광화학과 응용

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Introduction

- The fate of the excited molecule (physical processes).
- A molecule, photochemically promoted to an excited state, does not stay there for long. Excitations to S_2 and higher singlet states take place, but in liquids and solids these higher states usually drop very rapidly to the S_1 state (about 10^{-13} to 10^{-11} sec) by giving up the energy to the environment. This process is called an *energy cascade*.
- In a similar manner, molecules at different vibrational levels of S_1 cascade down to the lowest vibrational level of S_1.

- Therefore, in most cases, the lowest vibrational level of the S_1 state is the only important excited singlet state.

Introduction

- This state can undergo various physical processes:
- 1. A molecule in the S_1 state can cascade down to the ground state through the vibrational levels of the S_0 state. The process is called *internal conversion*.
- 2. Molecules in the S_1 state can cross to a T_1 state (*intersystem crossing*) without loss of energy and cascade down to its lowest vibrational level.
- 3. A molecule in the S_1 state drops to some low vibrational level of the S_0 state all at once by giving off the energy in the form of light. This process, which generally happens within 10^{-9} sec, is called *fluorescence* and is common for small molecules and rigid molecules (e.g., aromatic).
- 4. A molecule in the T_1 state may return to the S_0 state by giving up heat (*intersystem crossing*) or light (*phosphorescence*).
- 5. A molecule in an excited state (S_1 or T_1) may transfer its excess energy all at once to another molecule in the environment, in a process called *photosensitization*. The excited molecule thus drops to S_0 while the other molecule becomes excited.

- Physical processes

Physical Processes Undergone by Excited Molecules	
$S_0 + h\nu \longrightarrow S_1^v$	Excitation
$S_1^v \rightsquigarrow S_1 + \text{heat}$	Vibrational Relaxation
$S_1 \longrightarrow S_0 + h\nu$	Fluorescence
$S_1 \rightsquigarrow S_0 + \text{heat}$	Internal Conversion
$S_1 \rightsquigarrow T_1^v$	Intersystem Crossing
$T_1^v \rightsquigarrow T_1 + \text{heat}$	Vibrational Relaxation
$T_1 \longrightarrow S_0 + h\nu$	Phosphorescence
$T_1 \rightsquigarrow S_0 + \text{heat}$	Intersystem Crossing
$S_1 + A_{(S_0)} \longrightarrow S_0 + A_{(S_1)}$	Singlet-Singlet transfer (photosensitization)
$T_1 + A_{(S_0)} \longrightarrow S_0 + A_{(T_1)}$	Triplet-Triplet transfer (photosensitization)

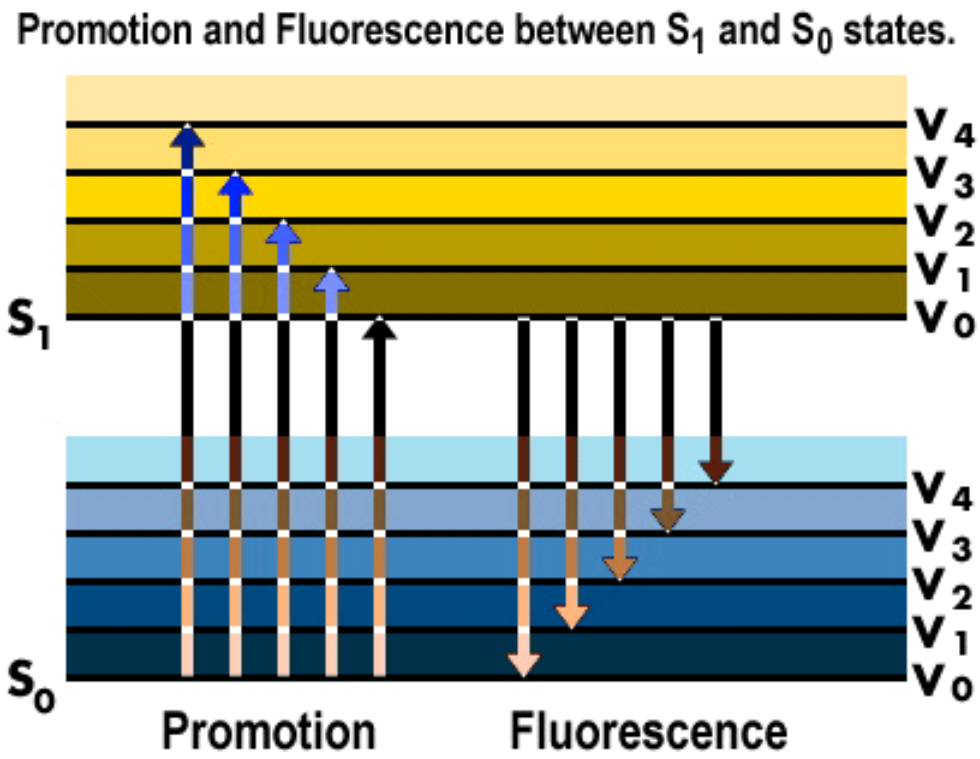
^{v}indicates vibrationally excited state
excited states higher than S_1 or T_1 are omitted

Fluorescence probe

- A fluorescent probe is a fluorescent chromophore designed to localize within a specific region of a biological specimen or to respond to a specific stimulus. In addition to the high detection sensitivity, the fluorescence process is sensitive to subtle changes in molecular environment. Therefore, the use of fluorescent probes is a powerful method to obtain information about the structure, function, and health of cells.

