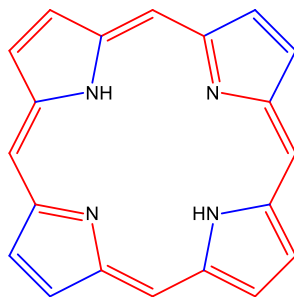Porphyrins are naturally occurring chromophores featuring a highly conjugated π-system. The simplest porphyrin structure is porphin (pictured).

Shade the conjugation pathway in porphin.

[2 marks]

The ring is conjugated over the red and blue lines above (i.e. over the entire ring).

How many π electrons are there in porphin?

[2 marks]

Each C=C and C=N contributes 2 electrons as does each –NH group. In total, this gives:

total number of π electrons = 9 × 2 (from C=C) + 2 × 2 (from C=N) + 2 × 2 (from - NH) = 26

Despite not obeying the Hückel's $4n+2$ rule, in each resonance form there is a path around the molecule which follows alternating single and double bonds. How many bonds comprise this path and how many π electrons are *along this path*? Does this path obey the Hückel rule?
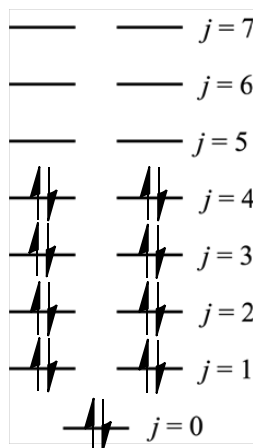
[4 marks]

The path coloured in red in the resonance form above follows alternating single and double bonds. There are 18 bonds along this path and 18 π electrons.

total number of π electrons along path = 7 × 2 (from C=C) + 2 × 2 (from C=N) = 18

Approximating porphin as a cyclic system, the allowed energy levels form degenerate pairs. Fill the following electronic energy diagram with π electrons.

[2 marks]

The 18 π electrons doubly occupy levels with $j = 0$ to $j = 4$ as shown below.

What are the j quantum numbers for the HOMO and LUMO?

[2 marks]

The HOMO is the 'highest occupied molecular orbital' and has $j = 4$, as above.
The LUMO is the 'lowest unoccupied molecular orbital' and has $j = 5$, as above.

From molecular orbital theory, the energy levels are given by

$$\varepsilon_j = 2\beta \cos\left(\frac{2\pi j}{N}\right).$$

If benzene absorbs at 260 nm, with a transition of -2β magnitude, estimate the spectroscopic value for β and thus calculate where porphin is expected to absorb given the above approximations.

[4 marks]

A wavelength of 260 nm corresponds to an energy of:

$$E = hc / \lambda = (6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1}) / (260 \times 10^{-9} \text{ m}) = 7.64 \times 10^{-19} \text{ J}$$

This corresponds to -2β so $\beta = -\frac{1}{2} \times 7.64 \times 10^{-19} \text{ J} = -3.82 \times 10^{-19} \text{ J}$

The ring in porphin has $N = 18$. The HOMO and LUMO have $j = 4$ and $j = 5$ respectively and so have energies:

$$\varepsilon_4 = 2\beta\cos(\frac{2\pi \times 4}{18}) = 2\beta\cos(\frac{8\pi}{18}) \qquad\qquad \varepsilon_5 = 2\beta\cos(\frac{2\pi \times 5}{18}) = 2\beta\cos(\frac{10\pi}{18})$$
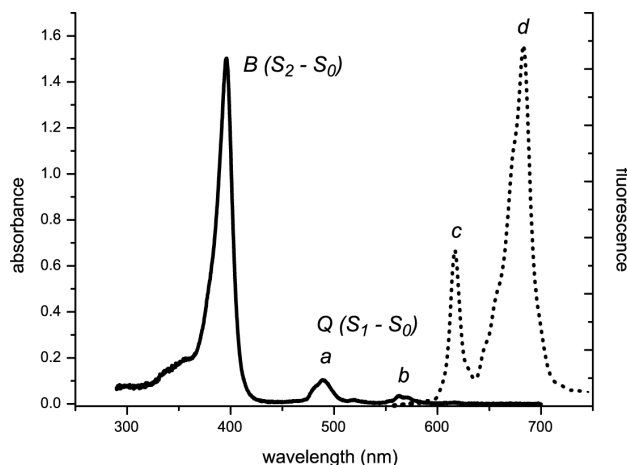
The transition energy is thus predicted to be:

$$\Delta\varepsilon = \varepsilon_5 - \varepsilon_4 = 2\beta\, [-0.174 - 0.174] = -0.695\beta = -0.695 \times -(3.82 \times 10^{-19} \text{ J}) = 2.65 \times 10^{-19} \text{ J}$$

