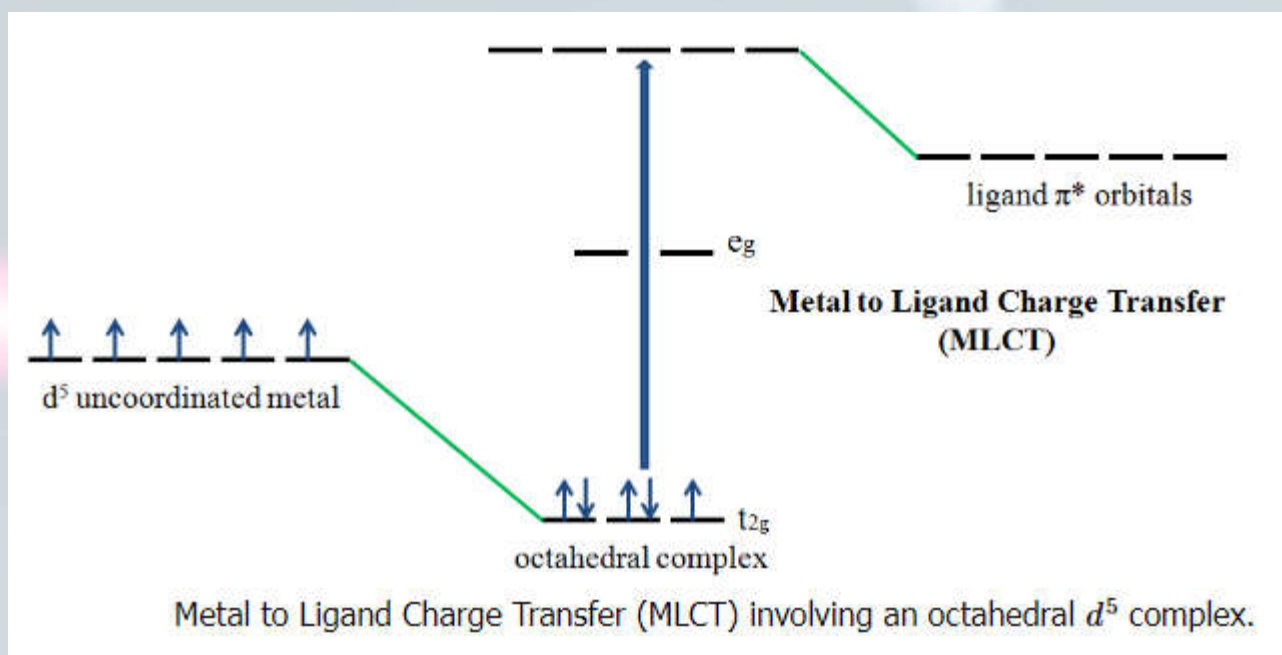


Ligand to Metal Charge Transfer (LMCT) involving an octahedral d^6 complex.



Metal to Ligand Charge Transfer (MLCT)

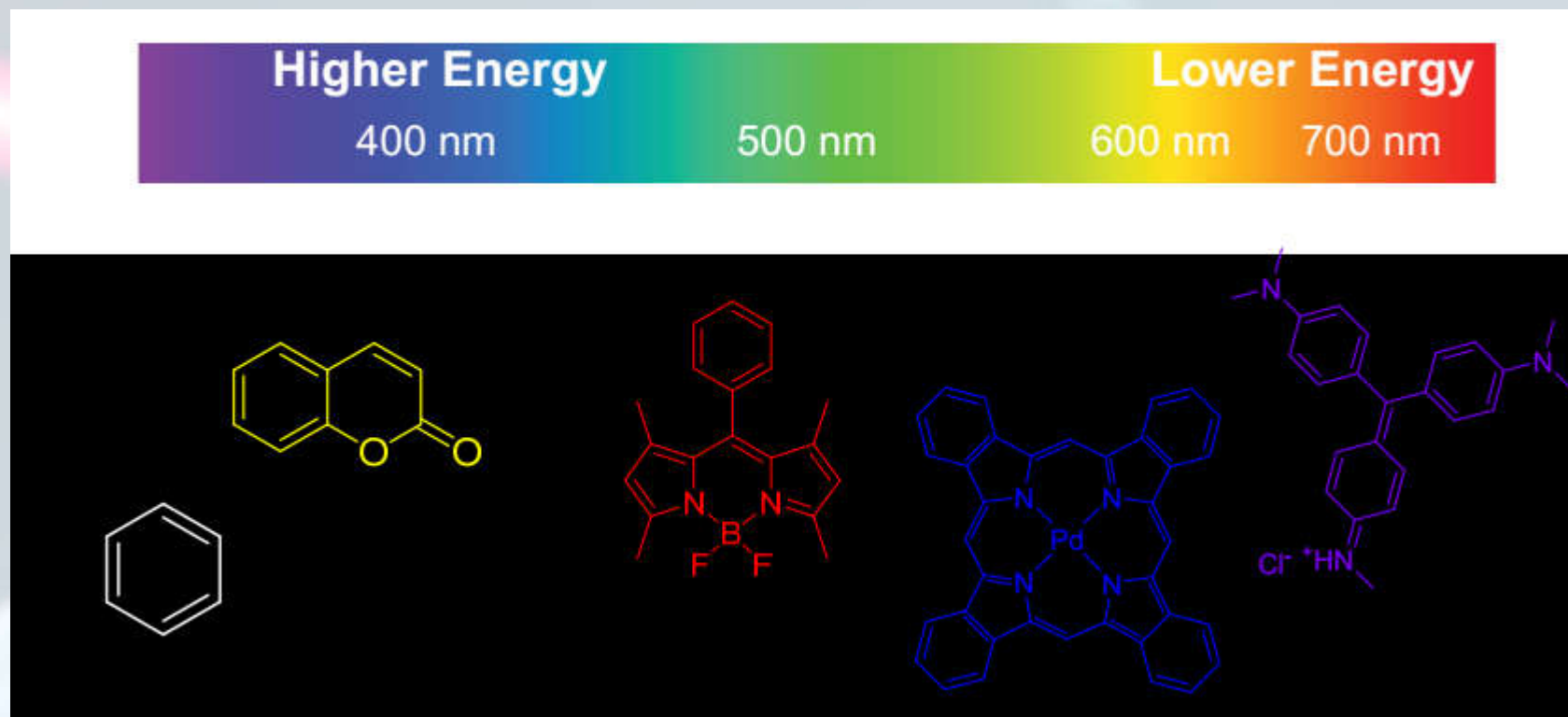
If the metal is in a low oxidation state (electron rich) and the ligand possesses low-lying empty orbitals (e.g., CO or CN^-) then a metal-to-ligand charge transfer (MLCT) transition may occur. MLCT transitions are common for coordination compounds having π -acceptor ligands. Upon the absorption of light, electrons in the metal orbitals are excited to the ligand π^* orbitals. Figure illustrates the metal to ligand charge transfer in a d^5 octahedral complex. MLCT transitions result in intense bands. Forbidden d–d transitions may also occur. This transition results in the oxidation of the metal.