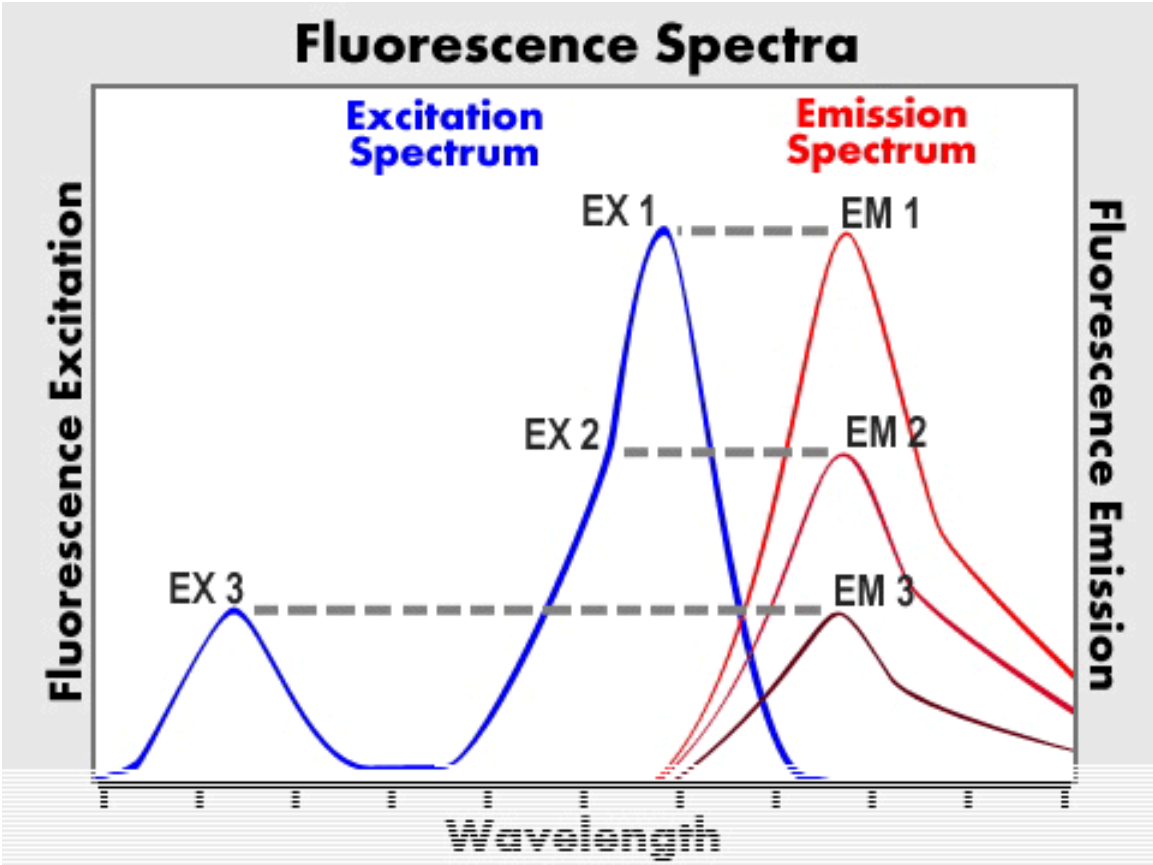
Fluorescence probe

- Transitions to vibrational levels



Fluorescence probe

- Excitation, emission spectra



Phtochemical terms

- The following properties are important for a fluorescent probe:
- 1. Extinction coefficient (α)
- The fluorescence output of a fluorescent probe depends on the efficiency with which it absorbs and emits photons. The extinction coefficient is the absorption efficiency reflecting the number of molecules making the transition and expressed by = E/*c*/ (where *c* is the concentration in moles per liter, / is the cell length in centimeters and E = log I_0/I, where I_0 is the intensity of the incident light and I of the transmitted light). The value of among fluorescent probes of current practical importance is around 5000 to 200,000 cm^{-1} mol^{-1}.
- 2. Quantum yield (ϕ)
- The emission intensity relates directly to the quantum yield, which is the ratio of the number of fluorescence photons emitted to the number of photons absorbed. For practical purposes, the quantum yield should be close to 0.4 or greater when the fluorescent probe is bound to the target and is in the solvent environment where the measurement is to be made. The fluorescence intensity of a probe is determined by the product of and .
- 3. Excitation wavelength
- Cells excited at wavelengths below 500 nm produce considerable autofluorescence that arises mainly from flavins, flavoproteins, NADH, etc. In situations where autofluorescence can swamp the probe fluorescence, it is useful to have the probe that can be excited at wavelengths above 500 nm.

Phtochemical terms

- 4. Photostability

  The same fluorescent probes can be repeatedly excited and detected, unless they are irreversibly destroyed in the excited state (an important phenomenon known as *photobleaching*). The photobleaching is commonly observed under intense microscope illumination. It is generally not a problem in flow cytometry because the sample only remains in the laser beam a short time.

- 5. Excited-state lifetime (τ)

  This is the average time that a molecule remains in the excited state. Short fluorescence lifetimes permit the greatest sensitivity to be achieved since multiple excitations can be achieved if the molecule is quickly relaxed after a prior excitation event. Most fluorophores have emission lifetimes in the order of nanoseconds. In cases where scattered light and autofluorescence of short lifetimes create interference with the desired fluorescence signal, it is desirable to use long-lived fluorochromes in combination with an appropriate photomultiplier tube.

- 6. Minimal perturbation by probe

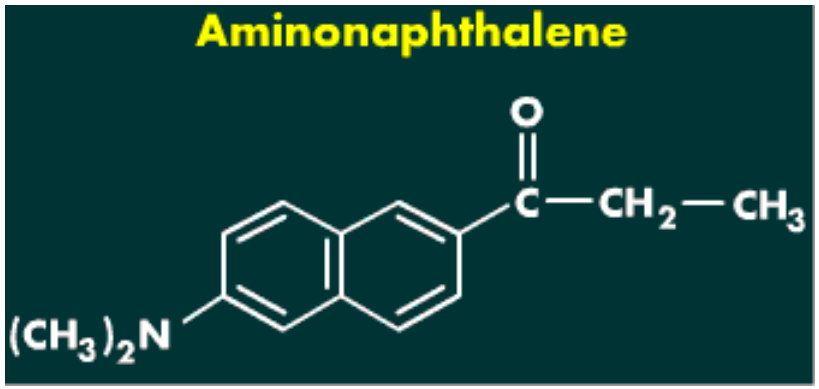
  The probe should not perturb the function of the cell, organelle, or target molecule by reacting with key groups in active sites or by causing nonspecific binding of a labeled protein, or by causing steric perturbations because of its size. The probe should also not be phototoxic.

• Environmental Sensitivity of Fluorescence

- Fluorescence spectra and quantum yields are in general more dependent on the environment than absorption spectra and extinction coefficients. This spectroscopic sensitivity of fluorescent probes to the surrounding environment makes the method versatile for probing the behavior of cells. Many environmental factors exert influences on fluorescence properties. It should be mentioned that R. Boyle (1626-1691) was the first to establish two main environmental facts regarding fluorescence of organic compounds-that the phenomenon is most apparent in dilute solutions (*fluorophore-fluorophore interactions*) and is greatly affected by acids and alkalies (*interactions with hydrogen and metal ions*).

Fluorescence probe – polarity

- 1. Environmental polarity.
- Fluorescence spectral shifts to longer wavelengths occur in a polar solvent because energy of the excited state is lost to the solvent when polar solvent molecules reorient around the more dipolar structure of excited fluorophores shortly after excitation. This characteristic is commonly observed with fluorophores that have large excited-state dipole moments. For example aminonaphthalene fluorophores are effective probes of environmental polarity in, for example, a protein's interior.



2. Fluorophore-fluorophore interactions.

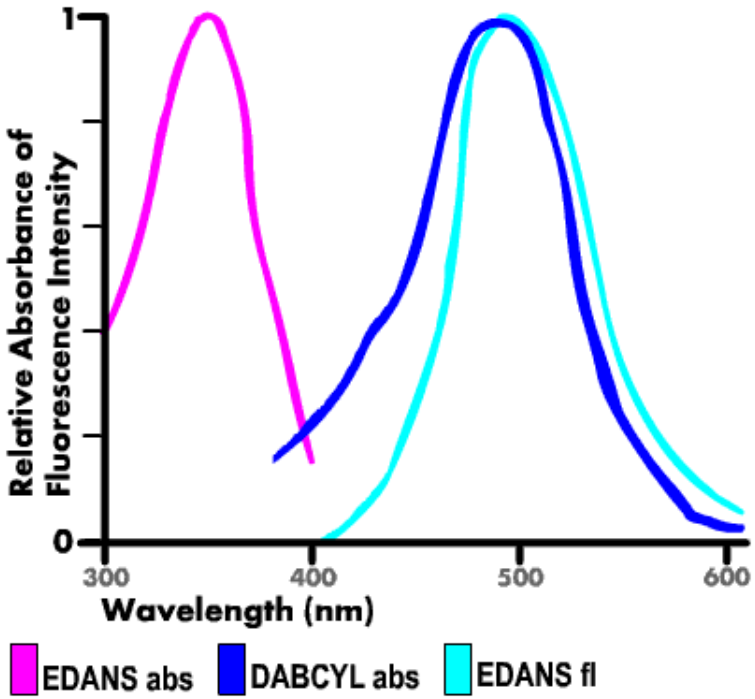
The quenching of one fluorophore by another (*self-quenching*) occurs in the case of high loading concentrations or labeling densities. This is the basis of protease detection in which protease-catalyzed hydrolysis of the heavily labeled and almost totally quenched protein substrates relieves the intramolecular self-quenching, thus yielding brightly fluorescent peptide fragments.

