

Organic Electronic Materials 2025 Mock Exam

Solutions

Disclaimer: The following solutions are indicative and meant to guide your understanding; they are not exhaustive or written in full exam-style detail.

Part 1 (X points)

1. Define and compare a semiconductor, a conductor and an insulator.

See the solution of question 1 of exercise sheet 1.

2. What types of organic molecules can exhibit semiconducting properties, and why?

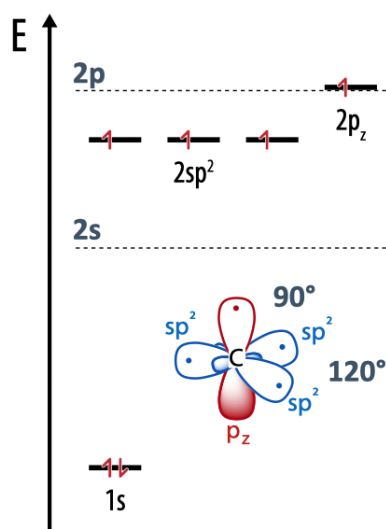
Conjugated molecules as they comprise pi orbitals that give rise to electrons delocalization and smaller bandgap than non-conjugated molecules.

3. Define the notion of the density of occupied states and explain how it can be determined.

The density of occupied states represents the state that are populated at a given temperature and correspond to the product of the density of states times the Fermi Dirac distribution at this temperature.

4. In which hybridization state are the carbons involved in the naphthalene molecule? Draw the associated energy diagram as well as sketch of the shapes and orientations of the corresponding atomic/hybrid orbitals.

The carbons involved are in sp^2 hybridization state.



5. Is the naphthalene molecule stable? Why?

Yes because it is a planar cyclic conjugated system and it satisfies the Hückel rule ($4n+2$ pi-electrons or $2 \cdot n+1$ pi-bonds).

6. Let's consider you want to estimate the π -energy levels and the associated π -orbitals of naphthalene:

- a. Give a synonym for the term "orbital" from a mathematical description point of view.

Spatial part of a wavefunction or spin independent wavefunction.

- b. What general equation should you try solve to get the energy levels and the associated orbitals? Use the bracket notation. Name and give the physical meaning of this equation and the elements that appear in it. Which are the approximations you should you make to simplify the problem? Name the theory from which these assumptions come.

The time independent Schrödinger equation $\hat{H}|\psi\rangle = E|\psi\rangle$ (please note that it is the bracket notation that is asked here) should be solved.

Schrödinger equation is a differential equation that describes the allowed states (stationary state wave functions ψ) of an electron in quantum system.

- H Hamilton operator, set of operations that describes the total energy of the quantum system.*
- E is the energy associated to the stationary state wave function ψ , ie the eigenvalue of the Schrödinger equation associated to the eigenvector ψ .*

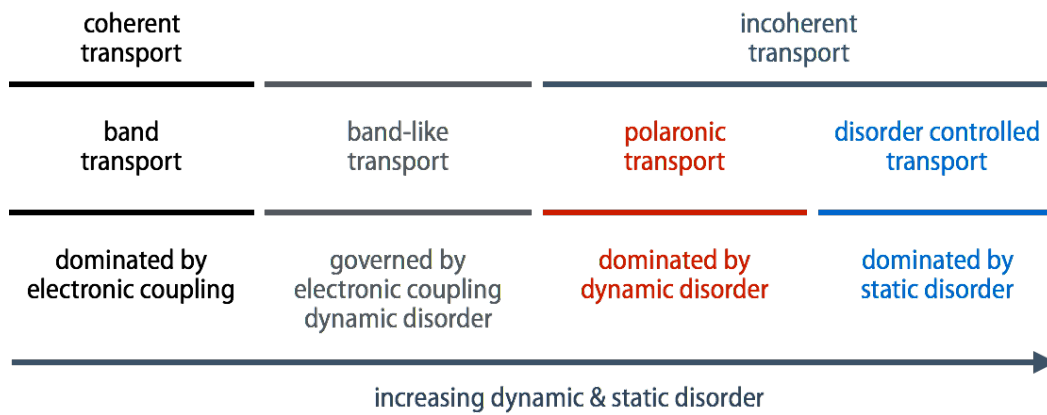
~~7. Define the notion of the density of occupied states and explain how it can be determined.~~

This was a formatting mistake, sorry for the inconvenience. See question 3.

