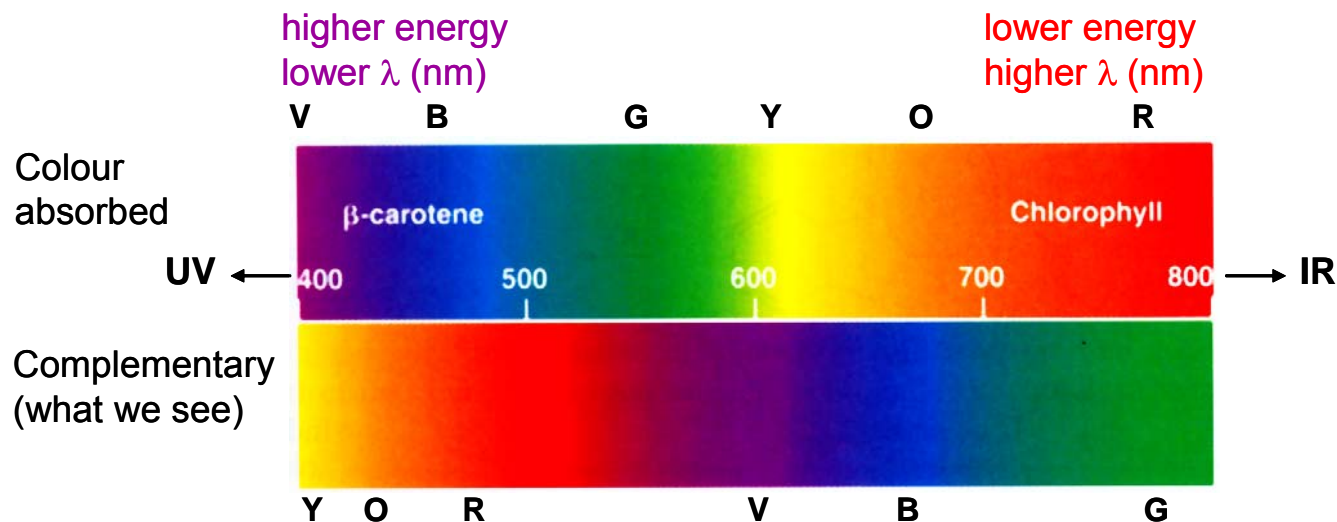


Chem 2223b Intersession 2008: Colours and Chromophores

- This section discusses the absorption of light by organic compounds, the related photophysical processes, and the spectroscopic methods used to measure light absorption and emission. Examples of important chromophores will be introduced.
- Background material, from Chem 2213a or otherwise, that is important includes:
 - Primary colours and the colours of the rainbow
 - Relationship between wavelength and energy
 - Bonding and hybridization
 - Conjugation and resonance structures
- After completing this section and Experiment 1, attempt:
 - Practice problems in the lab manual: all except for question #10
 - 2006 Midterm: 17, 18, 29, 30. 2006 Midterm Intersession: 22, 23, 26, 40.
 - 2007 Term Test #2: 7 to 11. 2008 Midterm: 1 to 5.

A. Colour

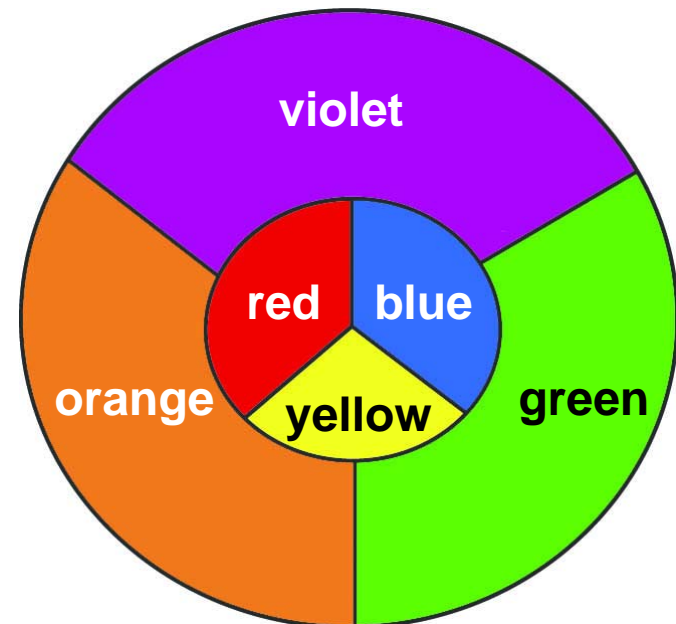
- White light is a continuum of different colours. If white light, such as sunlight, is passed through clouds or a prism, then it can be split up into its constituent colours, each of which has a different wavelength.
- When white light strikes an object or a substance, a specific colour component may be absorbed. The remaining colour components, which are not absorbed, are reflected or transmitted, and are what our eyes detect. We perceive this as the complementary colour of what is absorbed.
- This assumes that the absorbed component is a colour that our eyes can see. For example, the absorption of UV by an object would not be observable.



- Using this complementary-colour system, we can approximate the colour of light absorbed by some everyday objects and substances.

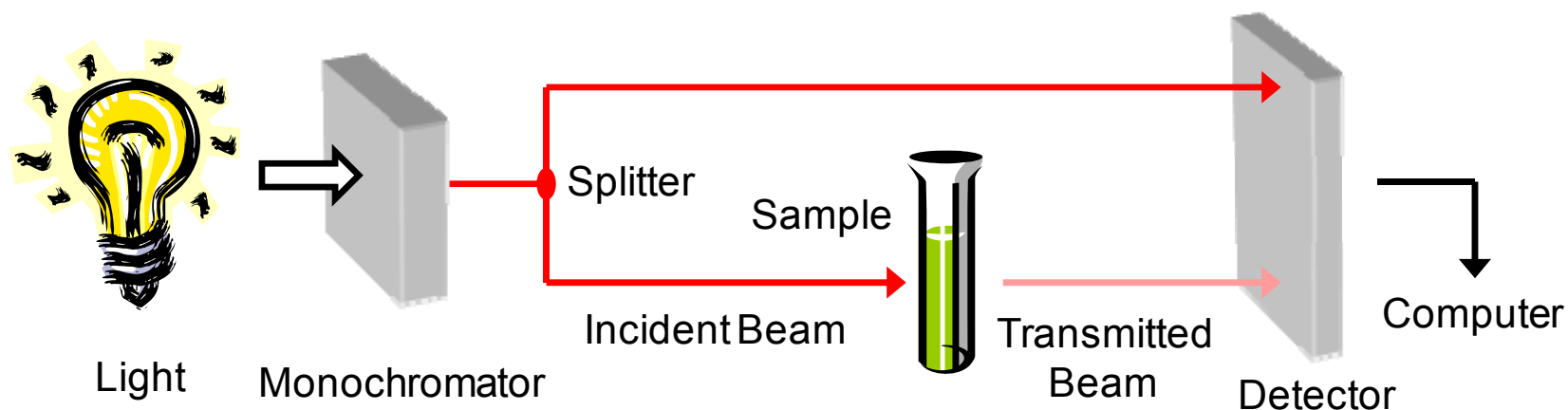
Item	Colour we see	Colour absorbed
Carrots	Orange	Blue
Lab coat	White	None (everything reflected)
Water	Clear and colourless	None (everything transmitted)
Leaves	Green	Red
Mud	Black	Everything absorbed

- A colour wheel may serve as a useful, qualitative way of remembering complementary colours.
- It is only qualitative because colours are not discrete: for example, orange spans a range of wavelengths.