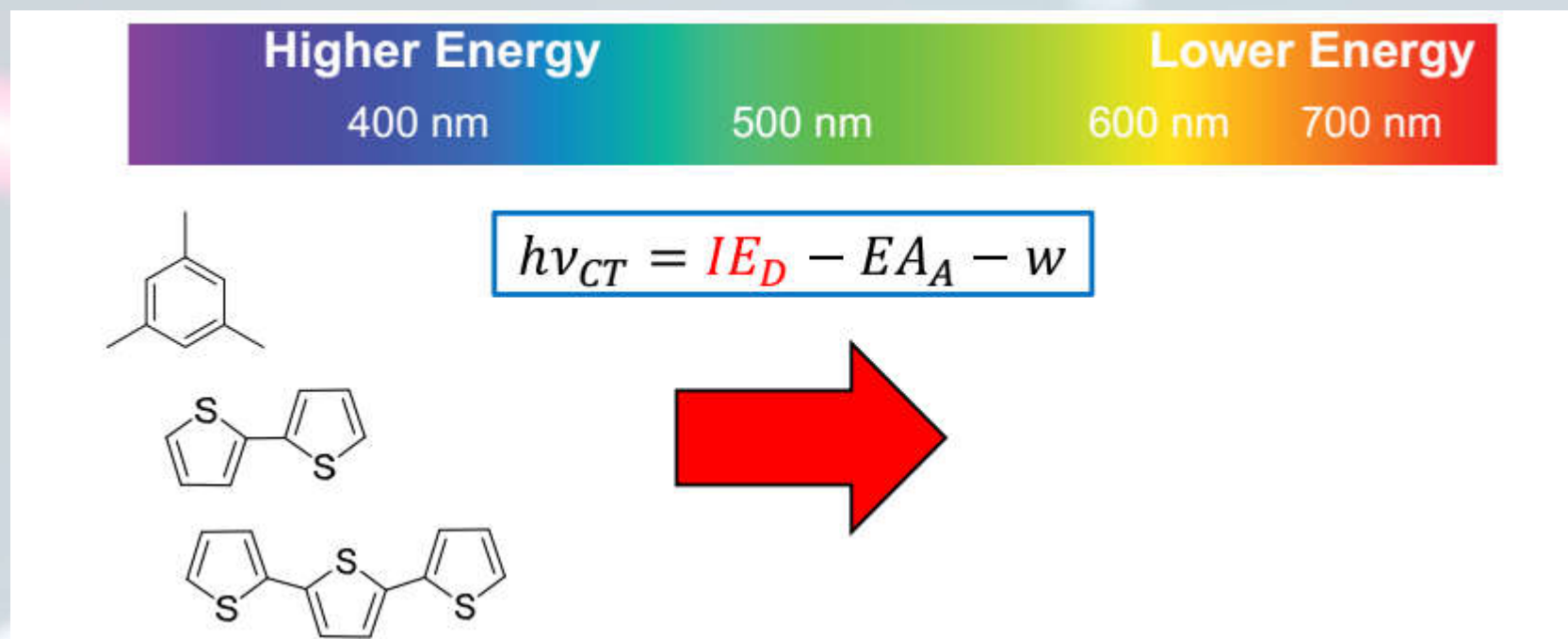
The Laporte selection rule states that electronic transitions between two gerade (g) states are forbidden; electronic transitions between two ungerade (u) states are forbidden; and electronic transitions between a gerade state and an ungerade are allowed.

Why is CT Absorption Significant?

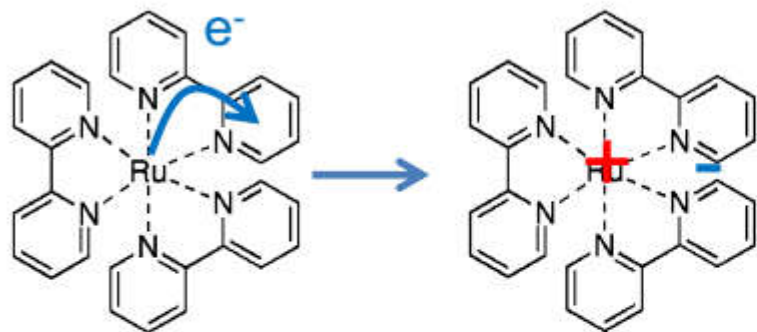
In one molecule: Color change with significant structural change.



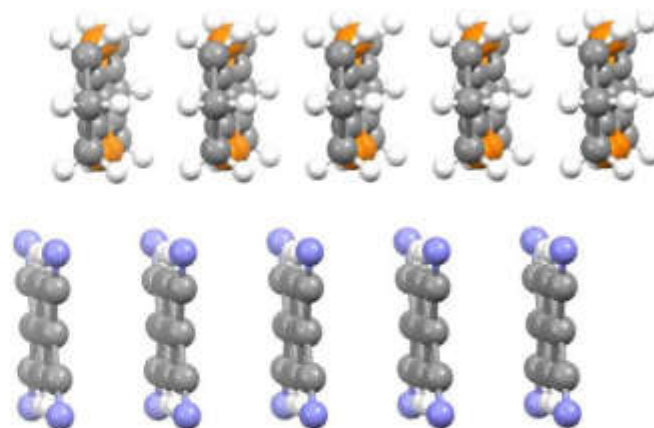
Color change by changing donor or acceptor, which can be very small structural change!



Charge-Transfer (CT) Absorption: Importance



Widely observed in inorganic molecules as metal-to-ligand charge-transfer (MLCT) absorption.

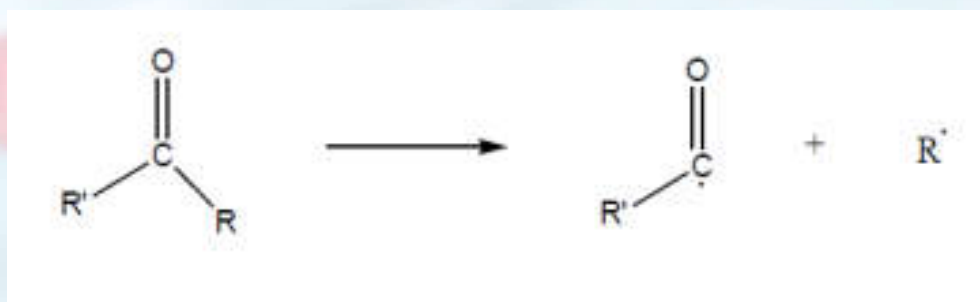


Applications in organic semiconductors; Implications in organic solar cells etc...