동영상

http://laxmi.nuc.ucla.edu:8248/M248_98/synprob/part1/en_sens2.html

Fluorescence probe – Energy transfer

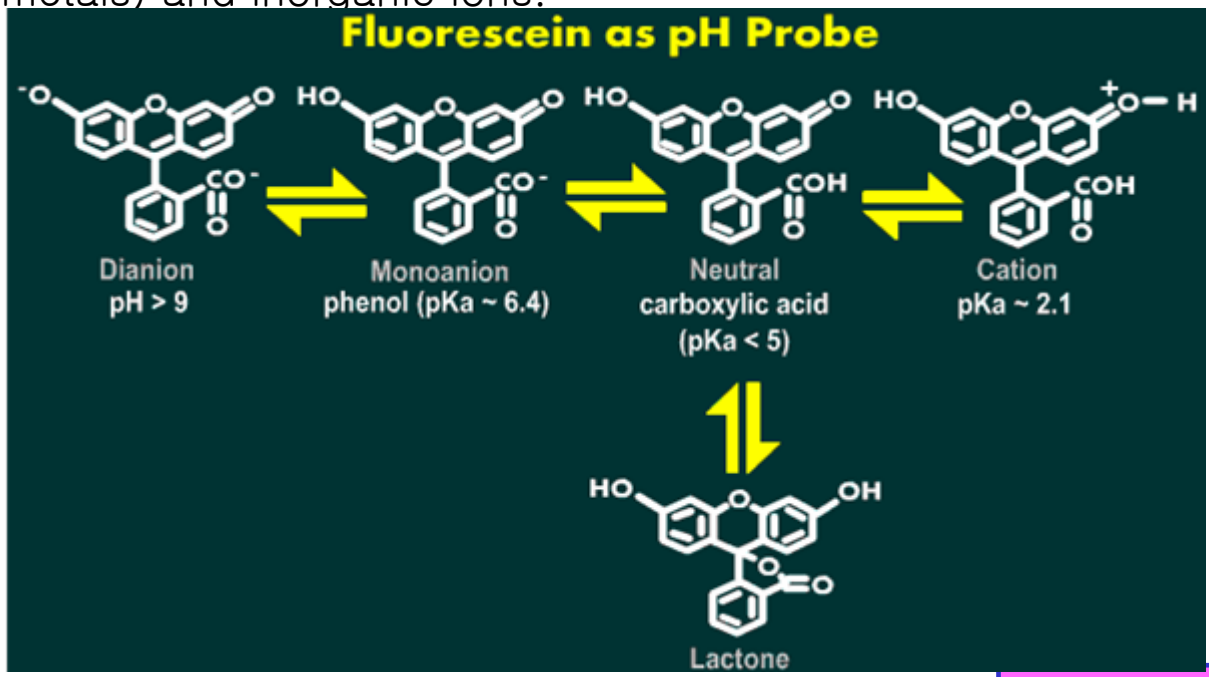
- *Fluorescence resonance energy transfer* is a distance-dependent interaction between the electronic excited states of two fluorophores in which excitation is transferred from a donor molecule to an acceptor molecule without emission of photon.



Fluorophore-fluorophore interactions have been employed to monitor a wide array of molecular assembly or fragmentation processes

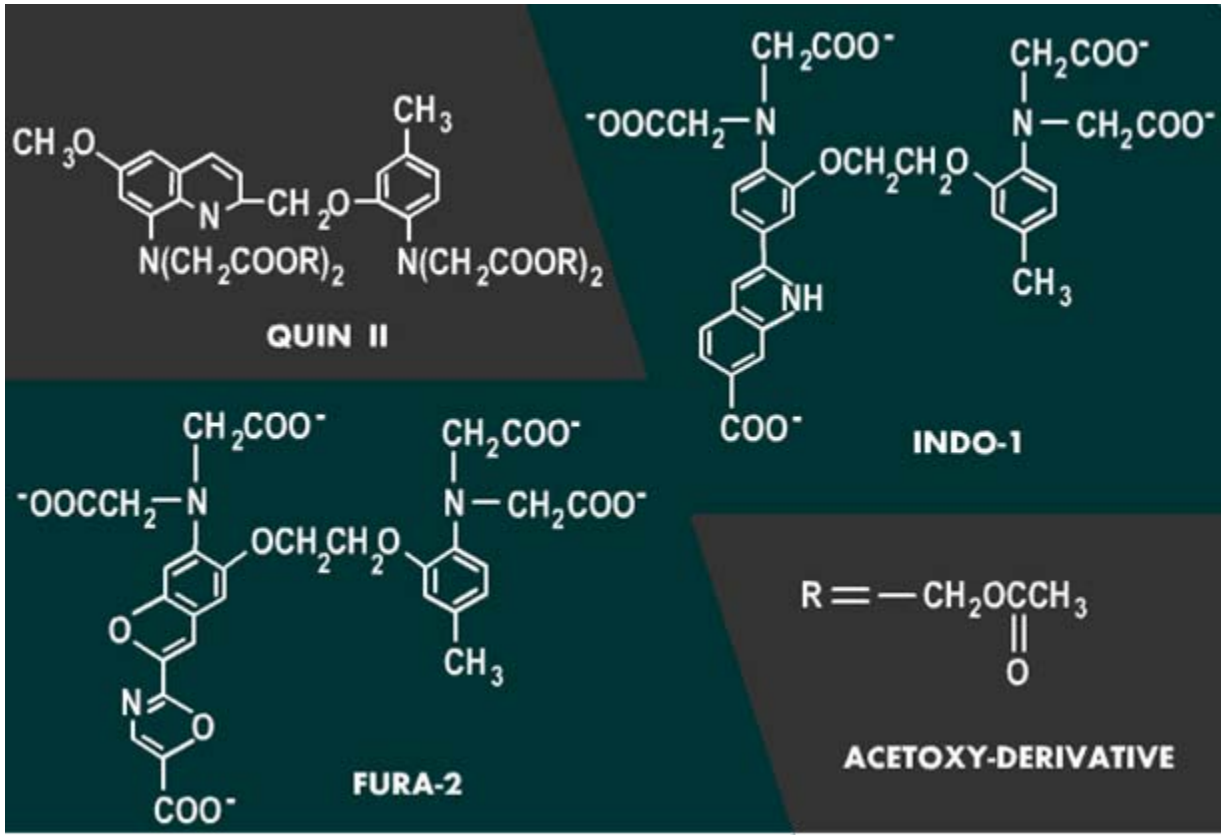
Fluorescence probe – pH, metal ion

- 3. Interactions with hydrogen or metal ions.
- The binding of hydrogen or metal ions changes the electronic structure of a number of fluorophores, thus affecting the absorption properties and/or the fluorescence properties of the probes. For example, various fluorescein-labeled proteins have quantum yields (ϕ) in the range of 0.2 to 0.7 at pH 8 which drop off rapidly with decreasing pH. Rhodamine, on the other hand, is much less sensitive to pH and is still fluorescent in acidic compartments of cells or in the presence of acidic fixatives. This characteristic has been utilized to develope probes for pH, calcium (and other metals) and inorganic ions.