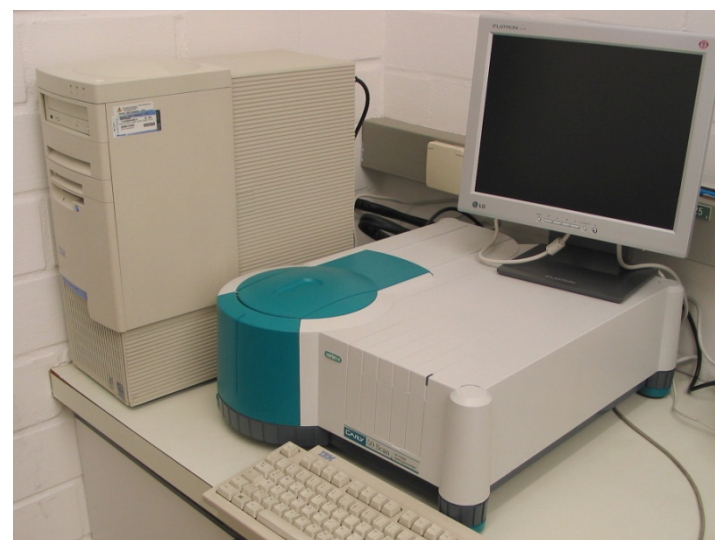


B. Measuring Colour Absorption

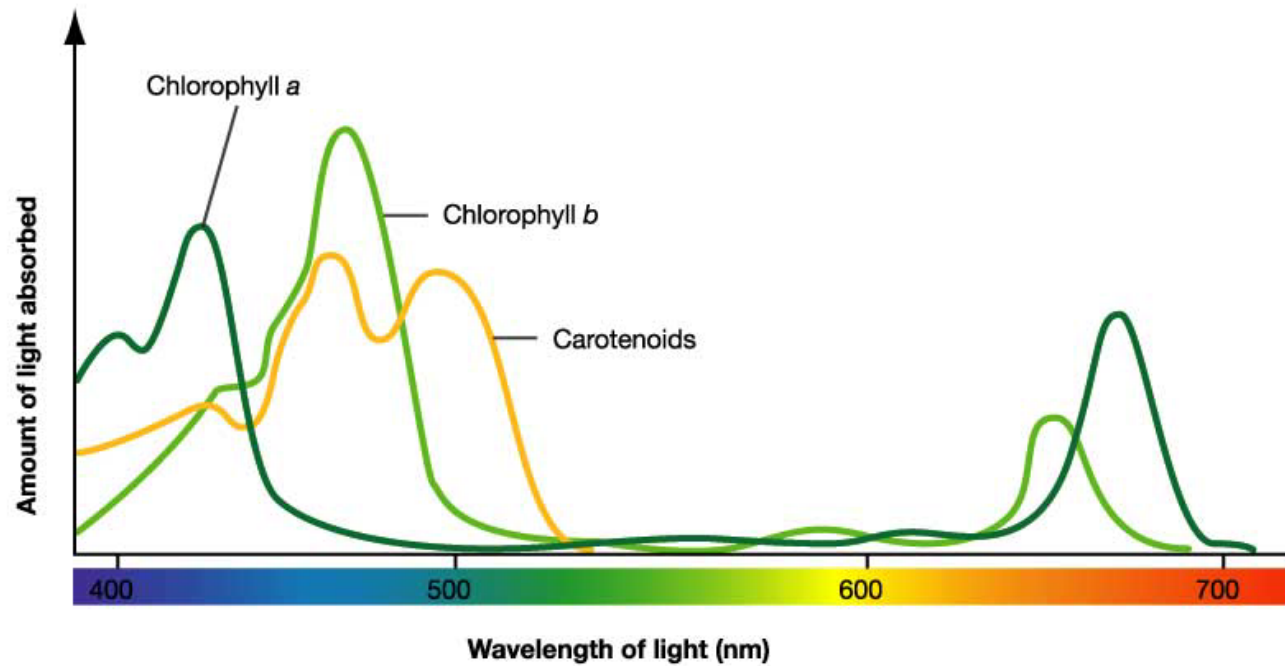
- The colours and their intensities absorbed by a chemical compound dissolved in solution can be measured by passing light through it. This technique is called **UV-Visible Absorption Spectroscopy** (commonly referred to as UV-vis).



- The detector measures the transmitted and reference beams, and the difference in intensity of these two beams corresponds to the amount of light absorbed by the sample.



- The instrument, known as a UV-vis spectrometer, scans a range of wavelengths and outputs an **absorption spectrum** (plot of light absorbed as a function of wavelength).

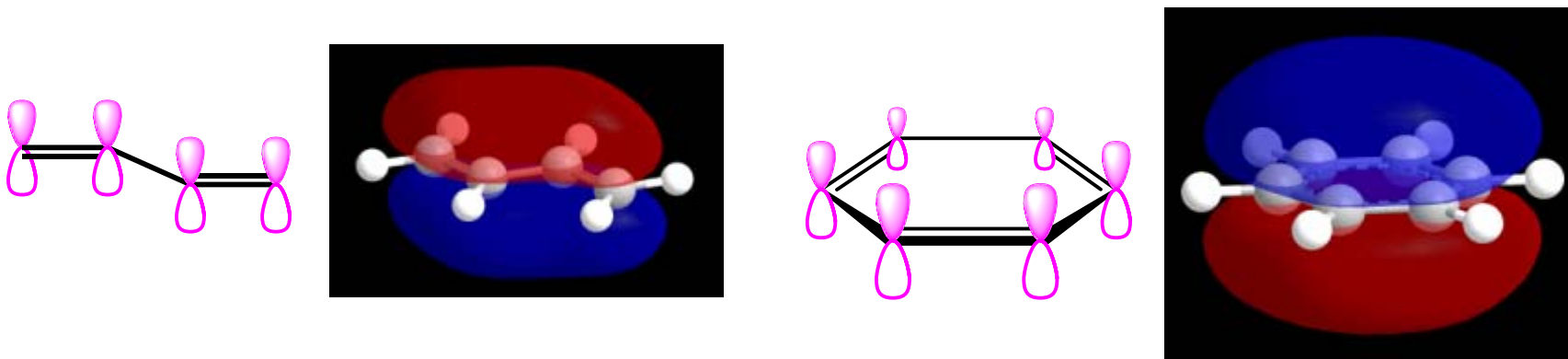


- For a compound to absorb light, it needs to possess structural features called **chromophores**. These are functional groups or parts of molecules that absorb light.
- The most-common chromophores are those with extended conjugation with or without the presence of polar/charged groups.

C. Photophysical Processes

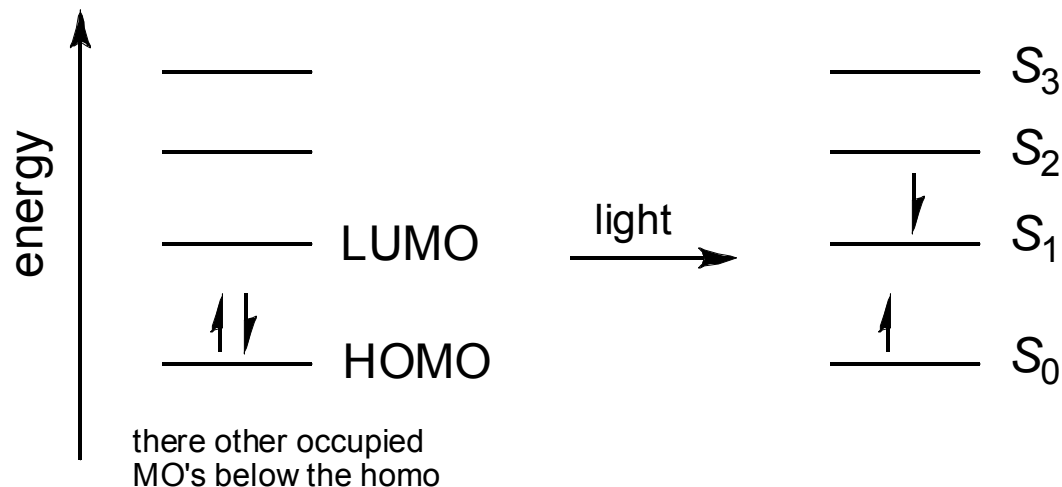
1. Molecular Orbital Theory and Absorption

- The p orbitals of conjugated π bonds and aromatic compounds interact together to form a large orbital known as a *molecular orbital* (MO).