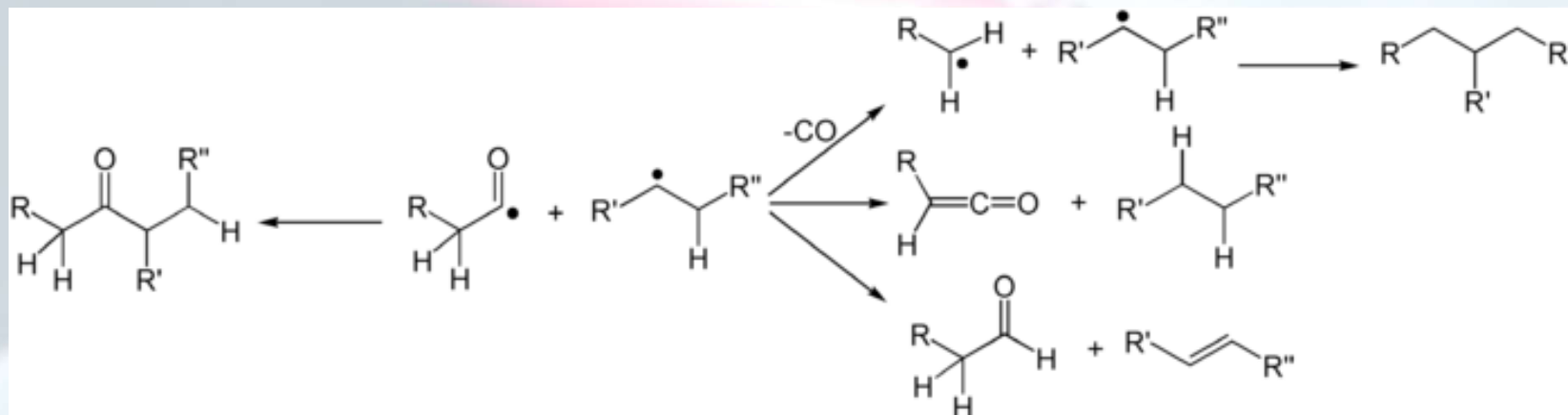
Fate of excited molecules:

- Both singlet and triplet states undergo chemical reaction but due to longer lives, mostly triplet states react chemically and singlet states have physical decay.
- Chemical reactions :

1. Simple Cleavage into Radicals:

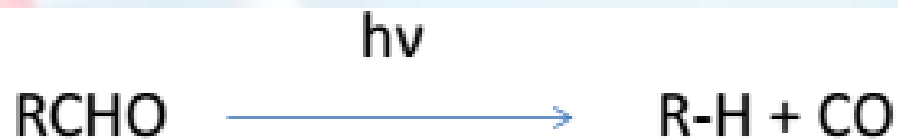


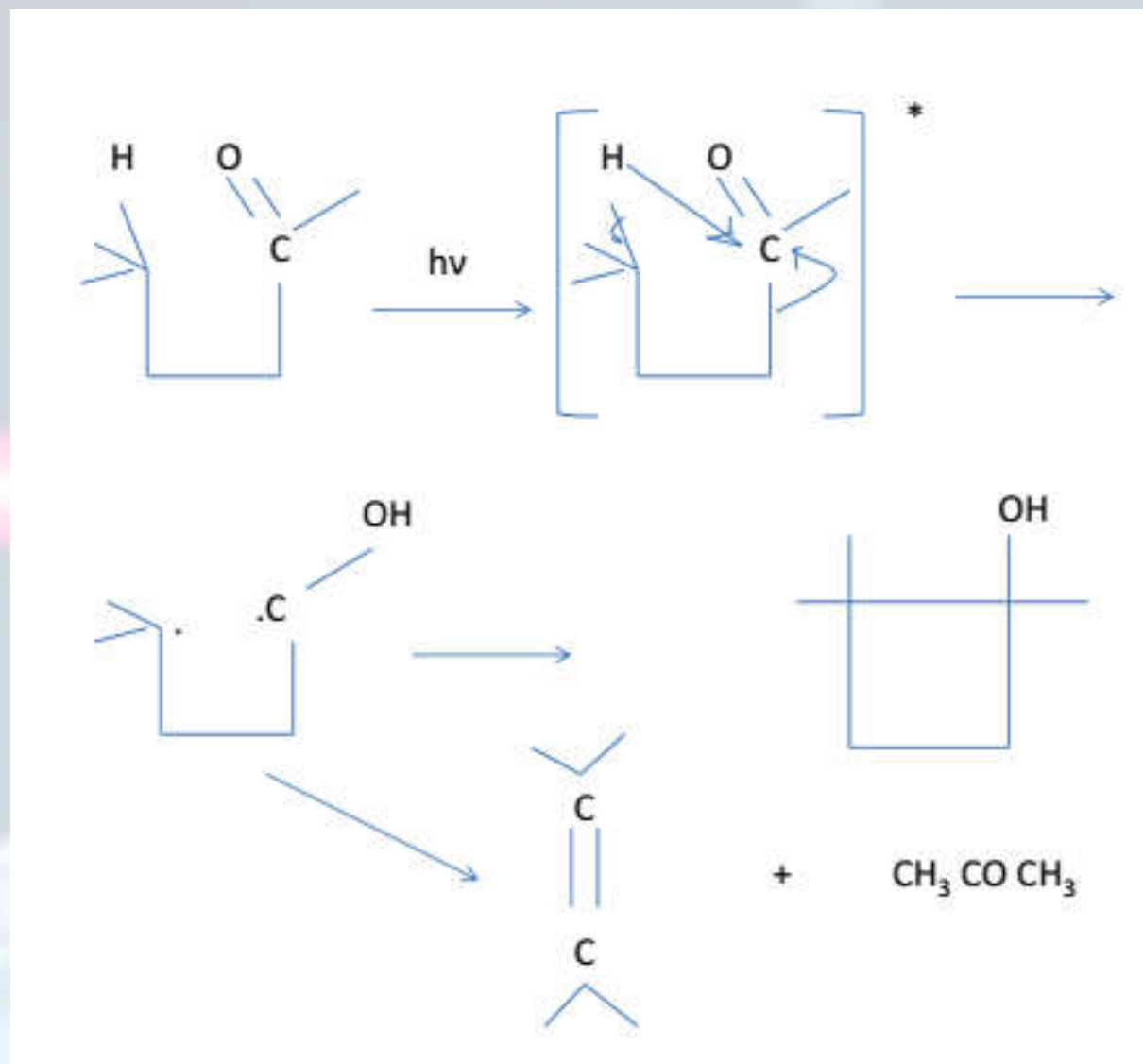
- Aldehydes and ketones absorb in 230-330nm
- Result from an $n - \pi^*$ singlet-singlet transition.
- Norrish type I reaction
- In secondary process acyl group loses CO group to give alkyl radical