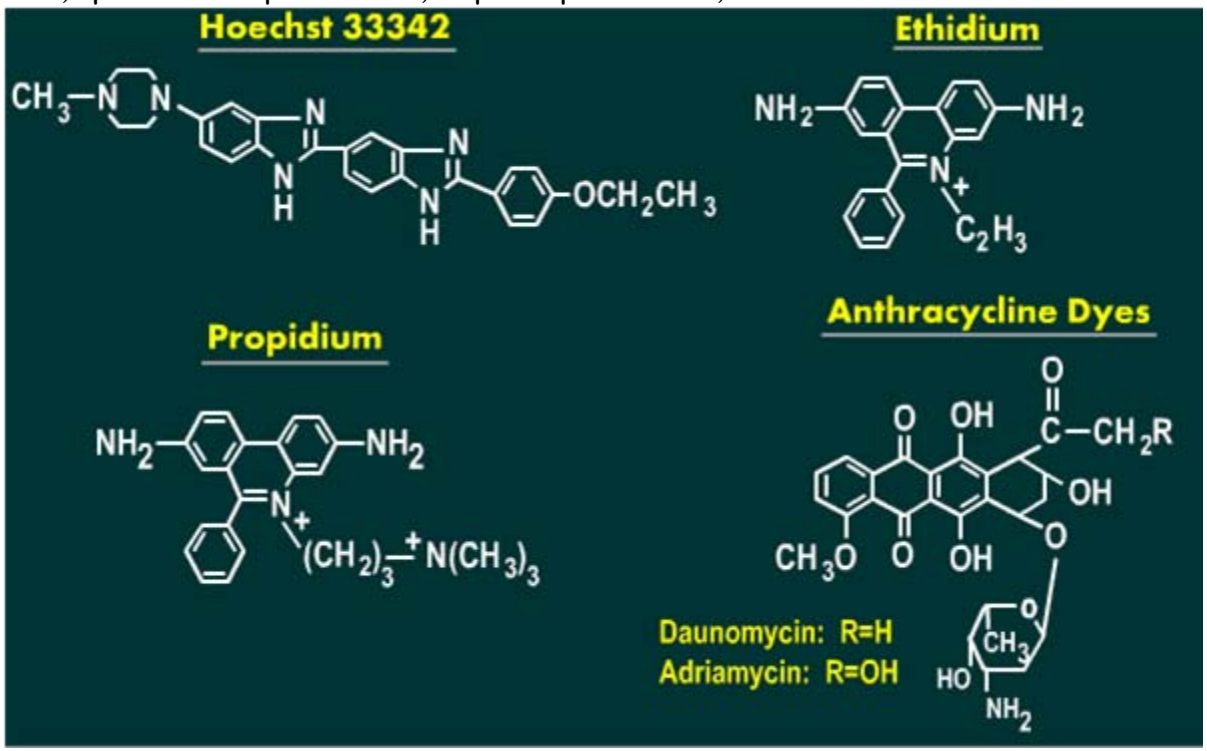
Fluorescence probe – Ca ion

The ester derivatives are membrane permeant. Cellular esterases convert the derivatives into the free-acid forms of the probes, which are trapped inside cells and are able to chelate calcium.

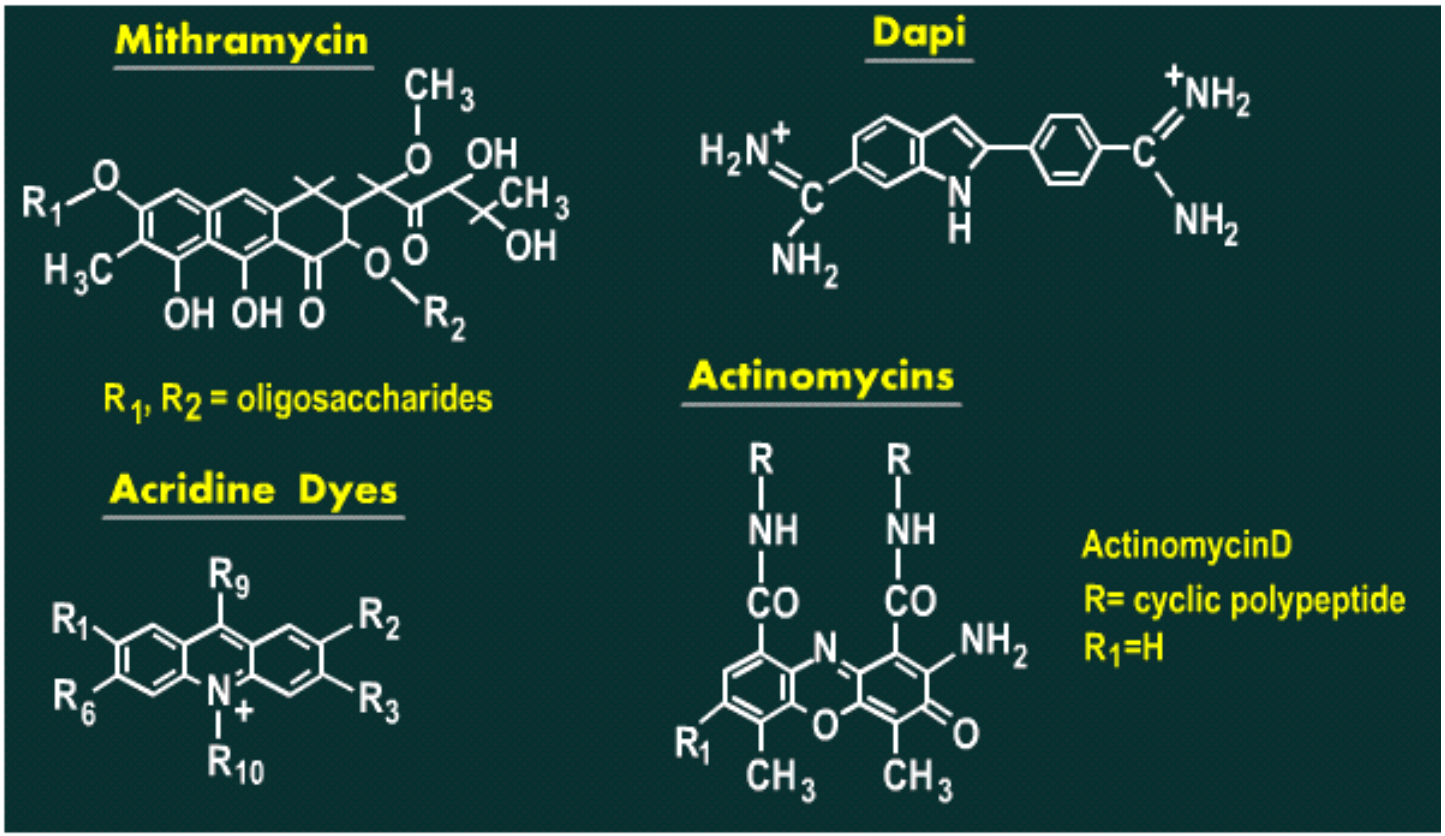


- 4. Interactions with biomolecules.

  Due to their particular structural nature, fluorescent probes can bind noncovalently to special biomolecules in cells in a specific or a non-specific fashion. The binding can affect dramatically the fluorescence quantum yield and wavelength, which is the basis of DNA and RNA probes, protein probes, lipid probes, etc.