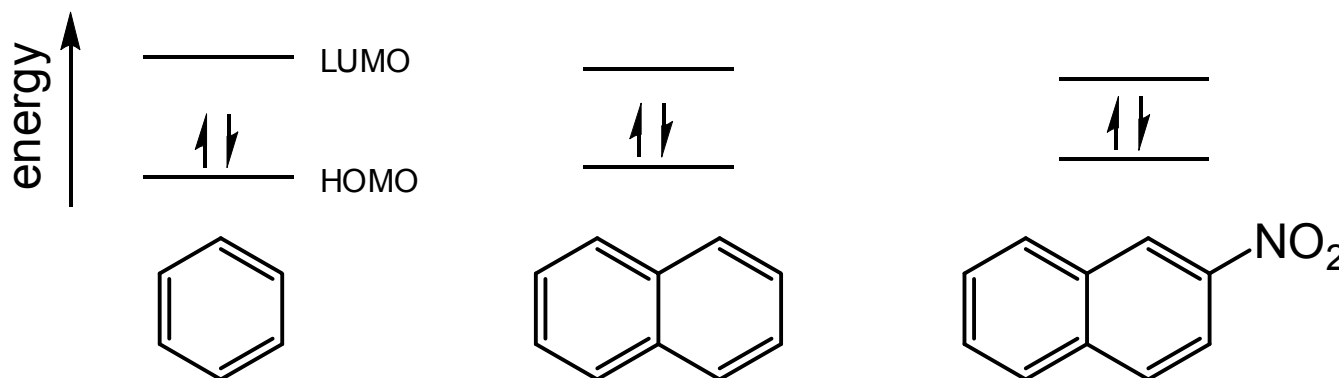


- π bonds are higher in energy than σ bonds. The MO derived from the π bonds is the one highest in energy that contains electrons, and it is termed the *highest occupied molecular orbital*, or HOMO. (MO theory is actually much more complicated!)
- MO's that are even higher in energy exist, but they are empty. The empty MO that is lowest in energy is the *lowest unoccupied molecular orbital*, or LUMO.

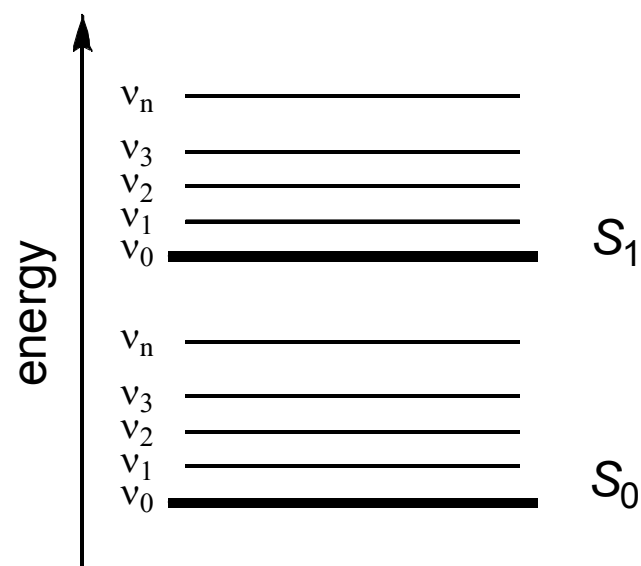
- Light absorption causes the excitation of an electron from the HOMO to the LUMO.
- The e^- have opposite spins and are said to be in a *singlet state*. The HOMO and LUMO are S_0 (ground state) and S_1 (lowest excited state), respectively.



- The HOMO/LUMO gap narrows when there is extended conjugation and when polar groups are also present. A smaller gap corresponds to a lower difference in energy, which results in the absorption of longer-wavelength light. (Particle-in-a-box theory).

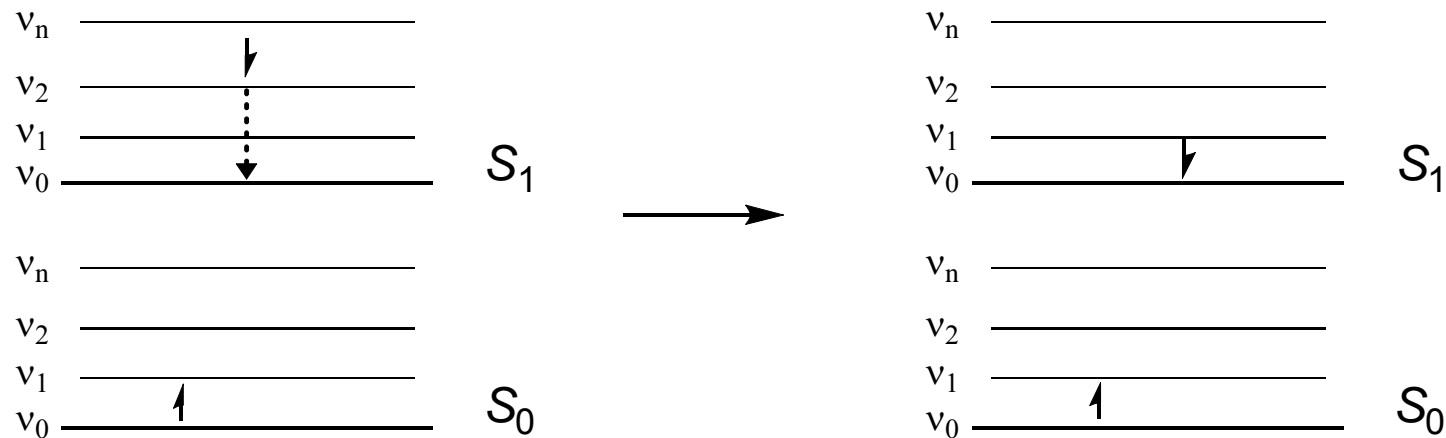


- For any molecule, the $S_0 \rightarrow S_1$ energy gap can be calculated, and it is a discrete number (*i.e.* one value). This suggests that the $S_0 \rightarrow S_1$ transition should occur at one, and only one, wavelength of light.
 - However, light absorption by molecules is observed not as a single wavelength, but as a band that spans a continuum of wavelengths. How can this be explained?
-
- Electronic-excitation energies are 200-400 kJ/mol, while vibrational energies are 10-40 kJ/mol (recall IR spectroscopy). As a result, concomitant vibrational excitation occurs with electronic excitation.
 - Within each S state, there is a series of vibrational levels (ground ν_0 and excited $\nu_1, \nu_2 \dots \nu_n$).
 - When a ground-state electron (S_0, ν_0) is excited to S_1 , a multitude of ν states are attained, resulting in an absorption band being observed.
 - If there is enough energy, S_2 is also accessible.