2- Decomposition into Molecules:

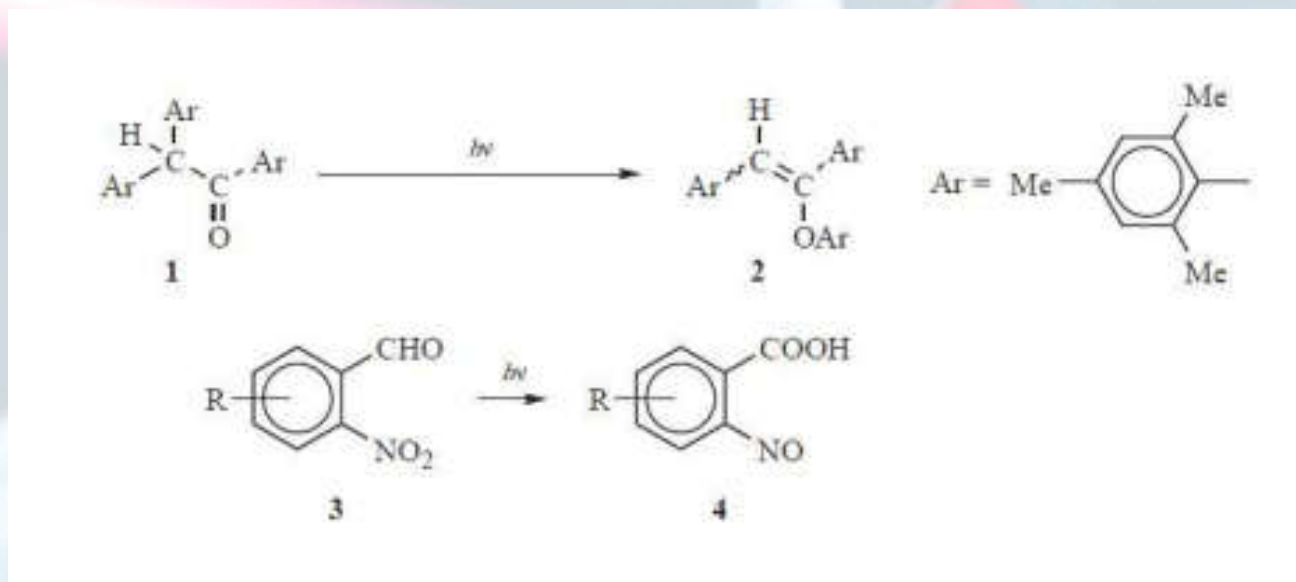
- Aldehydes (though not generally ketones) can also cleave in this manner
- Norrish type II reaction
- Involves intramolecular abstraction of the γ hydrogen followed by cleavage of the resulting diradical (a secondary reaction) to give an enol that tautomerizes to the aldehyde or ketone product
- Both singlet and triplet n, π^* states undergo the reaction.





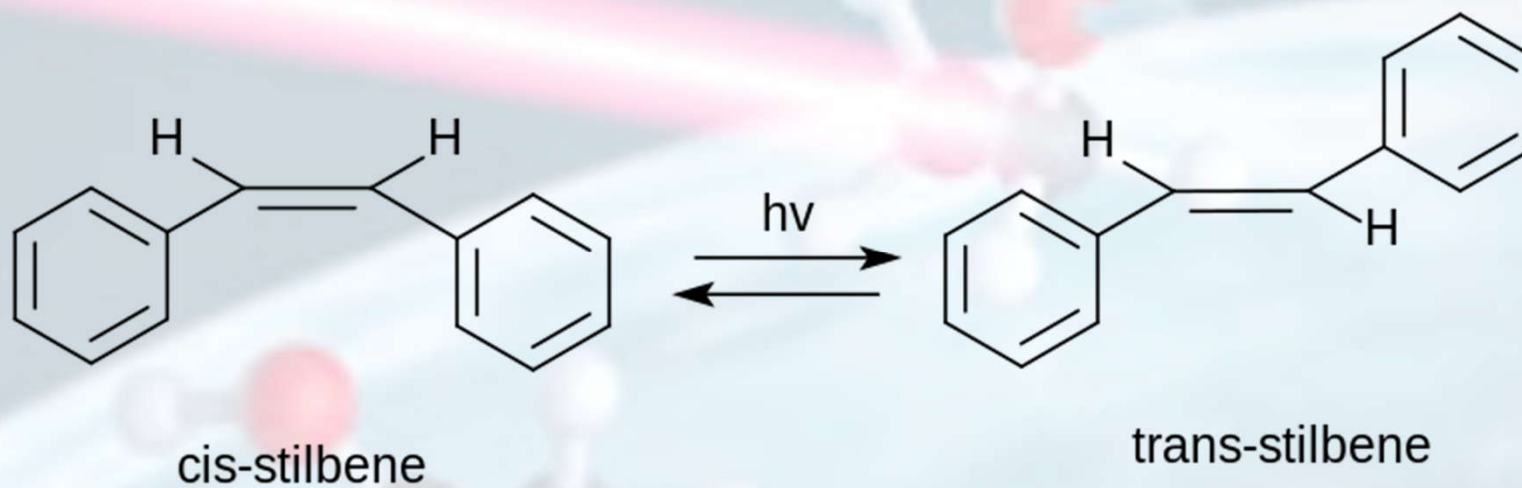
3- Intramolecular Rearrangement:

Trimesityl compound to the enol ether, and irradiation of onitrobenzaldehydes to give o-nitrosobenzoic acids.