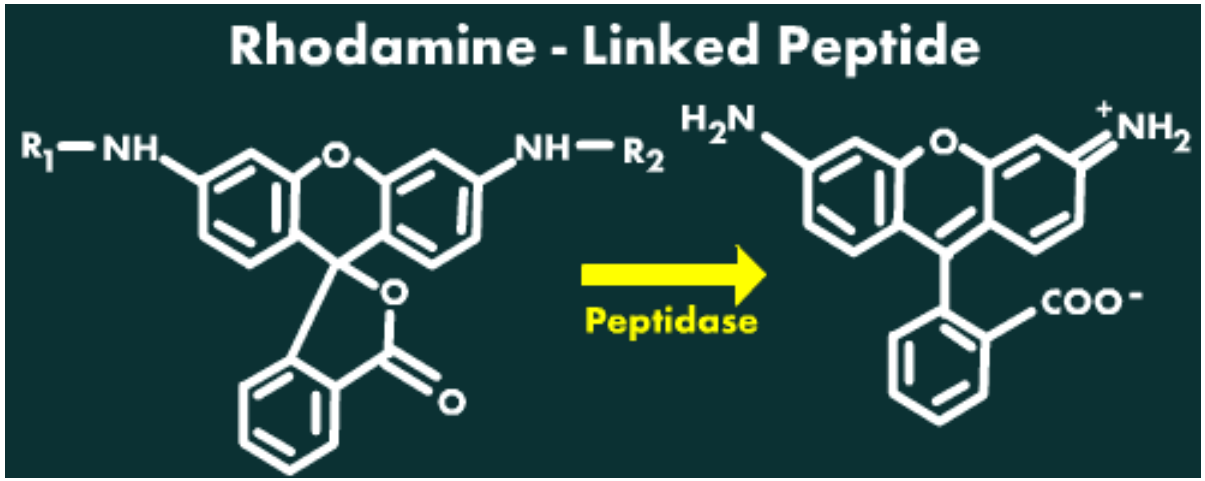


- 4. Interactions with biomolecules.
  - DNA Probes-2



Fluorescence probe – enzyme

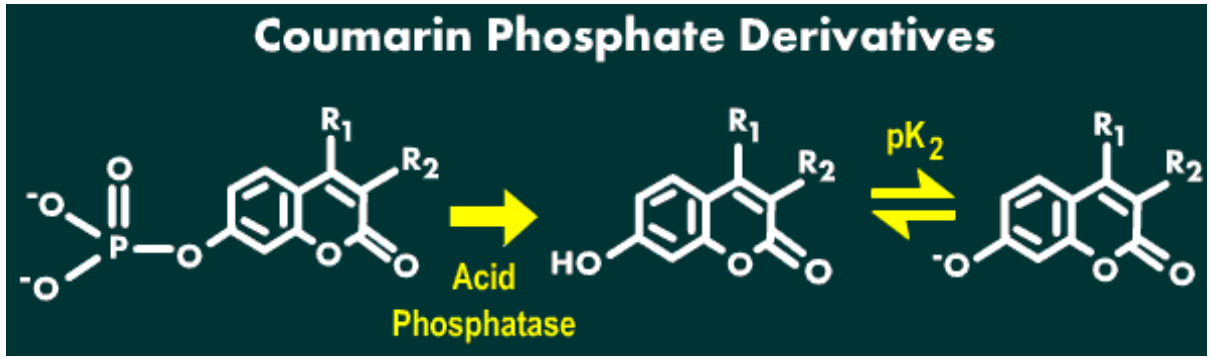
- Fluorogenic enzyme substrates are fluorescent probes that are converted by specific enzymes into products that have either increased fluorescence or shifted spectra. These are useful probes for monitoring enzyme activities. Due to their particular structural nature, fluorescent probes can bind noncovalently to special biomolecules in cells in a specific or a non-specific fashion. The binding can affect dramatically the fluorescence quantum yield and wavelength, which is the basis of DNA and RNA probes, protein probes, lipid probes, etc.
  - Fluorogenic Enzyme Substrates



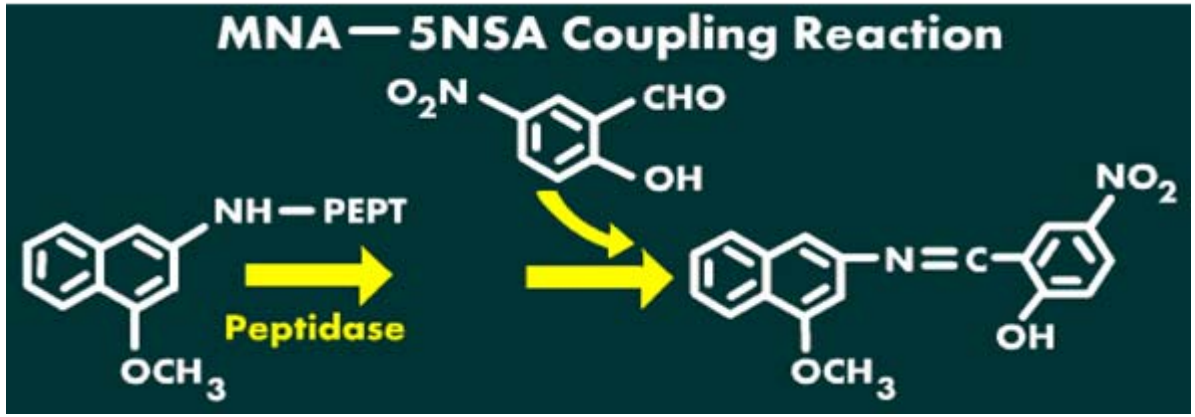
- R_1, R_2 = Peptides specific for the enzyme of interest.

Fluorescence probe – enzyme

- Fluorogenic Enzyme Substrates
- R_1, R_2 = Chosen to shift the fluorescence of these derivatives toward the visible region of the spectrum



•The free amino group, which is made available when the peptide bond of peptidyl-methoxynaphthylamine is hydrolyzed by a peptidase, couples with 5-nitrosalicaldehyde, which is present during the reaction, to form the insoluble red-orange fluorescing product.