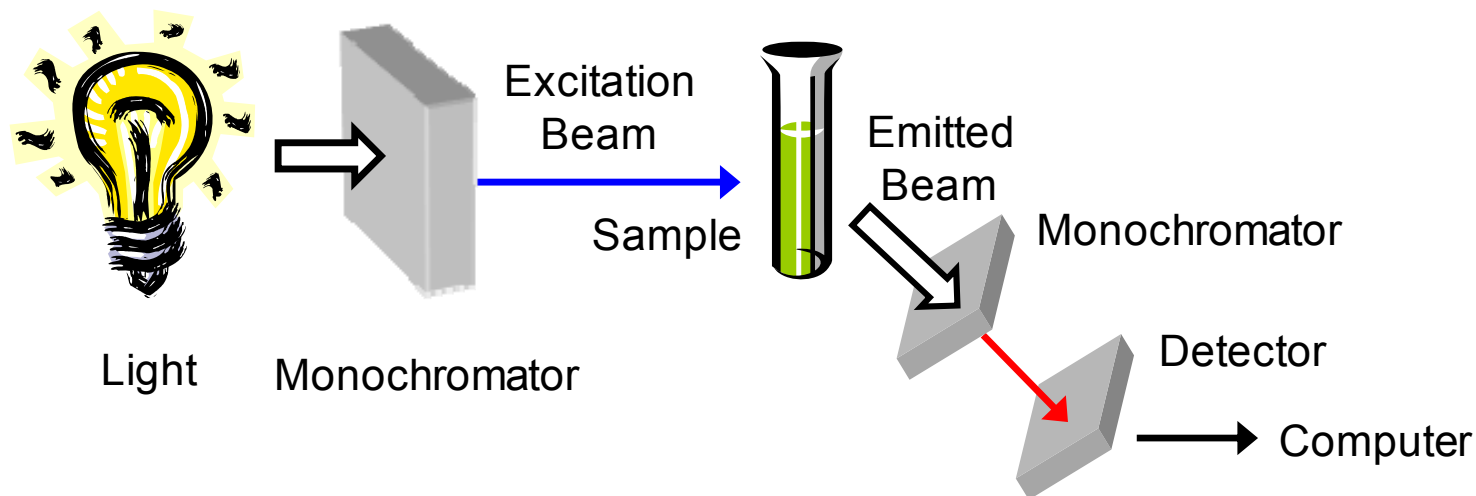
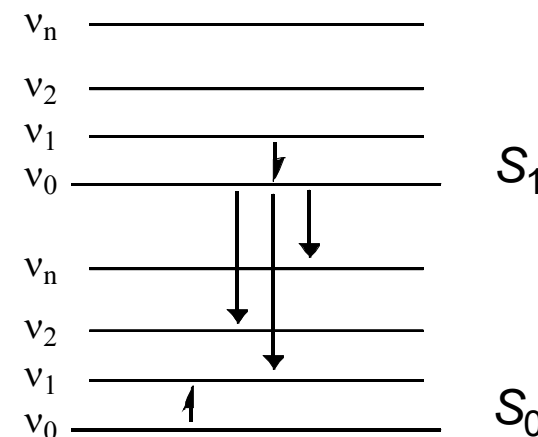
2. Events Following Light Absorption

- After the absorption of light, the system undergoes non-radiative **vibrational cooling**, also called *vibrational decay*, and the electron falls to the (S_1, ν_0) state. The process is very fast (ps timeframe), and the corresponding energy is released as heat.

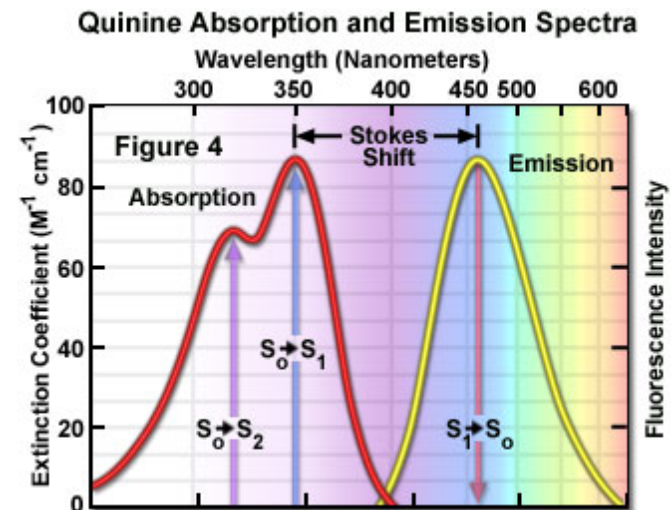
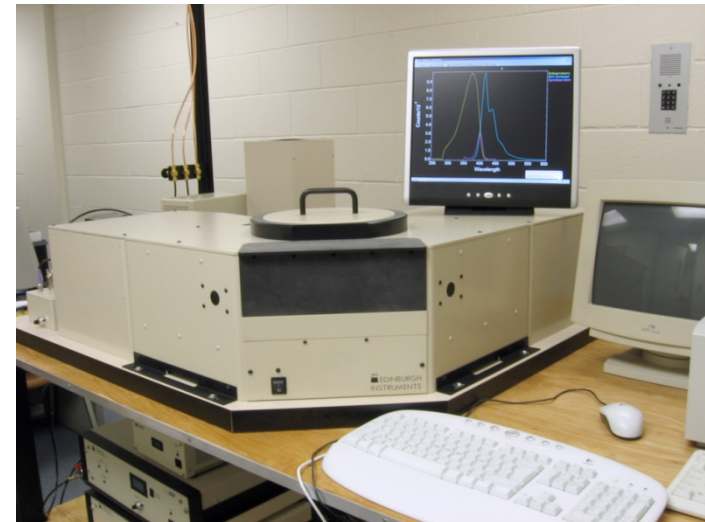


- Once at the (S_1, ν_0) state, various events can occur:
 - Fluorescence (an emissive/radiative process) caused by return to S_0
 - Internal conversion (a non-radiative process) to S_0
 - Intersystem crossing to the triplet state, and its associated processes
 - Energy transfer to another molecule (e.g. photosynthetic pigments)
 - Chemical reactions (e.g. formation of T-T base pairs in DNA)

- **Fluorescence** occurs relatively quickly (ns - μ s) and is a radiative process (emissive)
 - The electron returns to S_0 , but rarely ν_0 , so the emission is of a higher wavelength than the excitation wavelength.
 - Electrons arriving at (S_0, ν_n) subsequently return to (S_0, ν_0) by vibrational cooling.
 - Fluorescence can be measured using an instrument known as a *fluorescence spectrometer (fluorimeter)*.



- Notable features of a fluorimeter:
 - Usually, only the wavelength of maximum absorption, as determined from the absorption spectrum, is used to excite the sample.
 - To maximize sensitivity, the emission is monitored perpendicular to the excitation beam.
- A *fluorescence emission spectrum* plots fluorescence intensity as a function of emission wavelength. Both absorption and emission can be plotted on a single graph. With the anti-malarial drug quinine:
 - $\lambda_{\text{abs}} \text{ max} = 350 \text{ nm}$ (used for excitation)
 - $\lambda_{\text{em}} \text{ max} = 460 \text{ nm}$



- **Internal conversion** occurs when the electron returns to S_0 , but does not release light (non-radiative). The energy is lost as heat.

- Internal conversion can be fast or slow, depending on the molecule.

- For example, in nucleobases, this process is ultrafast, reducing the risk of DNA damage by quickly deactivating a high-energy state.

- *Proceedings of the National Academy of Sciences*, **2007**, 104, 435.
- Bases were excited with UV light (time zero), and their decays back to ground state were monitored over a few ps.