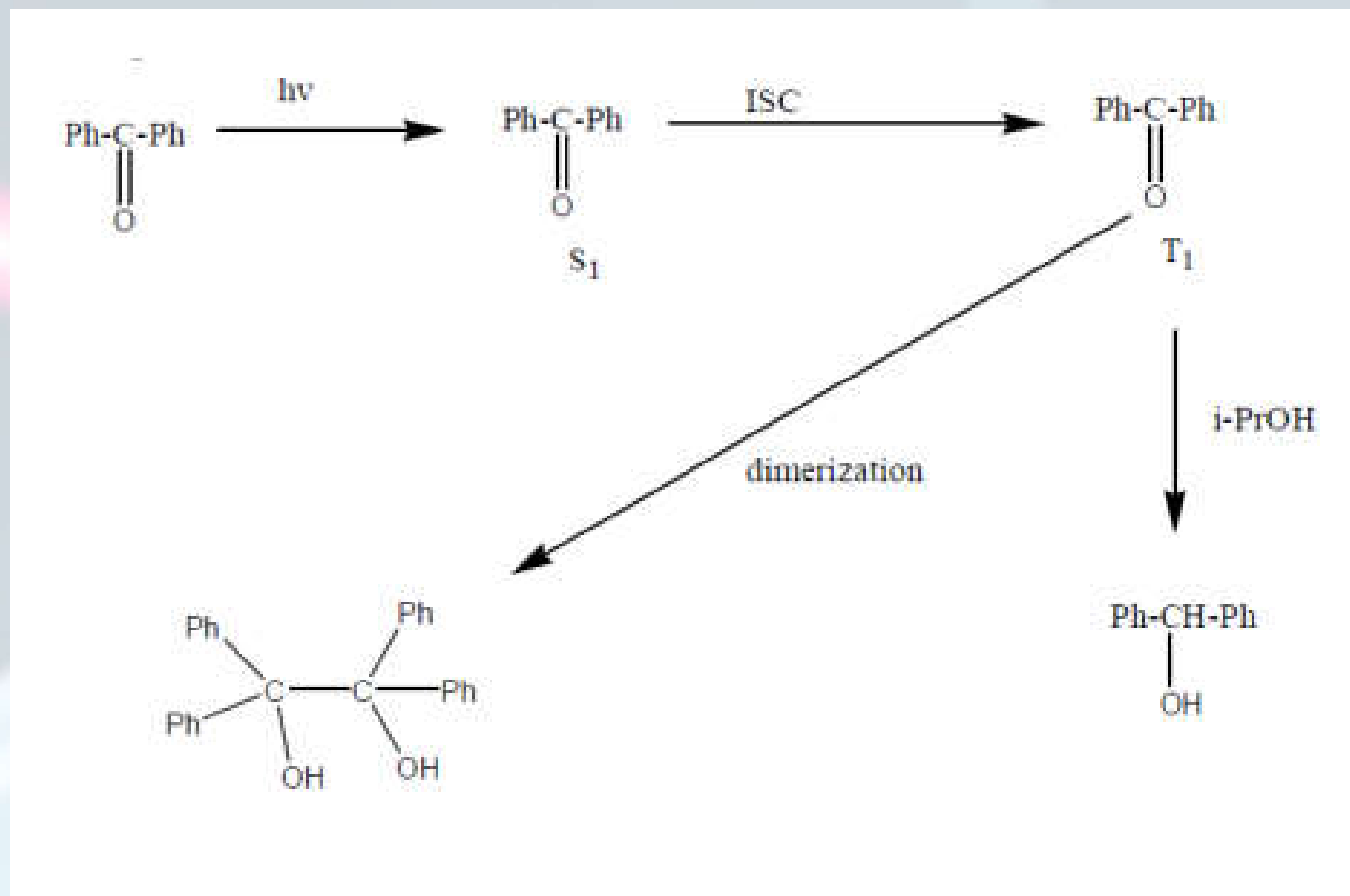


4- Photoisomerization:

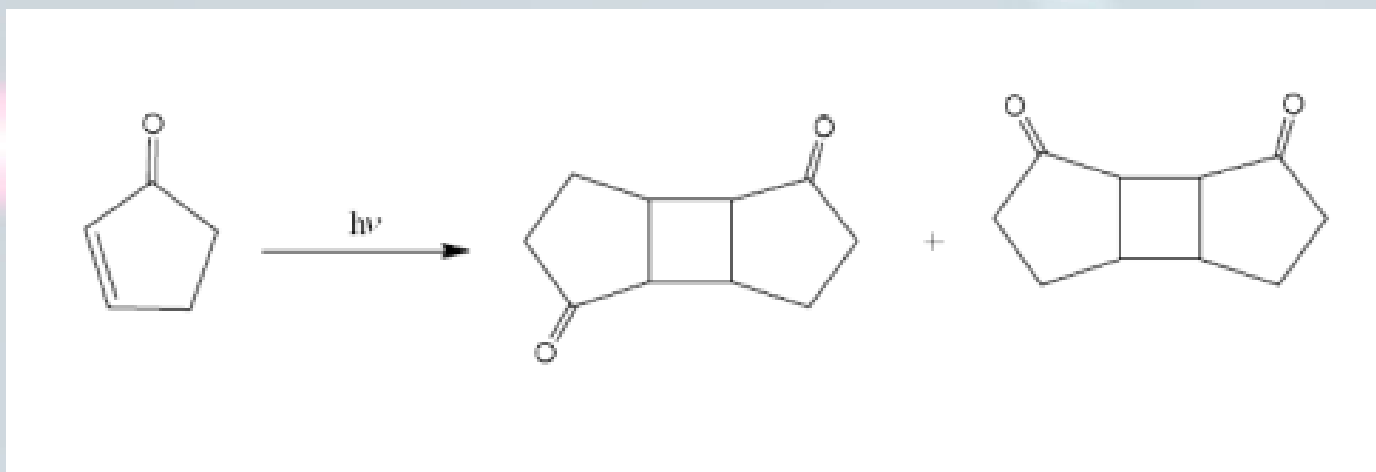
- cis trans isomerization
- e.g. cis stilbene to trans stilbene



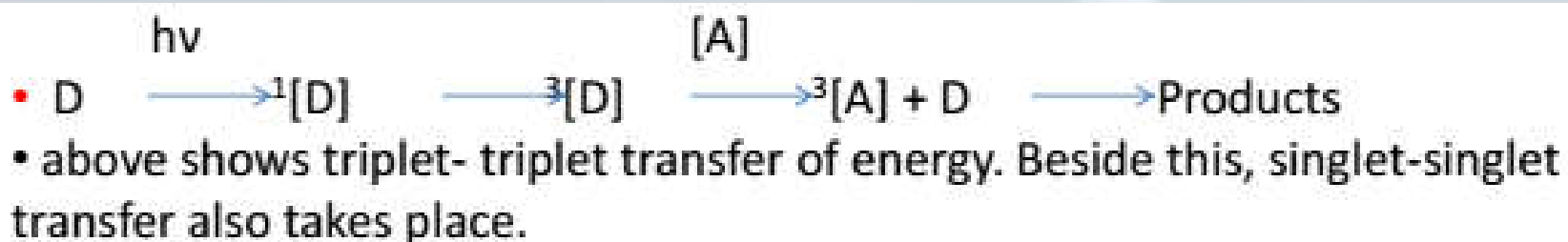
5- Hydrogen-Atom Abstraction:



6- Photodimerisation:

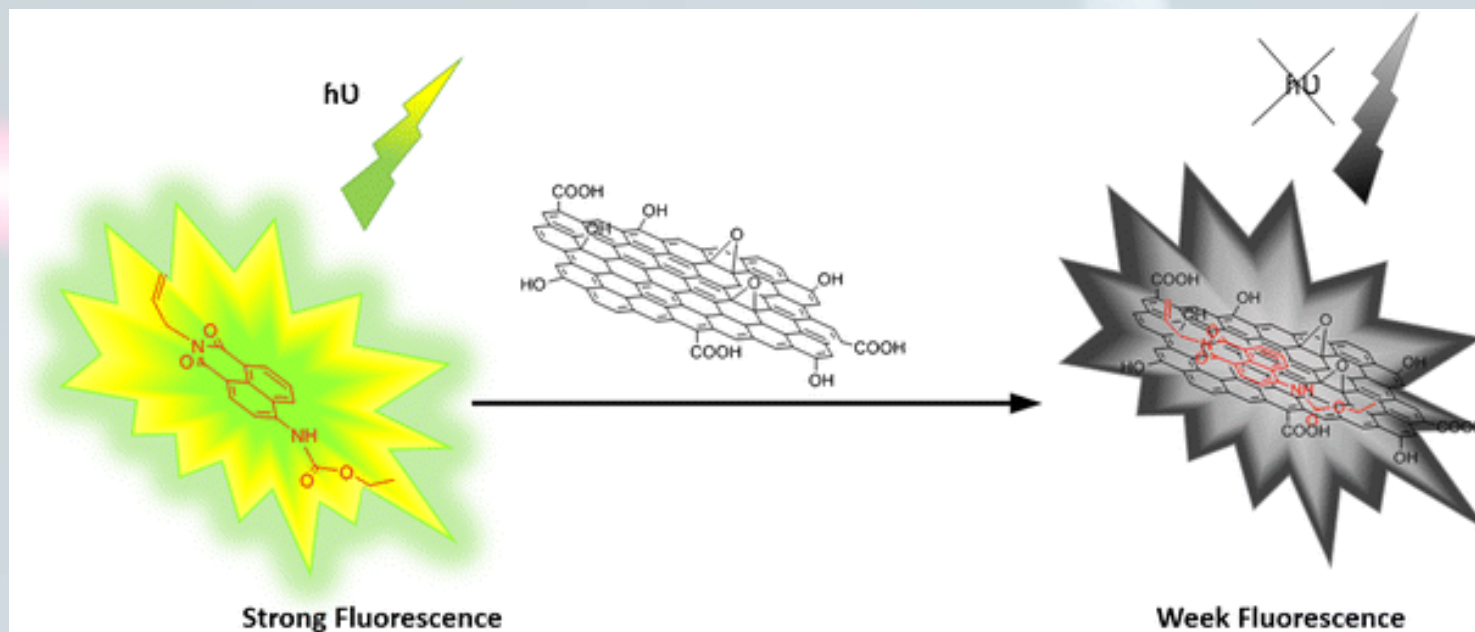


Energy transfer:

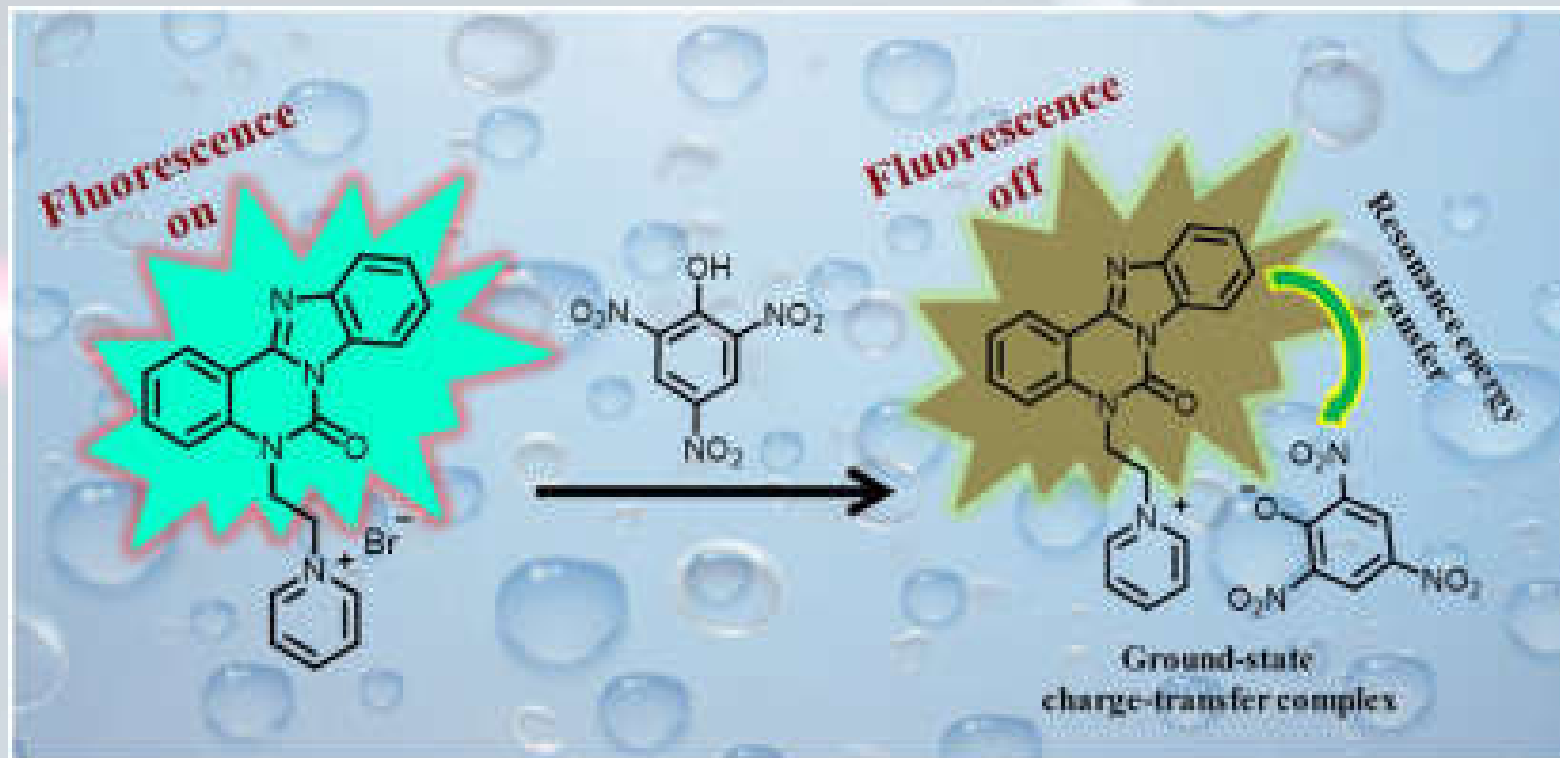


Triplet-triplet (TT) energy transfer requires two molecular fragments to exchange electrons that carry different spin and energy.