8. Why do most organic semiconductors have better conductivity than diamond at room temperature?

Because despite their lower mobility they have a larger concentration of charge carriers.

9. Distinguish the different possible transport mechanisms governing charge transport in organic materials and name the main physical effect by which each regime is dominated. For each case, indicate if majority of the charge carriers are localized or delocalized.



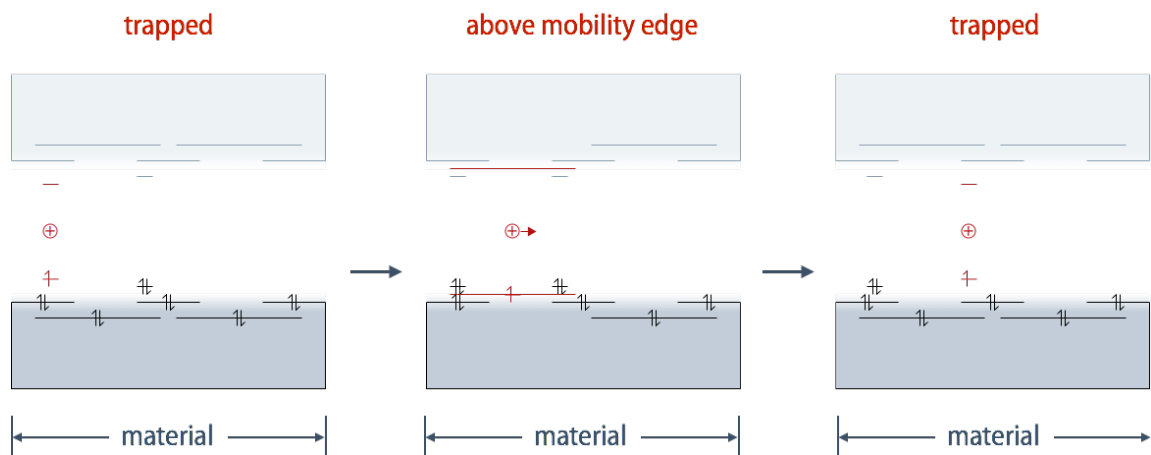
10. Qualitatively compare the MO energy level diagrams of ethylene, butadiene and octatetraene. Explain the evolution of the LUMO levels and optical gaps of these molecules.

See lecture slide 91.

11. Describe how charge transport occurs in the “multiple trap and release” model. Explain the two competing (in fact, opposing) effects of the temperature on the charge carrier mobility according to this model.

Definition of MTR model: see lecture slide number 289.

- *Band diagrams*

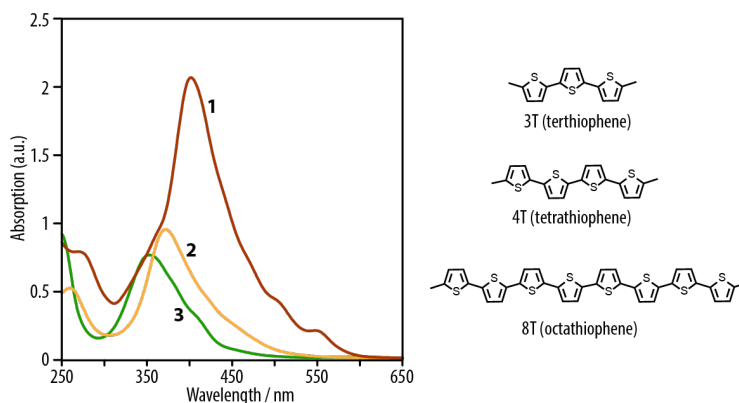


- *Charge carriers trapped in localized states at band edge*
- *Charge promoted with (thermal) energy above the mobility edge into a more extended state that allows it to be drifted in an electric field.*
- *Subsequent charge re-trapping into a localized state.*

Temperature effect

- *Increasing thermal energy allows for better promotion into delocalized states (1 pt) but decreases the extent of the delocalized states (i.e. localizes delocalized states)*

12. In the following graph the absorption spectra of three different oligothiophene derivatives (in dilute solution) are plotted. Which spectrum corresponds to which molecule? Explain the shift of the peak maxima of the absorption curves of the three molecules.



