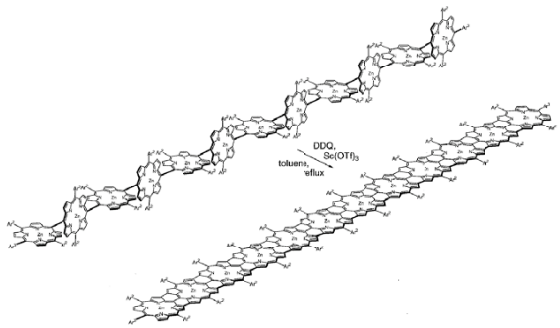
Core Course 2002
Homework Part II, Problem Set 1

In a recent issue of Science, investigators reported the synthesis and characterization of fused porphyrin systems, as illustrated here.



Scheme 2.

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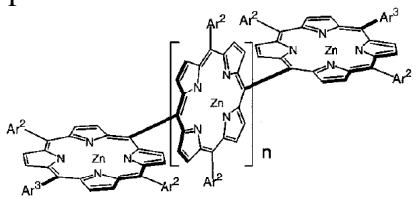
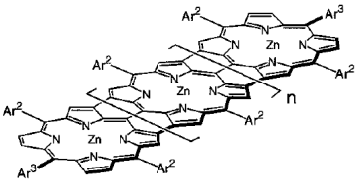
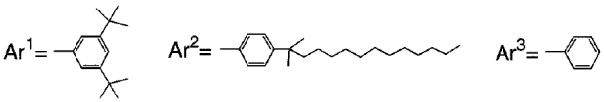
To be more complete, they characterized a series of constructs of varying lengths and measured their absorption properties. Absorption spectra are shown below:



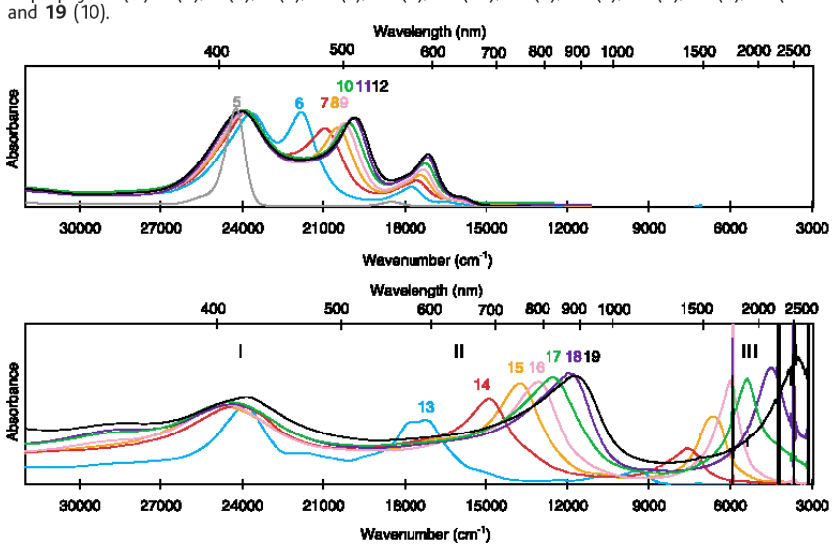
7–12



14–19



Scheme 1. **1**, M = Cu, $R^1 = R^2 = Ar^1$; **3**, M = Zn, $R^1 = R^2 = Ar^1$; **6**, M = Zn, $R^1 = Ar^2$, $R^2 = Ar^3$; **2**, M = Cu, $R^1 = R^2 = Ar^1$; **4**, M = Zn, $R^1 = R^2 = Ar^1$; **13**, M = Zn, $R^1 = Ar^2$, $R^2 = Ar^3$. Number of porphyrins (*N*): **7** (1), **8** (2), **9** (3), **10** (4), **11** (6), **12** (10); **14** (1), **15** (2), **16** (3), **17** (4), **18** (6), and **19** (10).



1. Assuming that the largest fused system (19) is a one dimensional particle in a box, with box size 100 Å, calculate the energy (in cm^{-1}) of the predicted lowest energy electronic transition.

$$E_n = \frac{n^2h^2}{8mL^2} = \frac{\left(6.626x10^{-34}\,J\,s\right)^2}{8\left(9.109x10^{-31}kg\right)\left(100\text{Å}\,\frac{10^{-10}m}{\text{Å}}\right)^2}n^2 = \frac{\left(6.626x10^{-34}\right)^2}{8\left(9.109x10^{-31}\right)\left(10^{-8}\right)^2}\frac{J^2\,s^2}{kg\,m^2}n^2 = \left(6.025x10^{-22}\,J\right)n^2$$

Relating that to wavelength (we'll go to nm, and then back to cm^{-1}):

$$\lambda_{n\ to\ n+1} = \frac{hc}{E_{n+1} - E_n} = \frac{\left(6.626x10^{-34}\ J\ s\right)\left(2.998x10^{8}\ m\ s^{-1}\right)}{\left(6.025x10^{-22}\ J\right)\left(\left(n+1\right)^2 - n^2\right)} = \frac{3.297x10^{-4}\ m}{\left(n+1\right)^2 - n^2} = \frac{3.297x10^{5}\ nm}{\left(n+1\right)^2 - n^2}$$

$$\frac{1}{\lambda_{n\ to\ n+1}} = \frac{\left(n+1\right)^2 - n^2}{3.297x10^{5}\ nm}\frac{10^{7}\ nm}{cm} = \frac{\left(n+1\right)^2 - n^2}{3.297x10^{-2}}\ cm^{-1} = \left[\left(n+1\right)^2 - n^2\right]30.33cm^{-1}$$