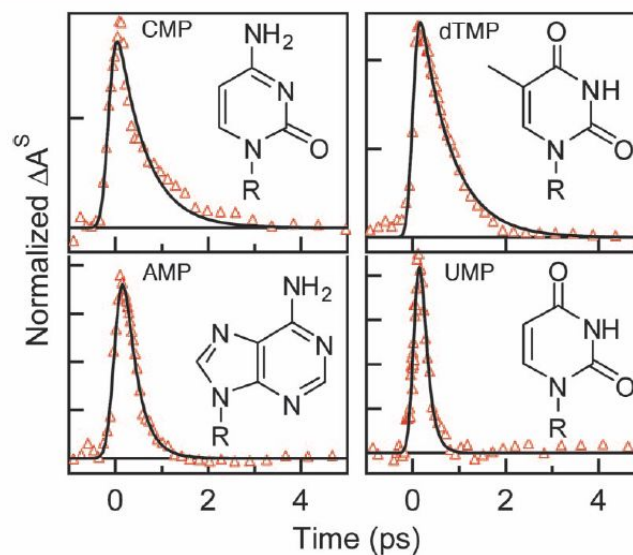
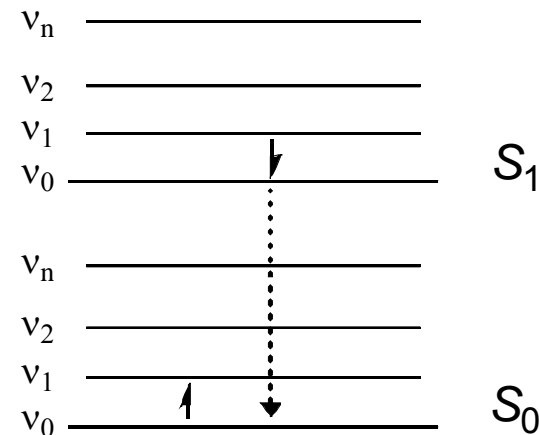
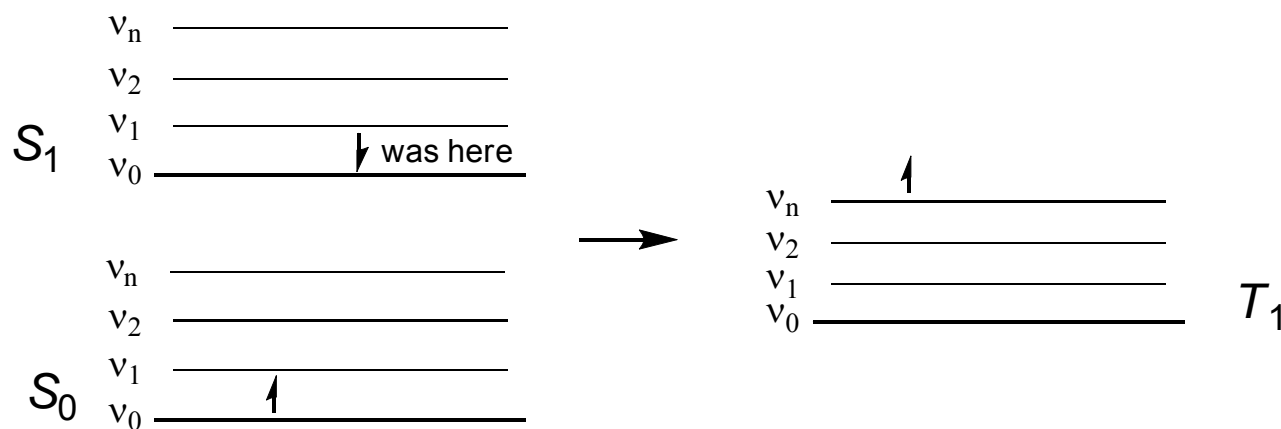
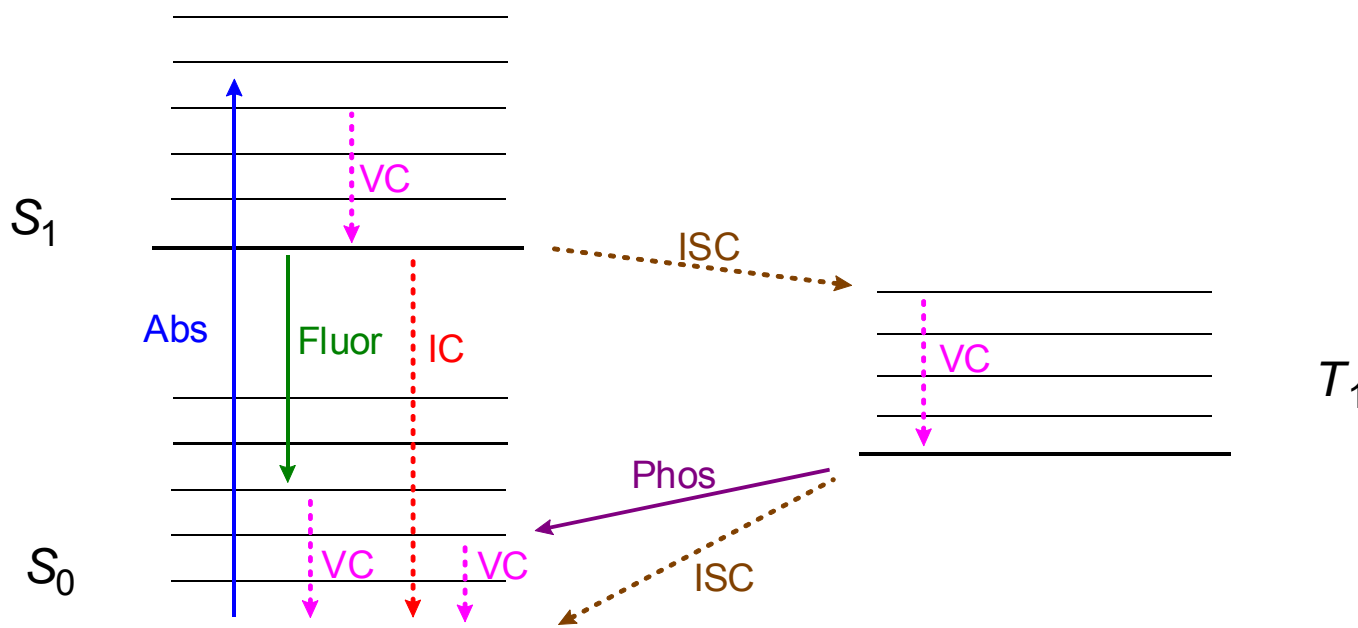


Fig. 3. Solvent-corrected transient absorption traces of CMP, dTMP, UMP, and AMP in pH 7 buffer pumped at 267 nm and probed at 570 nm. Structures of the bases are shown with R representing a ribose-phosphate group. Solid lines are from global fits to the data.

- **Intersystem crossing** occurs when the excited electron undergoes a *spin flip* and has the same spin as the other electron, resulting in an excited triplet state, T_1 .
 - Triplet states also have vibrational levels, so cooling to (T_1, v_0) occurs.
 - Return to S_0 can occur by non-radiative decay or by an emissive process known as **phosphorescence**. Phosphorescence is much slower than fluorescence, and it occurs on the μs - ms timescale.



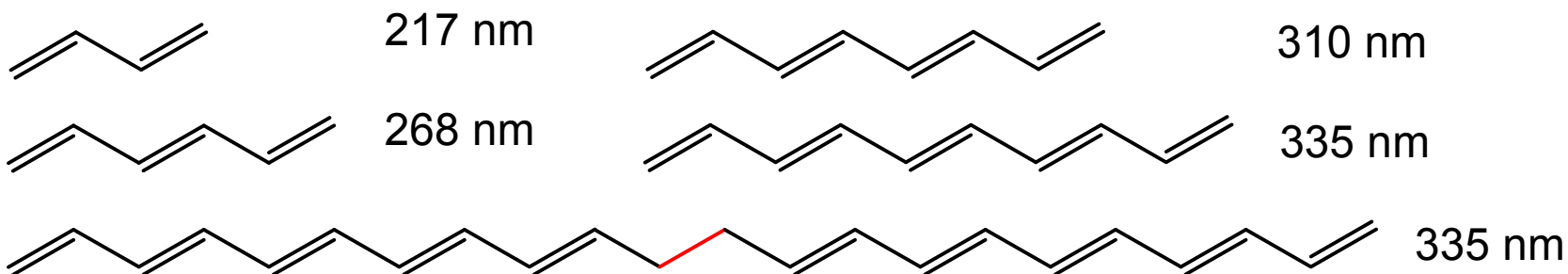
- A schematic known as a *Jablonski diagram* summarizes the photophysical processes. Non-radiative processes are shown in dashed lines.