3T -> 8T: Larger π -system -> higher degree of delocalization -> smaller HOMO-LUMO gap -> red shifted absorption

13. Explain on the example of two benzene molecules why face-to-face π - π stacking is never observed for regular aromatic molecules. What would happen if one of the two benzene molecules was perfluorinated?

Unfavorable quadrupolar moments typically stronger than attractive Van der Waals forces. Fluorinated and non-fluorinated would stack face-to-face.

Part 2 (X points)

14. We dissolve the following reactants in dry DMF under inert gas, and heat the flask to 80°C overnight (**Error! Reference source not found.**).

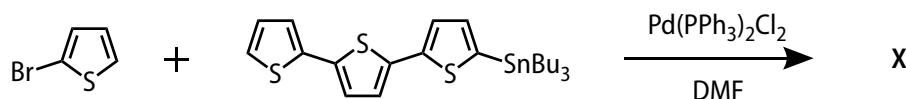
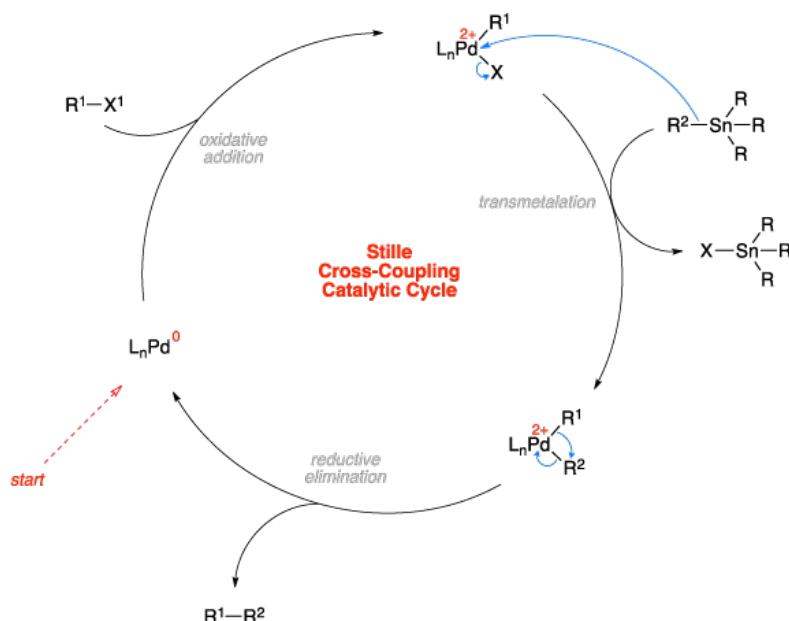


Figure 1 : Palladium-catalyzed reaction scheme

- a. What product do we obtain? What is the name of the reaction?

Quaterthiophene (the drawing of the molecule is expected), Stille coupling.

- b. Draw the detailed mechanism and name all individual steps.



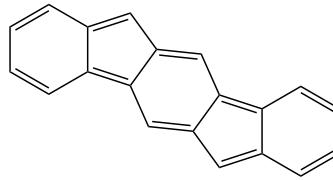
- c. Why is the reaction above often replaced with other palladium-based reactions?

Because of the use of organotin compound - SnBu_3 (toxic)

- d. What kind of molecular packing would be expected for the obtained product **X**? Explain briefly why.

Calamitic molecule, herringbone packing.

15. What is the shape type of this molecule? How do you expect this molecule to pack?



Calamitic, herringbone.