Finally, answer the question (two ways):

a) Assuming a simple situation with only 1 electron:

$$\frac{1}{\lambda_{1\ to\ 2}} = \left[\left(2\right)^2 - 1^2\right]30.33cm^{-1} = 91cm^{-1}$$

Not so great…

b) Treat it more realistically. From the Figure Legend, system (19) has 10 fused porphyrin rings. Counting π electrons in each porphyrin, I get about 24 electrons/porphyrin (anyone care to tell me otherwise?), leading to 240 electrons in the box in total. This means that the lowest 120 energy levels will be filled.

$$\frac{1}{\lambda_{120\ to\ 121}} = \left[\left(121\right)^2 - 120^2\right]30.33cm^{-1} = 7310cm^{-1}$$

The answer is off by about a factor of two (observed is 12,000 cm^{-1}). Not bad, given the approximations involved.

2. Assuming that the largest fused system (19) is a TWO dimensional particle in a box, with well size 100 Å x 7 Å, calculate the energy (in cm^{-1}) of the predicted lowest energy electronic transition.

$$E_{n_1,n_2} = \frac{h^2}{8m}\left(\frac{n_1^{\ 2}}{L_1^{\ 2}} + \frac{n_2^{\ 2}}{L_2^{\ 2}}\right) = \frac{\left(6.626x10^{-34}\ J\ s\right)^2}{8\left(9.109x10^{-31}kg\right)\left(\text{Å}\frac{10^{-10}m}{\text{Å}}\right)^2}\left(\frac{n_1^{\ 2}}{l_1^{\ 2}} + \frac{n_2^{\ 2}}{l_2^{\ 2}}\right) = \left(6.025x10^{-18}\ J\right)\left(\frac{n_1^{\ 2}}{l_1^{\ 2}} + \frac{n_2^{\ 2}}{l_2^{\ 2}}\right)$$

Note that I've switched from L to l, taking out units (in other words, l should be dimensions in Angstroms, but is unitless in the above…)

$$\lambda_{m,\mathrm{n}\ to\ m',\mathrm{n}'} = \frac{hc}{E_{m,n} - E_{m',n'}} = \frac{\left(6.626x10^{-34}\ J\ s\right)\left(2.998x10^{8}\ m\ s^{-1}\right)}{\left(6.025x10^{-18}\ J\right)\left[\left(\frac{m'^2}{l_1^{\ 2}} + \frac{n'^2}{l_2^{\ 2}}\right) - \left(\frac{m^2}{l_1^{\ 2}} + \frac{n^2}{l_2^{\ 2}}\right)\right]} = \frac{32.97nm}{\left[\left(\frac{m'^2 - m^2}{l_1^{\ 2}} + \frac{n'^2 - n^2}{l_2^{\ 2}}\right)\right]}$$

$$\frac{1}{\lambda_{m,\mathrm{n}\ to\ m',\mathrm{n}}} = \frac{\left[\left(\frac{m'^2 - m^2}{l_1^{\ 2}} + \frac{n'^2 - n^2}{l_2^{\ 2}}\right)\right]}{32.97nm}\frac{10^{7}\ nm}{cm} = \left[\left(\frac{m'^2 - m^2}{l_1^{\ 2}} + \frac{n'^2 - n^2}{l_2^{\ 2}}\right)\right]3.033x10^{5}cm^{-1}$$

Finally, answer the question (two ways):

a) Assuming a simple situation with only 1 electron:

$$\frac{1}{\lambda_{1,1\ to\ 1,2}} = \left[\left(\frac{1^2 - 1^2}{100_1^{\ 2}} + \frac{2^2 - 1^2}{7_2^{\ 2}}\right)\right]3.033x10^{5}cm^{-1} = 18600\ cm^{-1}$$

$$\frac{1}{\lambda_{1,1\ to\ 1,2}} = \left[\left(\frac{2^2 - 1^2}{100_1^{\ 2}} + \frac{1^2 - 1'^2}{7_2^{\ 2}}\right)\right]3.033x10^{5}cm^{-1} = 91.0\ cm^{-1}$$

Note that the lowest energy transition would be the latter (despite the fact that the former is fortuitously closer to the real value)…

b) Treat it more realistically. 240 electrons in the box in total. But life gets complicated… Have to use Excel or the equivalent (I did *not* expect you to go through this…). Evaluating a large range of n1 and n2, it turns out that 120th and 121st lowest energy levels are (43,2) and (29,3), corresponding to (100A,7A).

$$\frac{1}{\lambda_{43,2\ to\ 29,3}} = \left[\left(\frac{29^2 - 43^2}{100_1^{\ 2}} + \frac{3^2 - 2^2}{7_2^{\ 2}}\right)\right] 30.33x10^5\, cm^{-1} = \left(-0.1008 + 0.1020\right) 30.33x10^5\, cm^{-1} = 3640\ cm^{-1}$$

Whoops. Farther off than with 1D system (observed is 12,000 cm^{-1}). Still not bad, given the approximations involved.

3. Why measure spectra of constructs 7-12? Explain their spectra.

In these constructs, the π systems are effectively decoupled. The resulting spectra correspond to the isolated porphyrins, and so are independent of the numbered of linked systems.