D. Examples of Chromophores

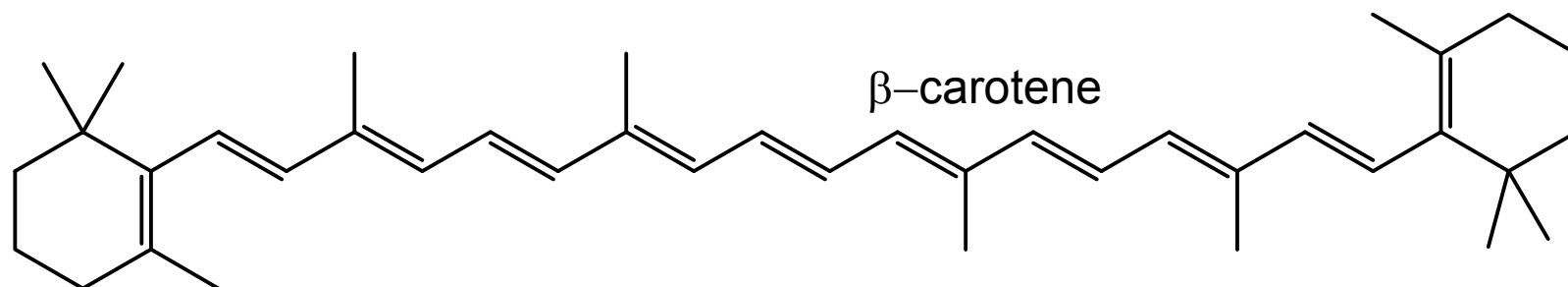
1. Conjugation Only

- If there is only conjugation, a long chain of conjugated bonds is needed to reduce the HOMO/LUMO gap to energies that correspond to visible light.
- Below are the wavelengths of maximum absorption of some alkenes



- Realize that it is continuous, extended conjugation that is important (*i.e.* the size of the molecular orbital), not the total number of double bonds.
- A compound with absorption at 335 nm would still be colourless, since it is in the UV region (not observed by our eyes).

- If we continue to increase the number of conjugated C=C bonds, then eventually we reach a point where the compound will absorb visible light (β -carotene ~ 475 nm).



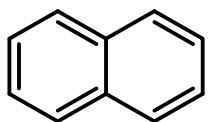
- The same also applies to aromatic compounds. Benzene is colourless, while at the extreme end, graphite is black because its sheets of fused rings absorb all colours.

benzene



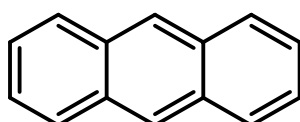
208 nm

naphthalene

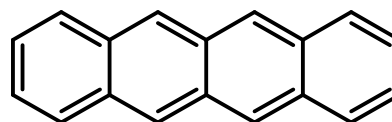


289 nm

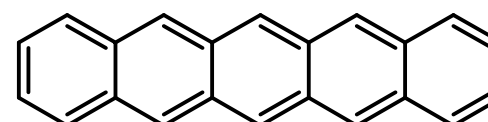
anthracene



379 nm



474 nm



580 nm

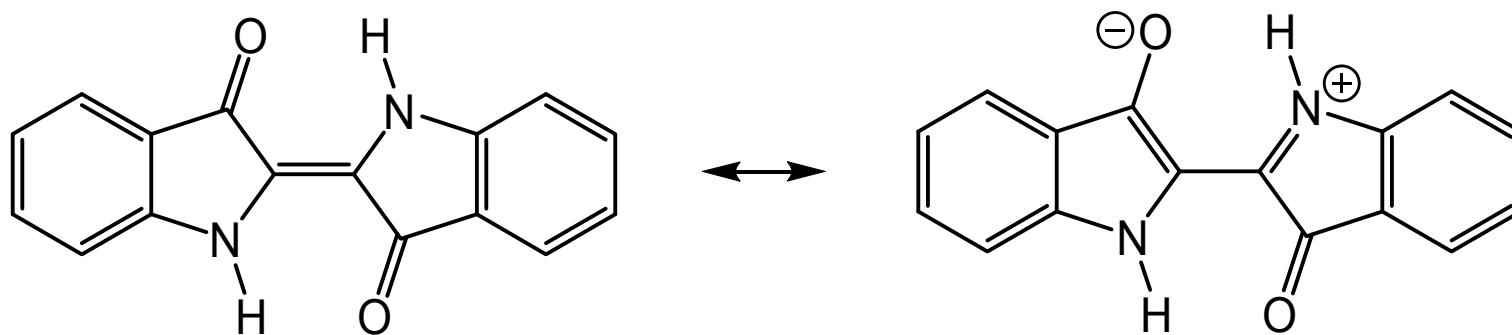
- You do not have to memorize wavelengths, but if given a choice of five structures, you should be able to pick out the one that is least/most likely to be coloured.

2. Conjugation + Polar or Charged Functional Groups

- If there are polar or charged functional groups present, then less conjugation is required for a molecule to exhibit colour. Some examples are described below.

a. Indigo

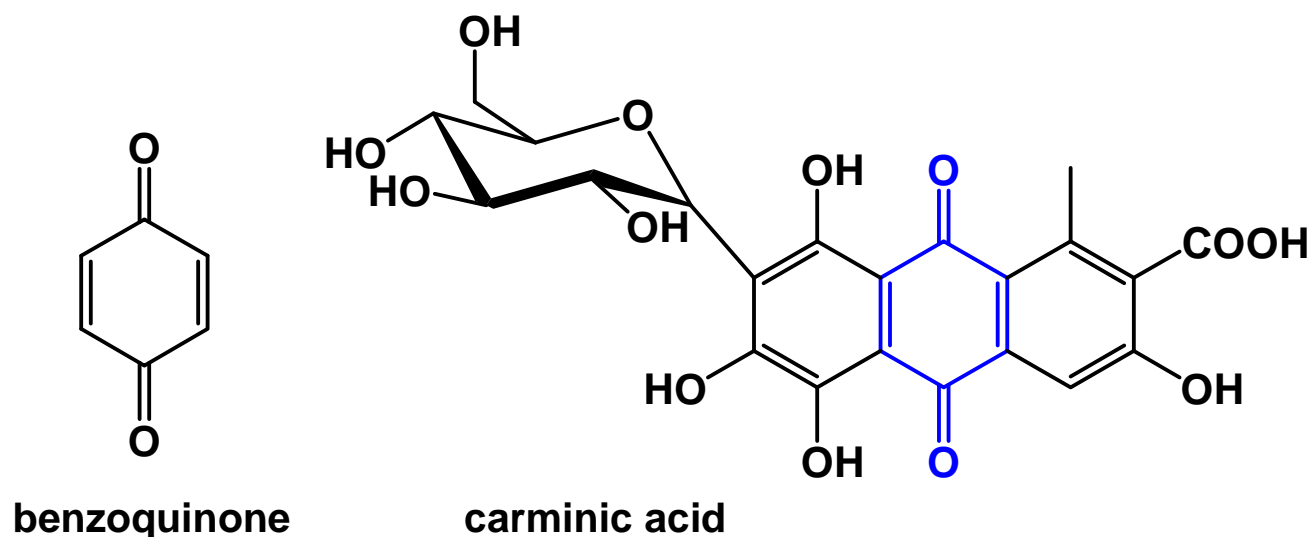
- An example is indigo, the dye found in blue jeans. We can draw resonance forms that show charge separation (polarity), a feature that is important for the molecule to act as a chromophore.