This corresponds to a wavelength:

$$\lambda = hc / E = (6.626 \times 10^{-34} \text{ J s})(2.998 \times 10^8 \text{ m s}^{-1}) / (2.65 \times 10^{-19} \text{ J}) = 749 \text{ nm}$$

The experimental porphin absorption spectrum is shown below. How does your prediction compare to the strong absorption of porphin?

The value is in approximately the right place for the longest wavelength peaks in the absorption spectrum (the Q band). It underestimates the absorption energy.

Experimentally, the HOMO-LUMO transitions give rise to two distinct band systems. The higher energy one is known as the Soret, or B band, and the lower energy one is known as the Q band. These are evident in the absorption spectrum. The fluorescence spectrum shown is due to 396 nm excitation. With the aid of a Jablonski diagram, explain how absorption in the B band yields fluorescence consistent with population with the upper state of the Q band system. Name all processes involved.
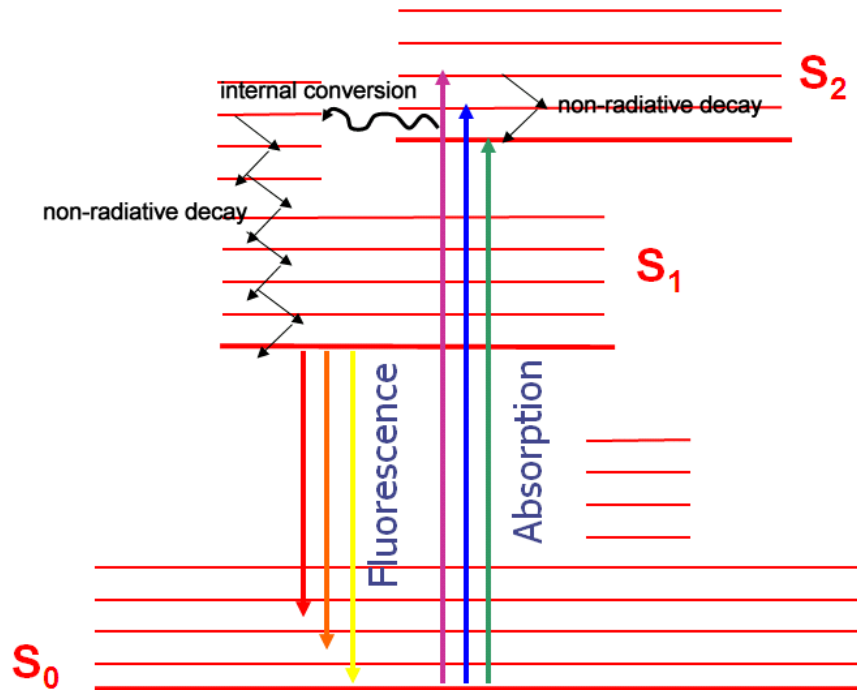
[4 marks]

Absorption at 396 nm occurs from the lowest vibrational level of the S_0 ground state to vibrational levels of the S_2 excited state.

This undergoes non-radiative decay to lose vibrational energy, via collisions with the solvent, to reach the lowest vibrational level of S_2. It also undergoes internal conversion to the S_1 excited state in which the excess electronic energy is transferred into a highly vibrationally excited level of S_1.

The vibrational energy of S_1 is lost through non-radiative decay, via collisions with solvent, until the lowest vibrational level of S_1 is reached.

Fluorescence then occurs from the lowest vibrational level of S_1 to the vibrational levels of the ground state, S_0.

The fluorescence yield of porphin is only 0.043. Explain possible processes which may explain non-unity fluorescence yield.

[2 marks]

Internal conversion from S_2 or S_1 to high vibrational levels of S_0 followed by non-radiative decay to the ground level of S_0 will yield no emitted photons. All of the absorbed light is converted via this non-radiative decay into thermal energy.

Intersystem crossing to a triplet state (or states) and subsequent phosphorescence could also be lowering the yield of photons via fluorescence.

