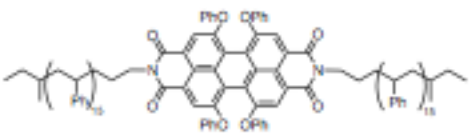
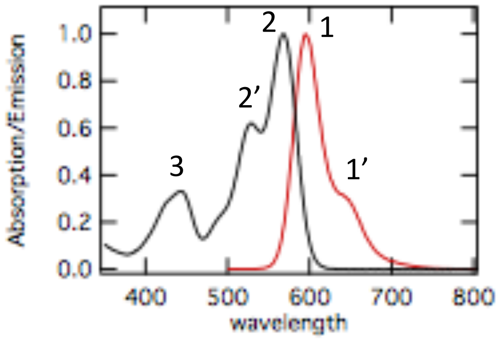
School of Engineering
Institute of Materials
Laboratory of Macromolecular
and Organic Materials

Organic Electronic Materials 2025 Exercise 4 (submit on 06.04.25)

1. Explain why the energy of a molecular system in its electronic ground state is always higher than the energetic eigenvalue associated with this state.
2. Draw the MO energy level diagram of butadiene with the electrons and draw the same diagram after promotion of one electron from the HOMO to the next higher orbital upon photon absorption. Why does the wavelength of the absorbed photon not correspond to the HOMO-LUMO gap? Which energy does it correspond to? Draw a transition corresponding to this promotion of electron in a Jablonski diagram. Briefly explain the difference in representation between a Jablonski diagram and a diagram such as the first one you drew.
3. What are the electronic, vibronic, and spin conditions for a non-zero probability of an electron to be excited (this probability is related to an associated transition dipole moment)?
4. The absorption and emission spectra of a tetraphenoxyperylene bisimide are shown below. Which is which? Draw the four transitions associated with the peaks 1, 1', 2 and 2' on a relevant diagram. Explain the difference in wavelength between the peaks 1 and 2. Name both the principle and the rule that lead to this observation. To which transition could the peak 3 correspond to?





5. Single molecules of naphthalene, anthracene, tetracene and pentacene absorb at 200–300 nm, 250–400 nm, 280–500 nm and 450–600 nm, respectively in solution. What is the reason for this absorption shift?

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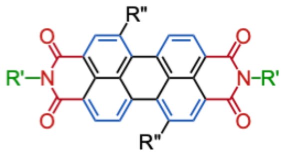
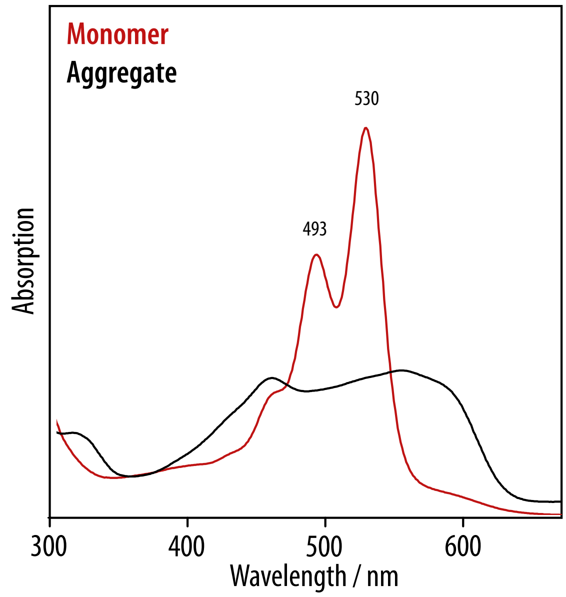
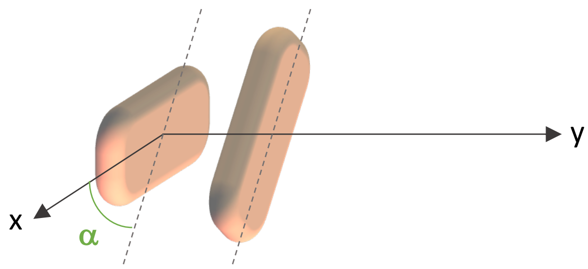
6. The absorption spectra of a perylene diimide derivative in its monomeric and aggregated form are given below. What can you say about the type of spectroscopic aggregates observed in this case?



perylene diimide



7. Kasha, *Pure Appl.Chem.* **1965**, *11*, 371–392: Two perylene diimide derivatives are stacked helically as represented on the figure below. Considering the absorption spectrum of the perylene diimide derivative in its monomeric form in the previous question, sketch the absorption and emission spectra of such a dimer in the cases where **α**=0°, **α**≈20°, **α**≈70° and **α**=90°.



Further Reading Suggestions:

- ‘Polarons, Bipolarons, and Solitons in Conducting Polymers‘ Acc. Chem. Res. 1985, 18, 309-315.
- “Mind the Gap”, Mater. Horiz. 2014, 1, 17.
- ‘Electronic Processes in Organic Semiconductors: An Introduction‘, Anna Kohler, Heinz Bassler ISBN: 978-3-527-33292-2; p.37: selection rules, p.48: absorption, p.98: Jablonski diagram, p. 99-107: Exciton coupling, p.136: Kuhn plots

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