16. Briefly define Keesom, Debye and London forces.

See slide number 118.

17. The absorption maximum of an asymmetrically substituted X in a thin-film is blue-shifted in comparison to its absorption spectrum in dilute solution (**Error! Reference source not found.**). What is the reason for this blue-shift? Explain this effect with the help of an energy diagram.

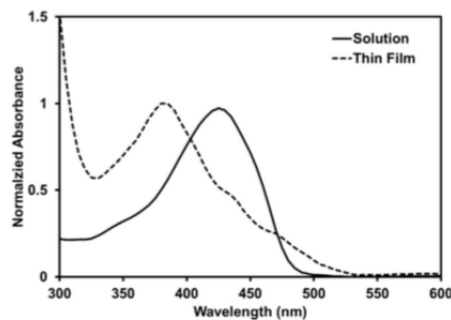
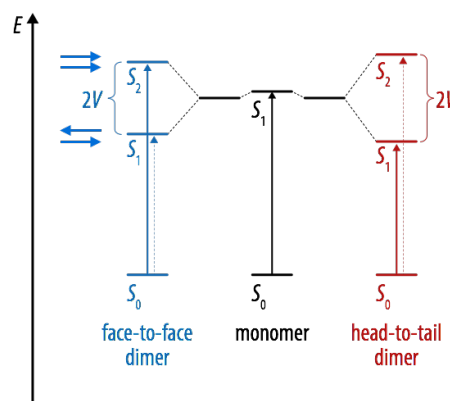


Figure 2 : Absorption spectrum of an asymmetrically substituted X in a thin-film (dashed) and in solution (plain)

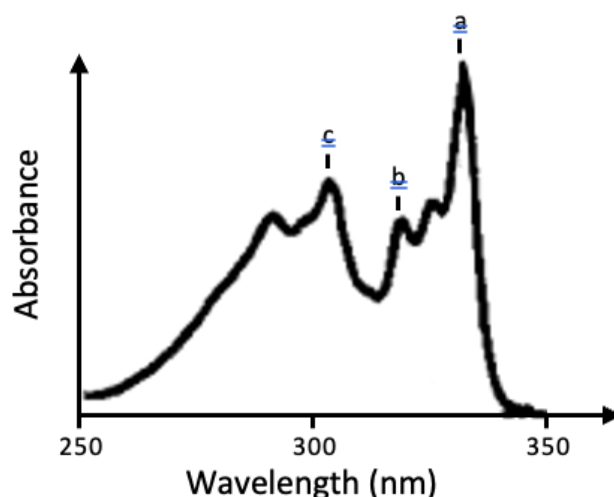
The distance between molecules in a thin film is much smaller compared to diluted solutions, so spectroscopic aggregates are observed due to dipolar coupling of the transition dipole moments.



(left side of this picture)

Splitting of the excited state, where due to the face-to-face packing in the film only transitions to the higher energy excited state are allowed (in-phase situation for the transition dipole moments). This results in a blue shift.

18. The absorption spectrum of a molecule is presented on the graph below. To which transitions do “a”, “b” and “c” correspond to?

