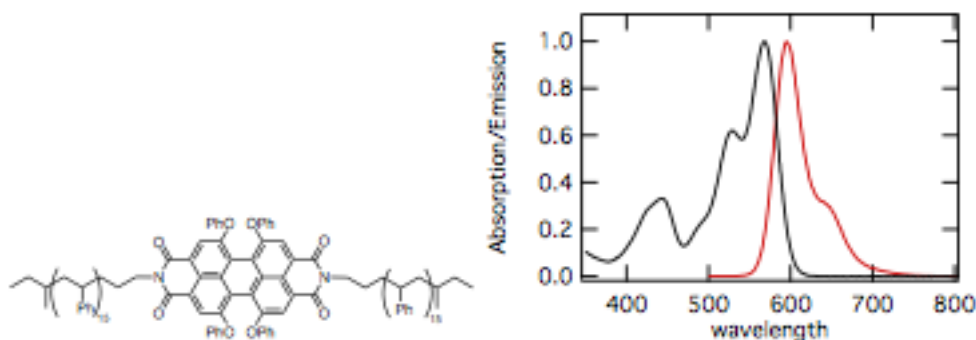


Organic Electronic Materials

Exercise 7

1. Naphthalene, anthracene, tetracene and pentacene absorb at 200–300 nm, 250–400 nm, 280–500 nm and 450–600 nm, respectively. What is the reason for this absorption shift?
2. The absorption and emission spectra of a tetraphenoxyperylene bisimide are below. Which one is which one? Try to assign the five peaks or shoulders observed in both spectra with the help of a Jablonski diagram!



3. What is the difference between the ground states of poly(acetylene) and “typical” benzenoid polymer semiconductors? Explain the difference using an energy diagram, showing the energy landscapes and the molecular structures.
4. Poly(*para*-phenylene) (PPP) and poly(flourene) are both benzenoid polymers. What is the structural difference between these two polymers? What is the consequence on the effective conjugation length, and consequently on their absorption and emission spectra?
5. Draw an energy diagram of poly(acetylene) and poly(phenylene) doped with a very small amount of an oxidant. Name the species formed in the case of the organic materials! Draw their chemical structures, and define what they are from an organic chemistry perspective.
6. J-aggregation of organic semiconductors as well as their aggregation in the solid state lead to a red shift of the absorption. Explain the difference between these two effects.

Reading suggestions:

‘Polarons, Bipolarons, and Solitons in Conducting Polymers’ *Acc. Chem. Res.* **1985**, *18*, 309-315.
“Mind the Gap”, *Mater. Horiz.* **2014**, *1*, 17.

Organic Electronic Materials

Exercise 8

1. How do you imagine the absorption spectrum of a pentacene film to differ from the one in solution? Explain why the molecular orbitals of crystalline pentacene give a narrower energy band gap than crystalline benzene.
2. What are the main factors that influence the extent of charge delocalization in a conjugated polymer? How does the charge localization (by dynamic disorder) affect the energy diagram of an organic semiconductor?
3. Describe the difference of the electronic interactions of two neutral molecules compared to those between one neutral molecule and a charged one.
4. How is the Fermi level defined? Where is the Fermi level in a neutral organic semiconductor? Where is the Fermi level of an n-type or a p-type semiconductor upon introducing the first negative or positive polaron defect, respectively?
5. How would you choose the material of an electrode that has to be in contact with an n-type organic semiconductor?

Organic Electronic Materials

Exercise 9

1. What would you expect, if you measure the charge carrier mobility of a single crystal of aromatic molecules at low temperature in three different crystallographic orientations? How does the mobility change with the increment of temperature?
2. Explain the difference between band transport and band-like transport. How would you determine which one is occurring in your material? Why would you expect none of these transport mechanism in polythiophene?
3. Tetrathiafulvalene (TTF) and Teracyanoquinodimethane (TCNQ) exhibit poor conductivity as pristine single crystal. What are the two main reasons for the remarkable conductivity of TTF-TCNQ composite crystal? How does the conductivity correlate to the charge carrier mobility and the charge carrier density in a material?
4. ‘Tunneling’ and ‘hopping’ are two of main charge transport mechanism in organic semiconductors. On which parameters do they depend? How can the static disorder affect the hopping mechanism?

Organic Electronic Materials

Exercise 10

1. How does charge transport occur in the “multiple trap and release” model? Describe the two competing (in fact, opposing) effects of the temperature on mobility according to this model!
2. Poly(3-hexylthiophene) (P3HT) is a semicrystalline polymer that typically forms fibrillar nanostructures. Explain why and describe in detail the molecular packing within such a fibril.
3. Explain why, at low molecular weights P3HT, the hole mobility increases while the crystallinity of P3HT decreases with an increasing molecular weight! Why does the mobility not increase further, above molecular weights of about 30'000? Describe the charge transport process through the entire bulk material in the case of such a semi-crystalline polymer!
4. Which different methods are feasible to characterize the morphology of organic semiconductor materials in thin films, from the Angstrom to the mm scale?