Fluorescence quenching:



- **A quencher is defined as a molecular entity that deactivates (quenches) an excited state of another molecular entity, either by energy transfer, electron transfer, or by a chemical mechanism.**

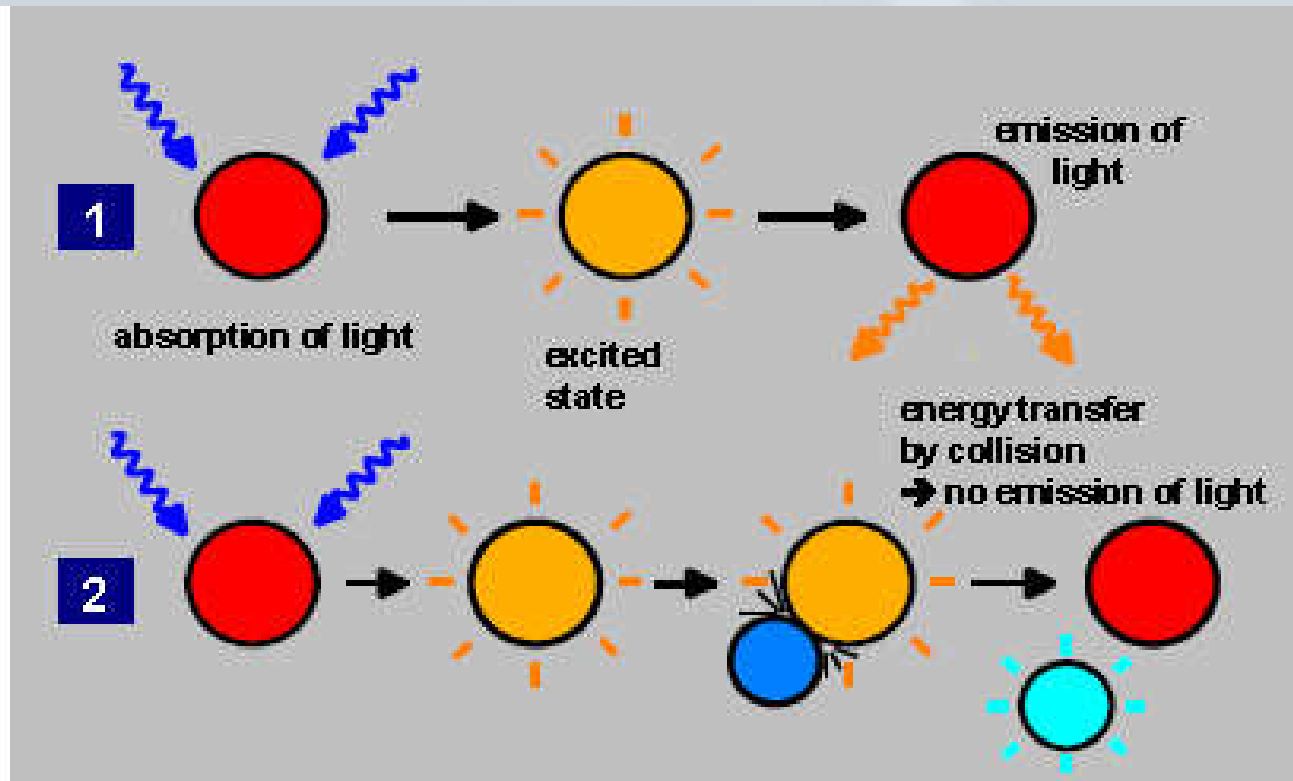


Fluorescence quenching:

Fluorescence quenching refers to any process that decreases the fluorescence intensity of a sample. A variety of molecular interactions can result in quenching. These include:

i) Collisional quenching

Quenching by collisional encounters between the fluorophore and quencher is called collisional or dynamic quenching. Energy of an excited electron in a molecule can be converted into other forms or transferred to the other molecule, preventing from the recombination with fluorescence.



ii) Relaxation through nonradiative processes:

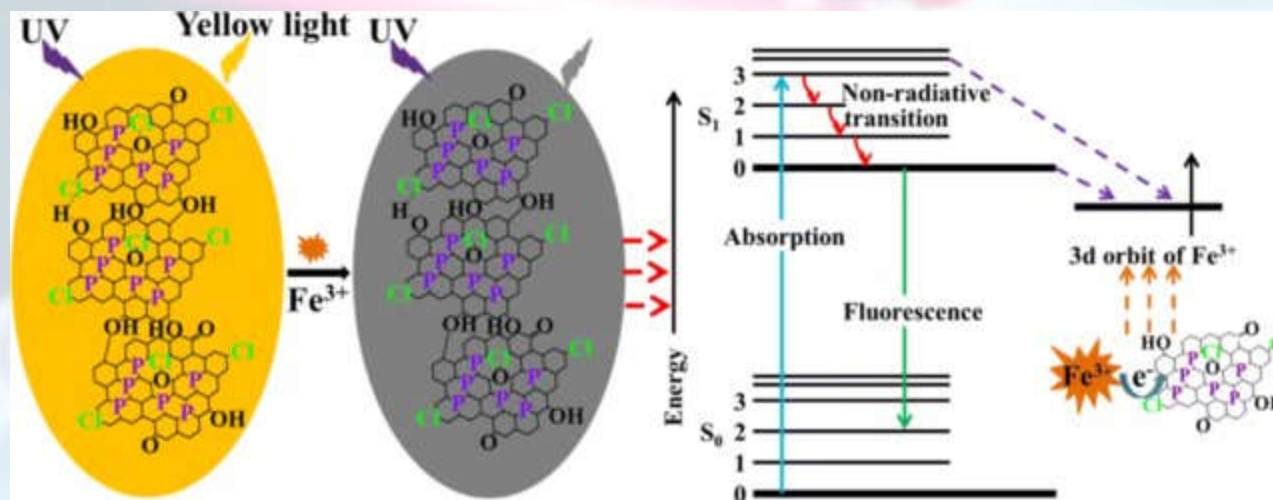
Energy of an excited electron in a molecule can also be converted into heat of the molecule (vibration) rather than the energy of a photon (photoemission).

iii) Excited-state reactions such as bond dissociation:

In some cases, such energy can be used to overcome a reaction barrier and thus triggers decomposition of the molecule or bond dissociation without photoemission.