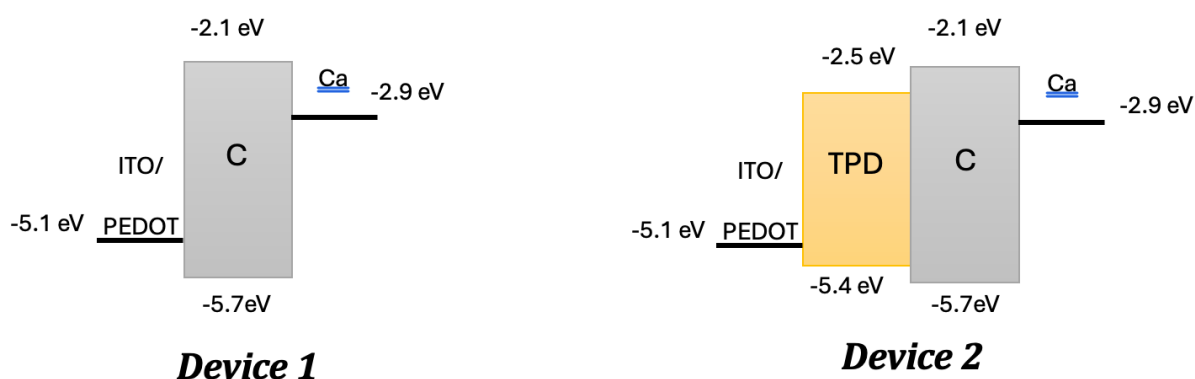


a: main absorption peak, transition from the ground state to the 1st electronic excited state

b: transition from the ground state to a vibrationally excited state of the first electronic excited state

c: transition to the second electronic excited state

19. Device number 2 presented below was created to improve the performance of device number 1. However, the second device led to poorer results. Explain what was the idea behind the addition of the TPD layer and why it actually reduces the efficiency?



TPD initially put as hole injection layer however on the LUMO side opposite then a blocking layer the electrons actually move from C to TPD and can no longer recombine in C.

20. Oligothiophene derivatives can be used as an active semiconducting layer in thin film transistors. On **Error! Reference source not found.**, two different characteristics (curves) are shown. Name these characteristics (curves) and describe briefly how you obtain them. What kind of important parameters can you extract from the first characteristic? Name them, briefly explain their meaning and how you can determine them.

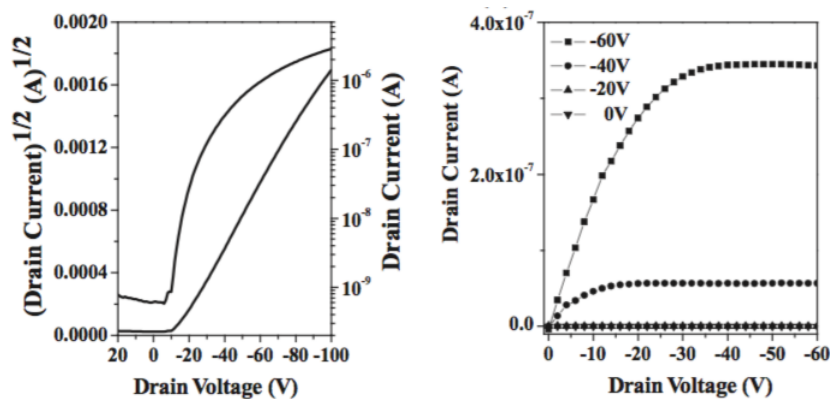


Figure 3 : Characteristics of an oligothiophene-based thin-film transistor.

Transfer curve: you keep the drain voltage constant and sweep the gate voltage and measure the drain current as a function of gate voltage.

Important parameters to be extracted:

-mobility: is a measure that determines the speed of charge carriers in E field and obtained from the slope of a plot of the square root of the absolute drain current I_D against the gate voltage V_G (2 pts)

$$\mu_{lin} = \frac{L}{C_{die} W V_D} \cdot \frac{\partial I_D}{\partial V_G}$$

$$\mu_{sat} = \frac{2L}{C_{die} W} \cdot \left(\frac{\partial \sqrt{I_D}}{\partial V_G} \right)^2$$

-Threshold voltage (V_{th}): is a measure when TFT is ON. threshold voltage V_{th} corresponds to the gate voltage axis intercept.

-on/off ratio describes the switch ability of a device, and is determined by plotting the absolute drain current I_D in a logarithmic scale against the gate voltage V_G

Output curve: you keep the gate voltage constant and sweep over the drain voltage and measure the drain current.

-FET like behavior meaning first linear regime; transition regime; saturation regime

21. Poly(phenylene) can be doped with either an oxidant or a reductant to improve its semiconducting properties. Give an example of a reductant used in this case and formulate the molecular structure as well as the energy diagram of the resulting doped state.

Reductant: Na / K / Li