- Recall that resonance structures are only ways to depict the different possible arrangements of electrons. The real structure is neither of these two, but rather, somewhere in between, known as the resonance hybrid.

b. Quinones

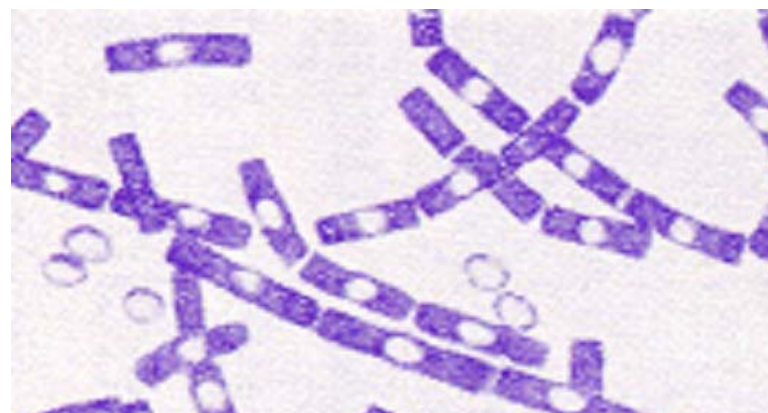
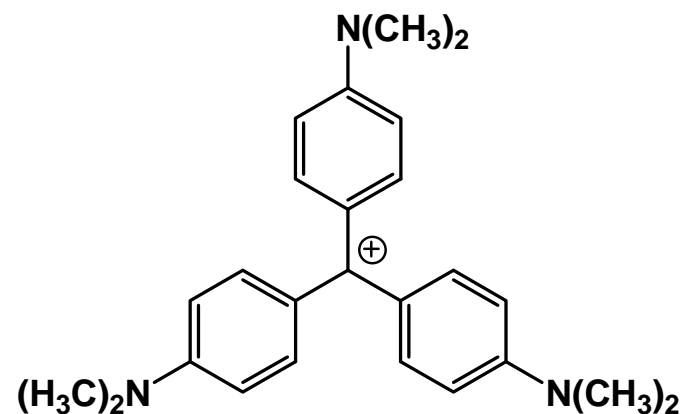
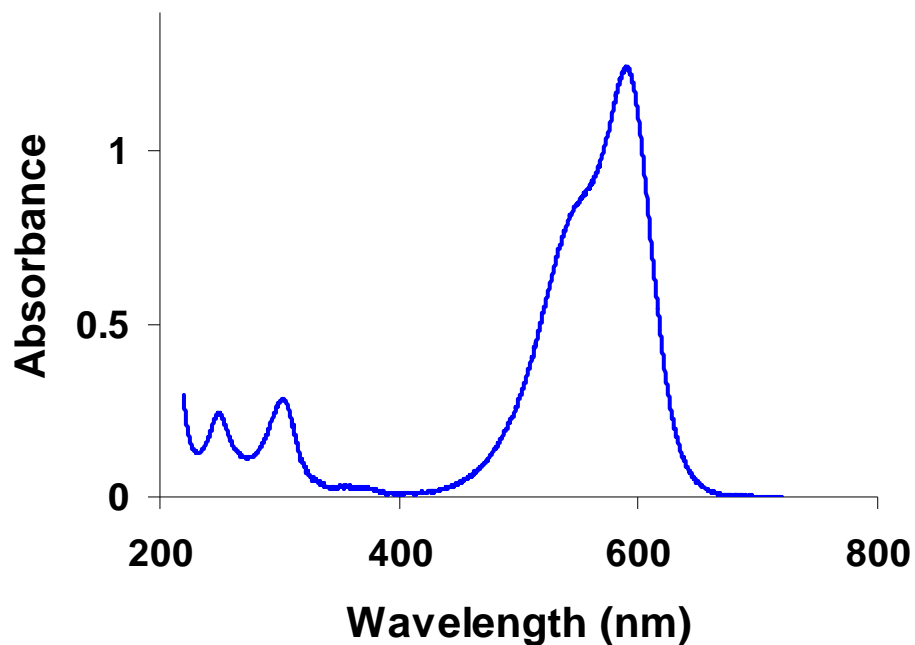
- Another common chromophore is the quinone group, based on the parent molecule benzoquinone. Benzoquinone itself is yellow, but when it is attached to other conjugated systems, such as hydroxyl groups, the molecule can be bright red.
- An **auxochrome** is a group or substructure that influences the absorption of the chromophore (changes the wavelength of absorption and/or intensity).



Carminic acid is an ingredient in the red pigment cochineal, isolated from a dried female insect living on a cactus. It was an important dye for wool and silk before the invention of synthetic dyes, but 7000 dried bugs (one pound) were needed for 0.1 lb of pigment.

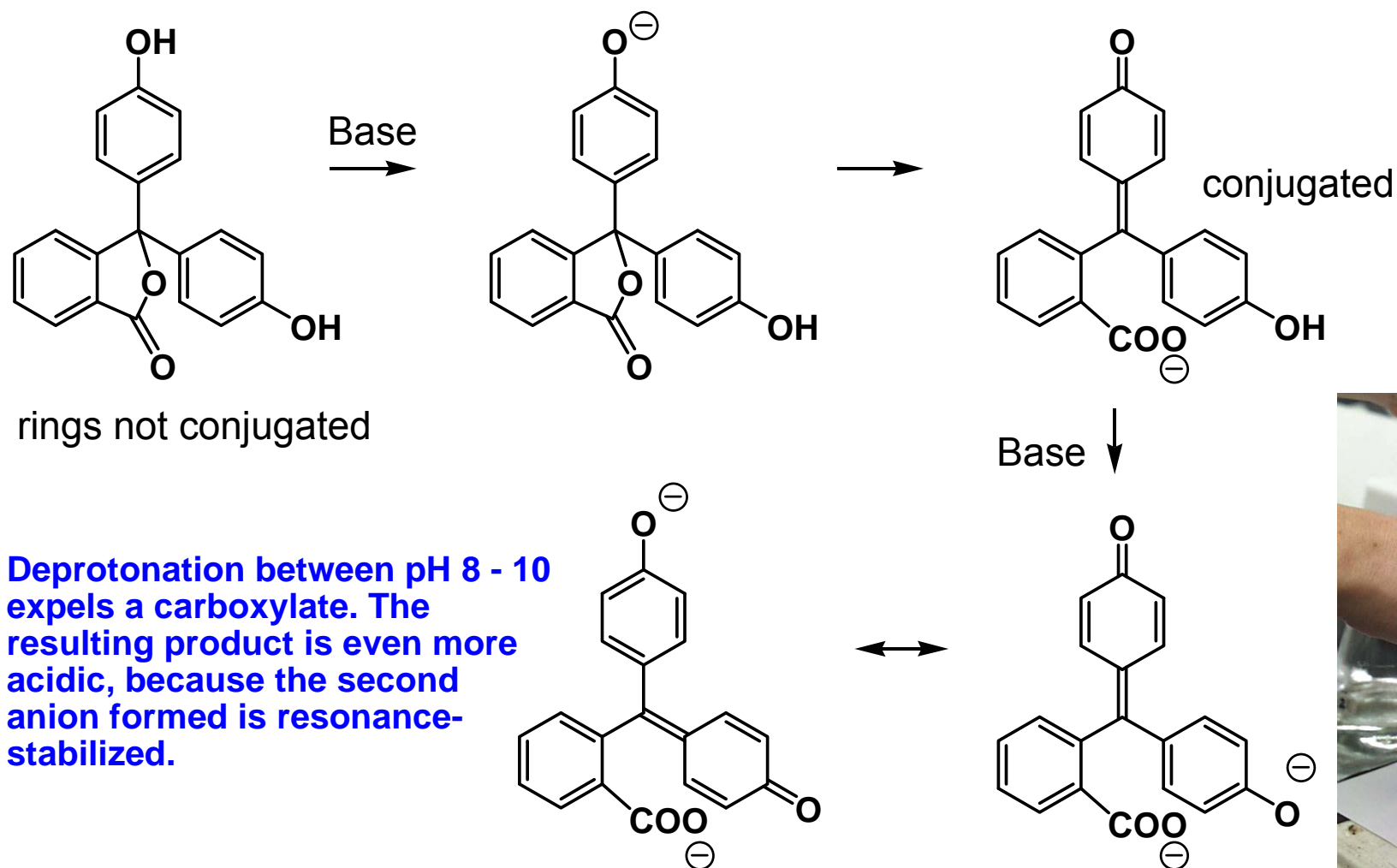
c. Triarylmethanes

- Chromophores comprised of a highly stable triarylmethane carbocation are present in these types of dyes. This carbocation is not only resonance-stabilized, but the empty *p* orbital also allows all three rings to be conjugated together.
- Crystal violet is a triarylmethane dye used in bacterial Gram stains (Anthrax shown)