Peaks *b* and *c*, as indicated, correspond to transitions between the ground vibrational levels in S_1 and S_0, with the small Stokes shift being due to solvent reorganization. With the aid of diagrams, and invoking the Franck-Condon principle, explain why bands *a* and *d* appear more intense than *b* and *c*.

[3 marks]

Because of the much higher mass of nuclei compared to the electrons, electronic transitions occur 'vertically': that is, electronic transitions occur without change in the nuclear positions. This is the Franck-Condon principle.

The most probable position of the nuclei in the lowest vibrational level of the ground state, S_0, is at the equilibrium geometry. If the equilibrium geometry in the excited state is displaced relative to the ground state, as represented by the red arrow in the scheme opposte, absorption from this point will lead to a vibrationally excited level in the electronic state S_1. This leads to the strongest line in the absorption spectrum.
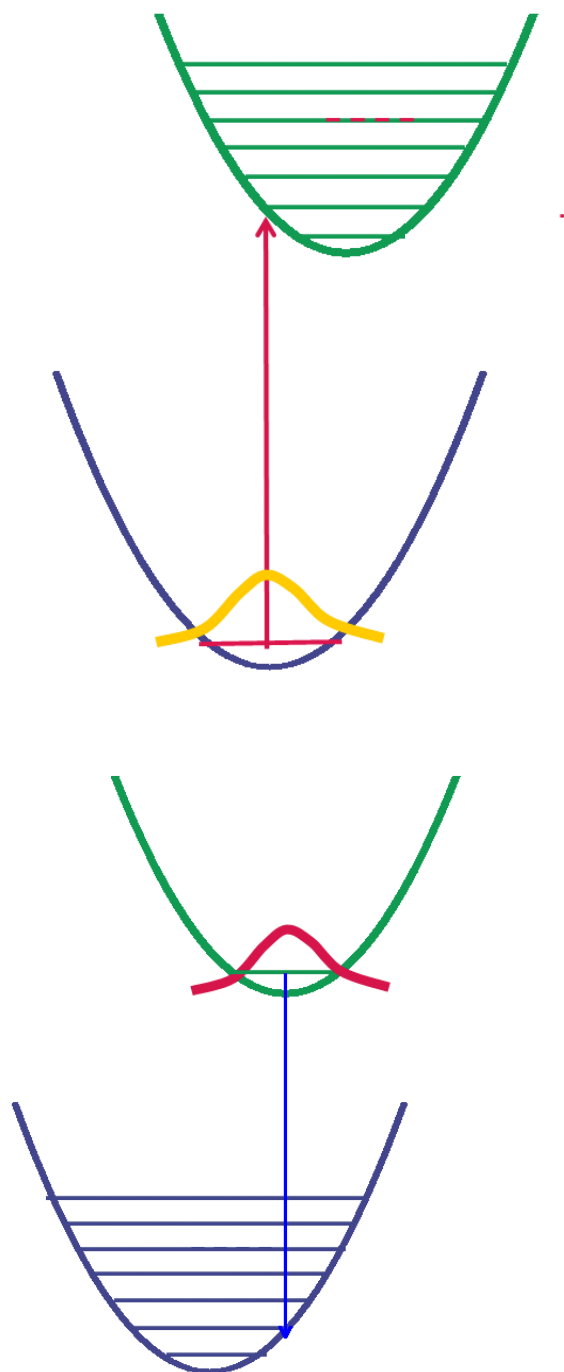
Only if the equilibrium bond lengths in the excited state are the same as those in the ground state does this strongest transition correspond to the transition to the ground vibrational level of S_1.

In the picture drawn, the vertical transition from the equilibrium bond length in the ground state leads to the $v' = 1$ level in the excited state and this is a stronger line than that to the $v' = 0$ levels.

Similarly, the most intense line in the fluorescence spectrum corresponds to the vertical transition at equilibrium geometry of the excited state. This is represented by the blue arrow in the scheme opposite and leads to a vibrationally excited level in the ground electronic state, S_0.

Unless the excited and ground states have the same geometries, this vertical transition does not correspond to emitted to the lowest vibrational level.

If the vibrational structure in the two states is similar, the most intense line in the absorption spectrum (0 → 1 above) is mirrored by the most intense line in the fluorescence spectrum (0 ← 1 to the right).

Total = 27