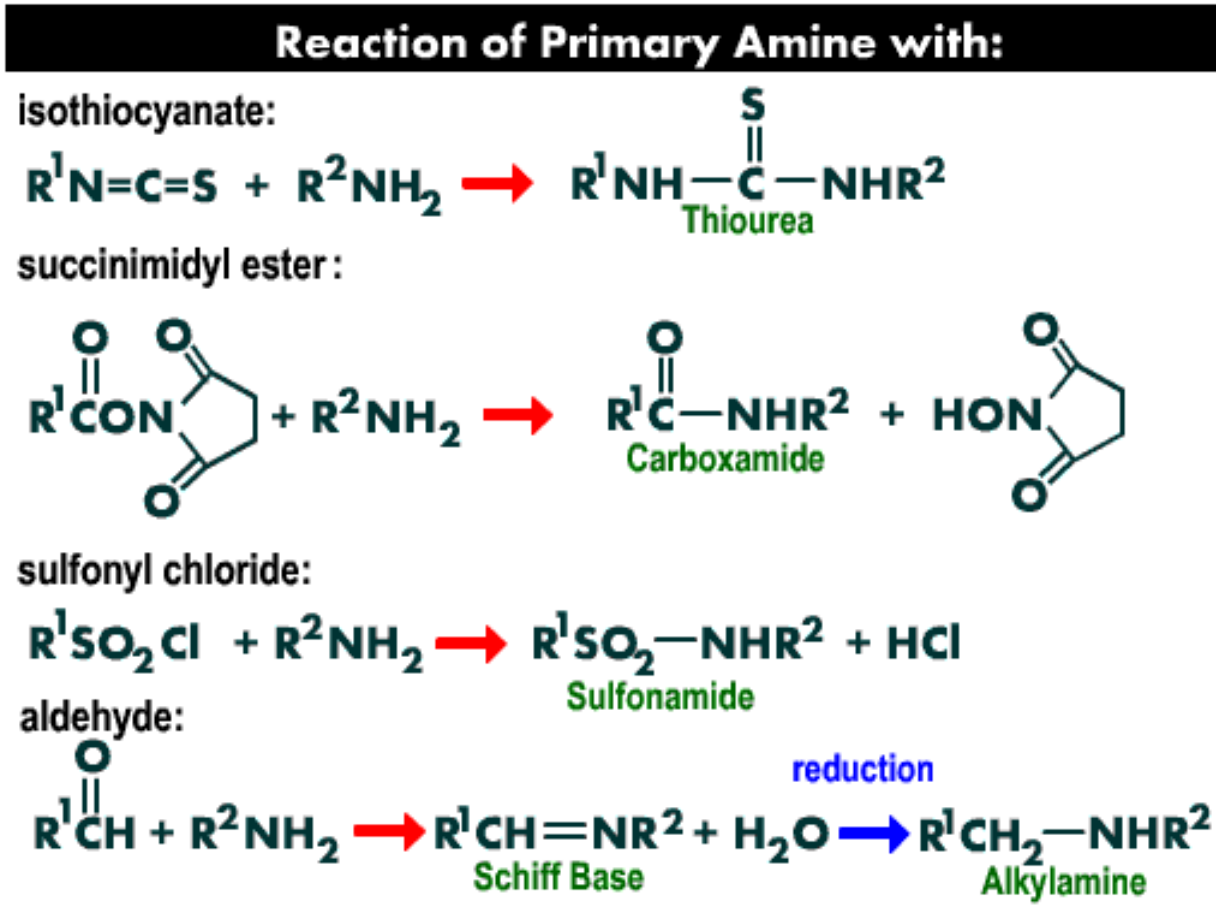


Fluorescence probe – covalent bond

- Covalent Labeling of Biomolecules

- Fluorescent probes can be used to tag proteins, nucleotides, lipids, oligosaccharides or other biological molecules. The fluorescence-tagged molecules are then used to localize and monitor interesting biological processes in living cells. The labeling reagent must have the proper reactivity and selectivity and should be soluble in aqueous solutions. It is also important that the fluorescence of the label should be insensitive to environmental pH and polarity. *Primary amines, thiols* and *aldehydes* are common functional groups available for biomolecules to covalently attach fluorescent probes.

Fluorescence probe – amine



Fluorescence probe – thiol

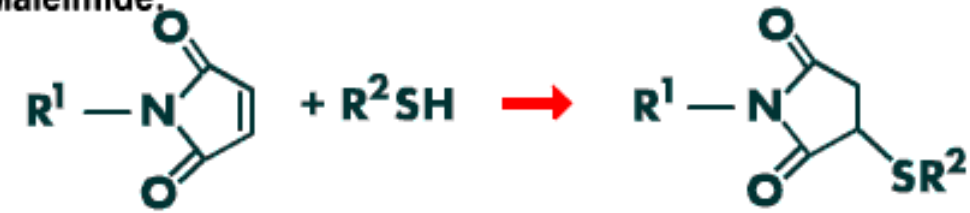
Reaction of a Thiol with:

Iodoacetamide:

Alky Halide or Haloacetamide

(X= I,Br,Cl)

Maleimide:



Thioether

Aziridine:

Thioether

Symmetric Disulfide:

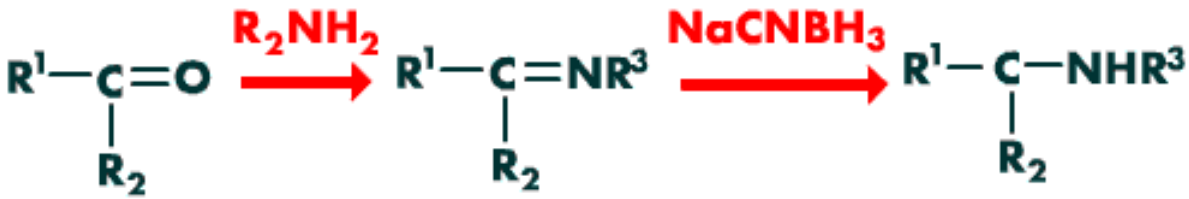
Mixed Disulfide

Fluorescence probe – hydrazine

Reaction of Aldehydes and Ketones with:

Hydrazine Derivatives:

Amine Derivatives:



Reference

- http://laxmi.nuc.ucla.edu:8248/M248_98/synprob/part1/photochem.html

Applications – media

- Micelles
- Vesicles
- Clays
- Cyclodextrin
- Porous materials
- Polymer network

Applications – reactions

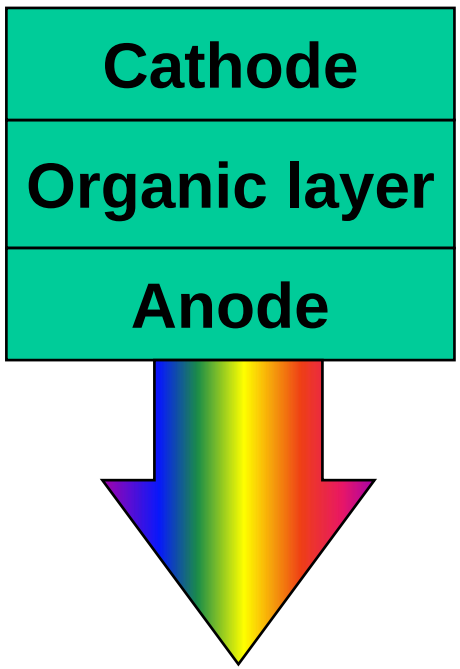
- Isomerizations
- 2+2 reactions
- Polymerization – radical reactions
- Color changing reactions
- Store energy

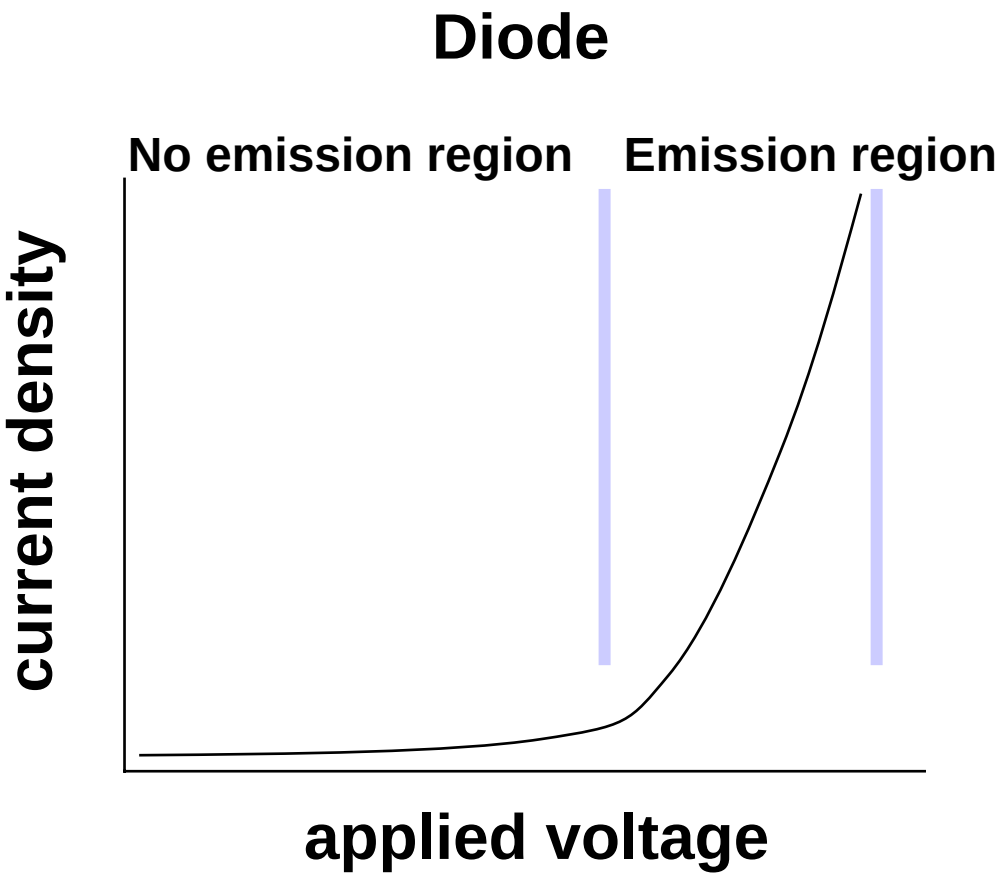
Overviews

- What is OLEDs?
- Organic materials for OLEDs
- Development of device structures
  - Improvement of interfacial properties using buffer layer
- Characterization of devices