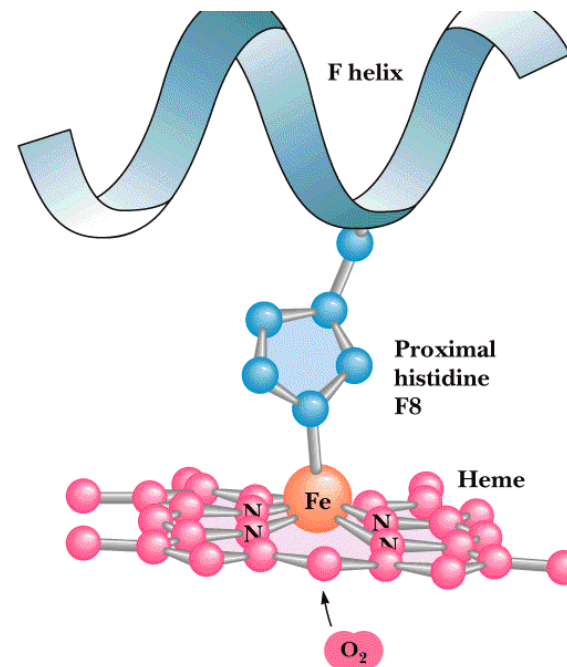
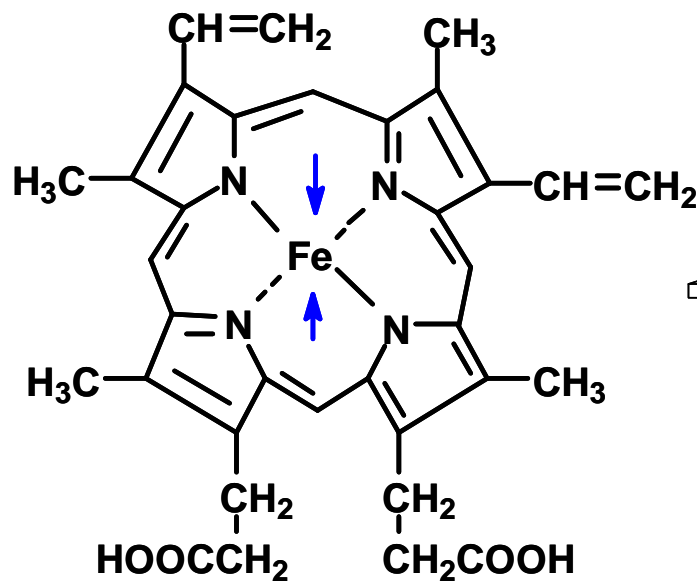
- Absorption maximum ~600 nm

- The pH indicator phenolphthalein is actually a triarylmethane dye that undergoes a reversible chemical reaction to convert a colourless molecule into a pink one.



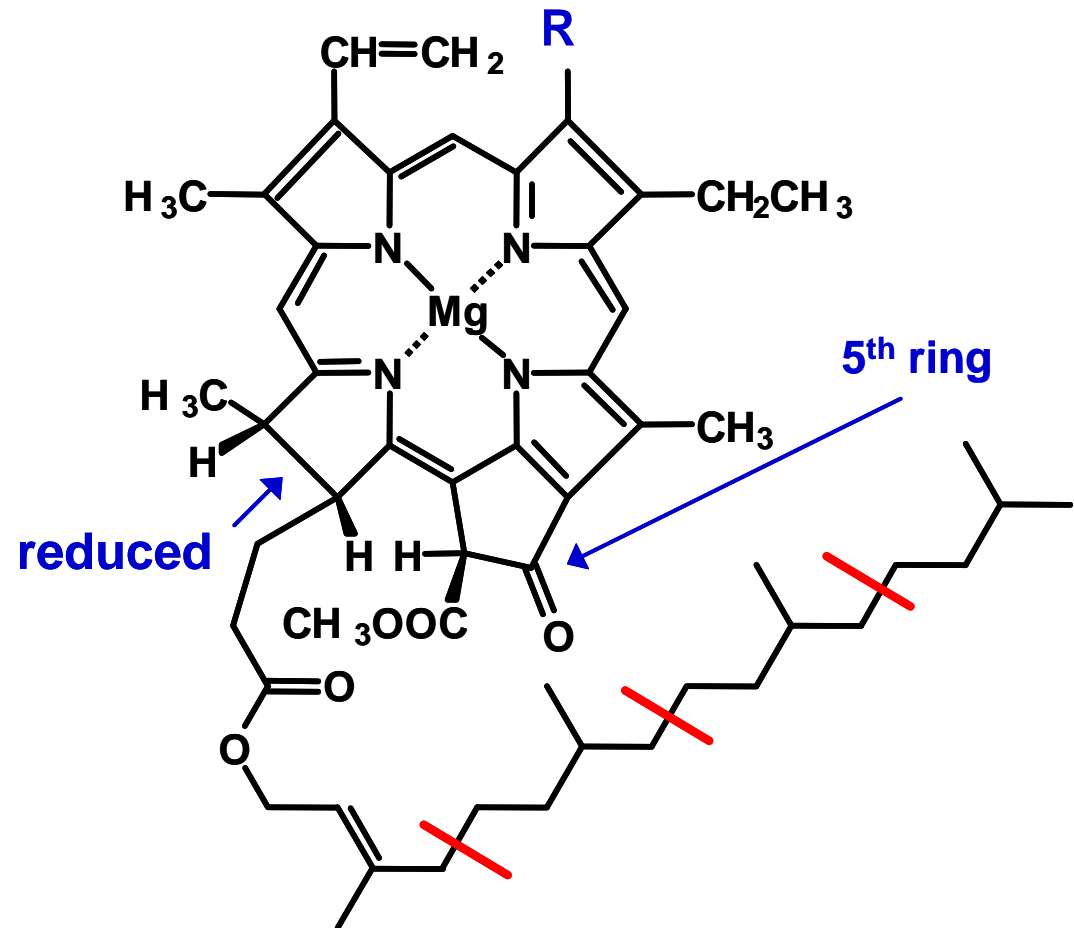
d. Porphyrins

- Porphyrins are chromophores consisting of a ring of highly unsaturated C and N. The colour of the porphyrin depends on the identity of the metal coordinated to N as well as the presence of other ligands coordinated to the metal.
- In hemoglobin, the porphyrin *heme* is planar. Histidine in globin protein holds the heme from one side using Fe^{2+} . On the other side, water or oxygen can coordinate to Fe^{2+} . (water = blue/purple, oxygen = red). Iron can have up to 6 coordinate bonds.



- Chlorophyll is another porphyrin, but it has some key differences from heme.

- Mg (4-coordinate)
- One C=C reduced
- Lipid tail that is a terpene (made from isoprene units)
- Extra ring
- Two forms:
R = CH₃ (*a*) or CHO (*b*)
- Appears green



- Why a hydrophobic tail? Photosynthesis occurs in thylakoids (chloroplasts).
- The *b* form absorbs at a higher wavelength due to the aldehyde auxochrome.

e. Diaryl Azo (or simply Azo)

- Roughly two-thirds of all synthetic dyes contain the diarylazo chromophore. The N=N permits the two aromatic rings to be conjugated together. Some uses:
 - Fabric dyes
 - Acid-base indicators
 - CD-R and DVD±R media
 - Artificial food colouring