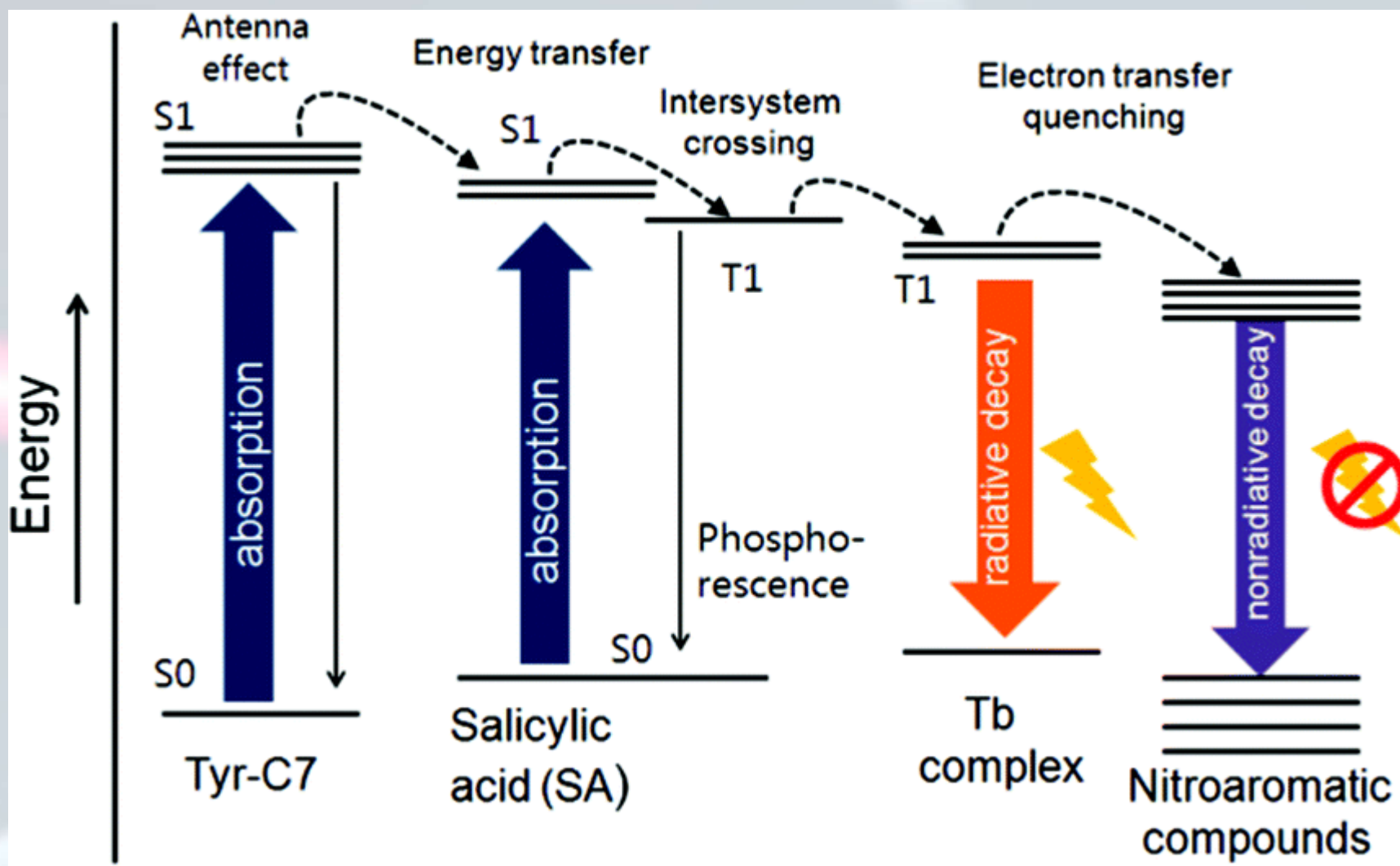
iv) Electron transfer

The excited electron can also be transferred to another molecule (inter-molecular electron transfer) or to another part of the same molecule (intra-molecular electron transfer). The latter case is likely to be occurred if the molecule has both electron donor and acceptor moieties.



v) Energy transfer:

The energy is itself able to be transferred to other molecules (inter-molecular energy transfer) or another moiety of the same molecule (intra-molecular transfer). The excited electron may emit a photon, but the released energy is used to excite another electron. This is a key process to understand the high efficiency of light-harvesting complexes in life.



Both static and dynamic quenching require molecular contact between the fluorophore and quencher. In the case of collisional quenching, the quencher must diffuse to the fluorophore during the lifetime of the excited state. Upon contact, the fluorophore returns to the ground state, without emission of a photon. In general, quenching occurs without any permanent change in the molecules, that is, without a photochemical reaction.

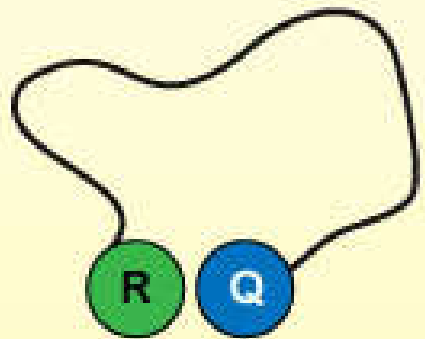
In static quenching a complex is formed between the fluorophore and the quencher, and this complex is nonfluorescent. For either static or dynamic quenching to occur the fluorophore and quencher must be in contact. The requirement of molecular contact for quenching results in the numerous applications of quenching.

Static Quenching

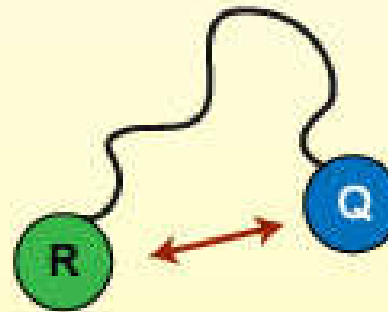
vs.

Dynamic Quenching

e.g. Forster (FRET)
Dexter (collisional)



vs.



strong coupling
→ intramolecular dimer

weak coupling