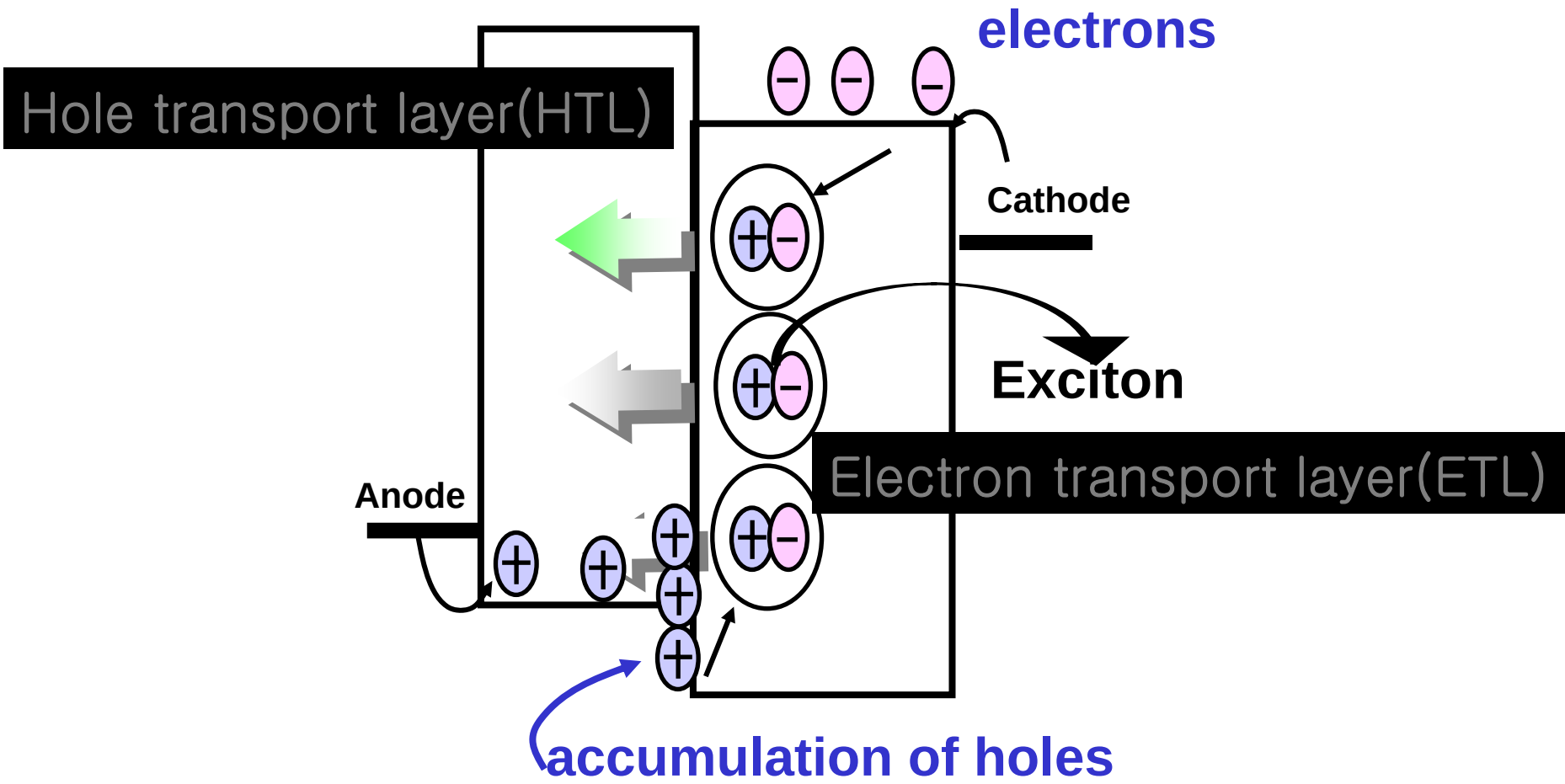
What is organic light emitting diodes(OLEDs)?

- Light emission from organic materials between electrodes





Light emission processes



Hole & Electron Conduction

- Electron conduction
  - Electron transfer
- Hole conduction
  - Electron transfer induced by positive charge.
  - Containing non-bonding electrons in the molecules.
  - Faster than electron conduction in most organic films (~100 times faster)

Development of device structures

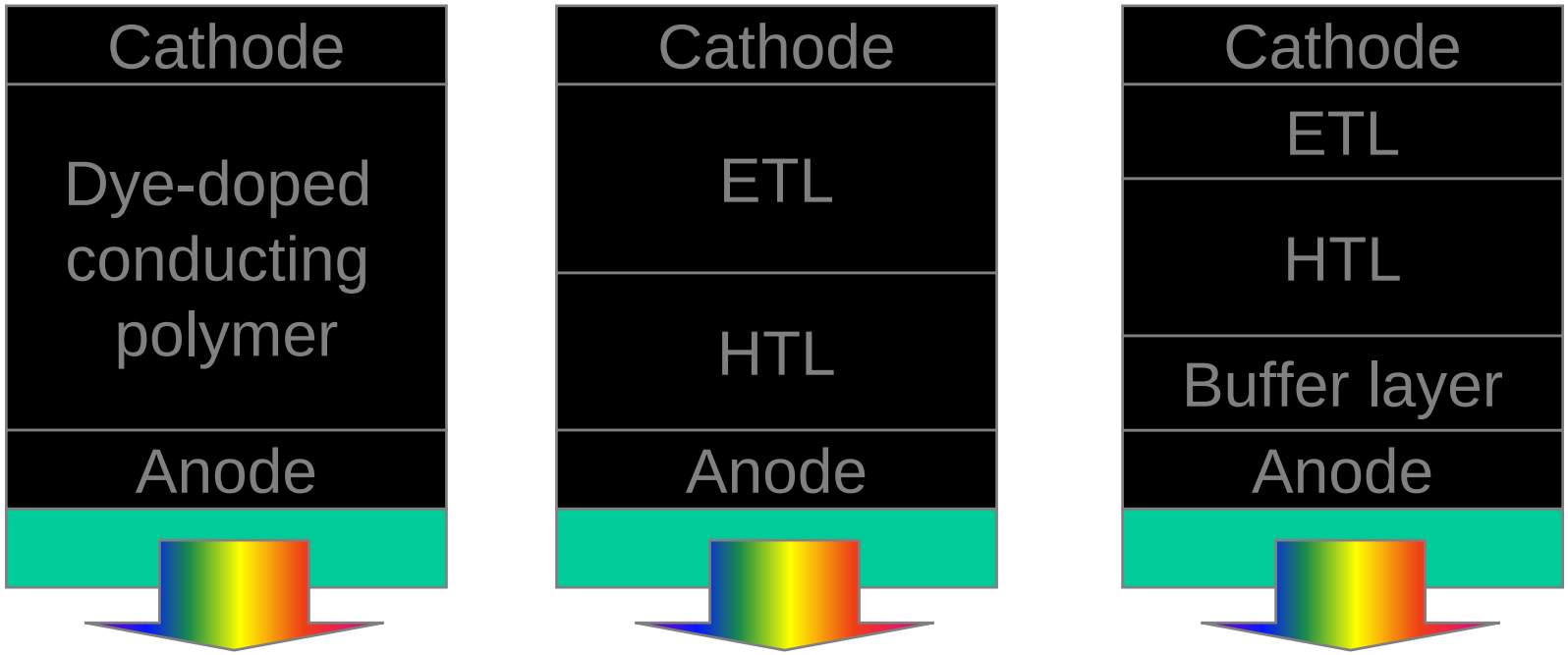
- Multi-layer system
- Buffer layer
  - to improve metal/organic interface
  - to improve carrier(hole) injection

Main Issues

- Interface of metal/organic layer
- Balancing holes and electrons at the emission region.
- Efficient formation of excitons

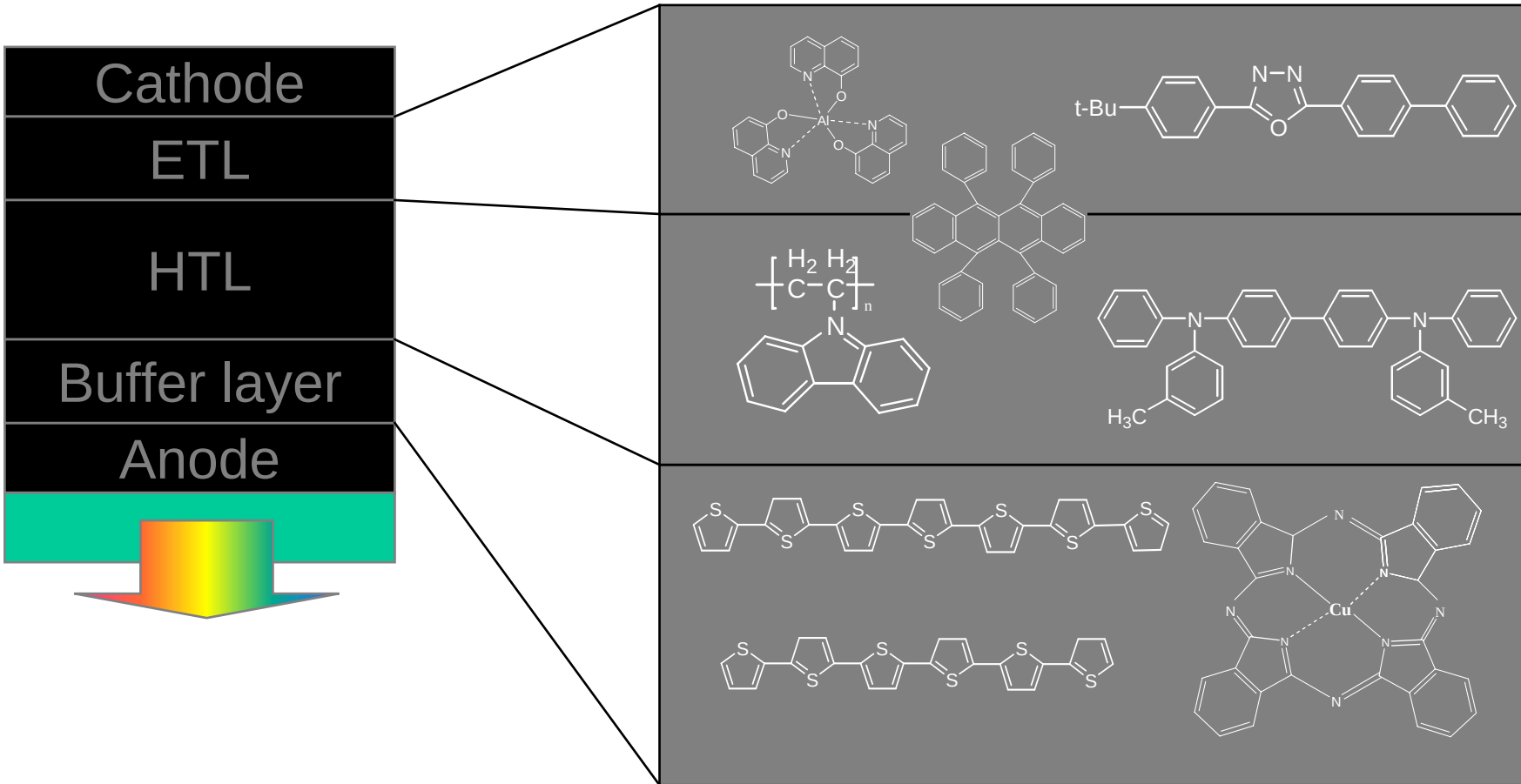
Systems

- Device structures for OLEDs



Multi-layer system

- Multi-layer system using buffer layer



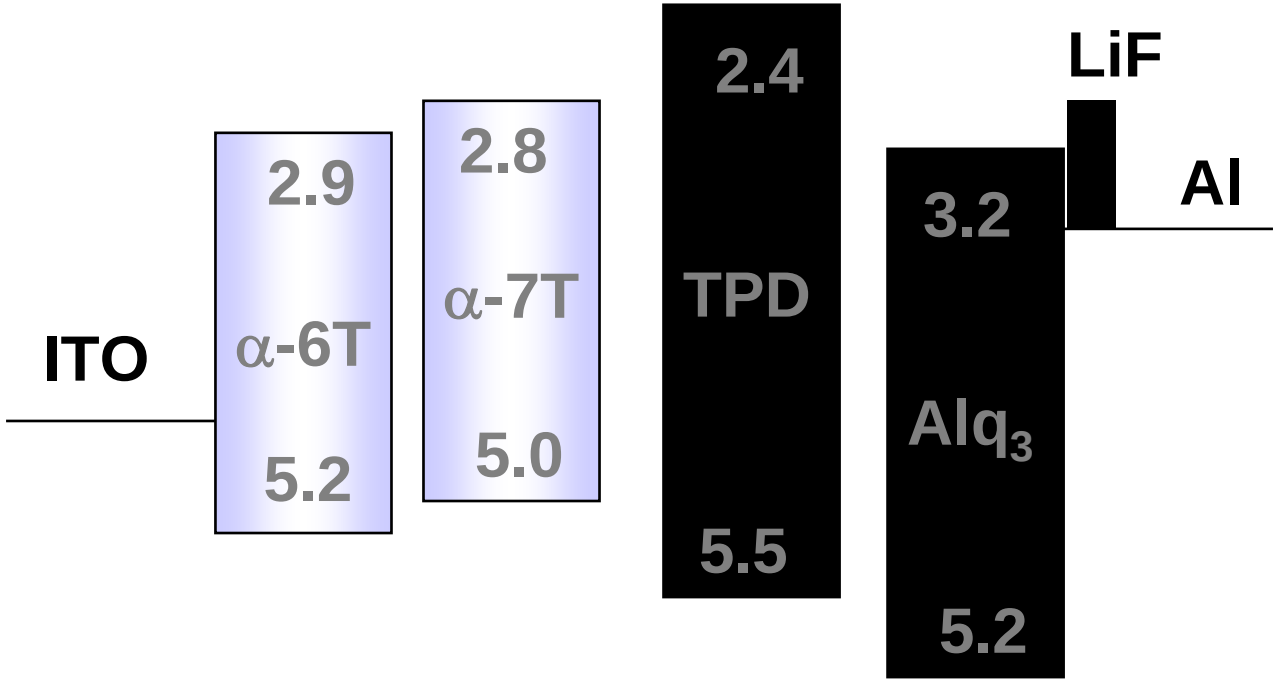
Buffer layer

- Buffer materials require
  - Low IP (ionization potential) [5.0 ~ 5.2ev]
  - Good surface morphology in solid film state
  - High conductivity and mobility of holes
  - High chemical stability in electric field
- Buffer materials provide
  - Lowered energy barrier at cathode/HTL interface
  - Sufficient hole carrier injected from cathode
  - Lowered turn-on and operating voltage
- *Buffer materials improve the device performance*

Characteristics of buffer materials

- Energy band diagram
- Surface morphology
- Lowering of energy barrier
- Hole injecting
- Hole conducting

Energy band diagram of buffer materials



- Lowered energy barrier
- Good surface morphology
- Good conducting property

Picture of OLED