Instructions for the practical course

TRAS

TRANSIENT ABSORPTION SPECTROSCOPY

Chair of Soft Matter Optoelectronics (EP II)

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1 Introduction

1.1 Colourfulness as a phenomenon

Colourfulness is a phenomenon of large fascination. The cultural use of dyes began already at the Stone Age. But even without the conscious use of dyes, the natural phenomenon of colourfulness can be observed, for example in the sky. The origins of this colourfulness are manifold and of different causes. Kurt Nassau describes fourteen reasons for colourfulness in [1]. From a scientific point of view, it is worthwhile to distinguish between them, as the underlying phenomena are of a very different kind. Electronic excitations on the molecular and atomic scale can cause the same colours as structural colours based on interference . However, the interaction with light is common to all of them and the characterisation of this leads to knowledge about the material, e.g. its electronic structure. In this experiment, coloured zinc complexes are to be investigated in an optical setup with regard to their transient absorption properties and thus the lifetimes of an excited tiplet state are to be determined under different experimental conditions. This experiment introduces the participants to the basic principles of transient absorption spectroscopy and shows possible applications of it.

1.2 Absorption and Extinction

The absorption of light of intensity I_0 on a path of length d through the absorbing medium of concentration c (see Figure 1.1) is described by Lambert-Beers law: [2,3]

$$\log\left(\frac{I_0}{I}\right) = \epsilon\, c\, d \tag{1.1}$$

ϵ is called extinction coefficient, because $E = \log\left(\frac{I_0}{I}\right)$ is the extinction. Using the absorption coefficient α it is: [2,3]

$$\ln\left(\frac{I_0}{I}\right) = \alpha\, c\, d \tag{1.2}$$

In this practical course an absorption spectrum $\left(1 - \frac{I}{I_0}\right)(\lambda)$ (see section 3.3) and the progress of the transient absorption $\Delta A(\tau) = -\log\left(\frac{I(\tau)}{I_{GZ}}\right)$, which depends on the delay between pump and probe pulse τ (see section 3.4), are distinguished. Note, that $I_{GZ} = I(\tau \to \infty)$.
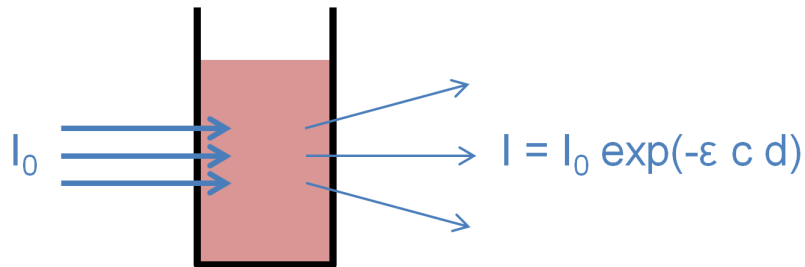

Abbildung 1.1: Schematic explanation of Lambert-Beer's law.

1.3 Electronic processes in organic matter

In the following, electronic processes in organic (semiconducting) molecules are considered. The energy levels of these systems can be described by molecular orbitals, which in turn can be combined from the atomic orbitals using the LCAO method. A concrete occupation of these molecular orbitals (configuration) is called a state. Examples of such states are shown in Figure 1.2. The highest occupied orbital is called HOMO (highest occupied molecular orbital), the lowest unoccupied orbital is called LUMO (lowest unoccupied molecular orbital). In addition a distinction is made between singlet and triplet states. In triplet states T_i the total spin (sum of the electron spins) is ± 1, so there are more electrons with one spin than with the other. In singlet states S_i the total spin is 0. The simplified representation in Figure 1.2 does not depict the electronic interaction within the excited states. Thus, the configurations shown in Figure 1.2 only represent the largest contribution in a linear combination of configurations in the configuration interaction (CI) model. This linear combination, as a state, better represents the actual conditions. [4]

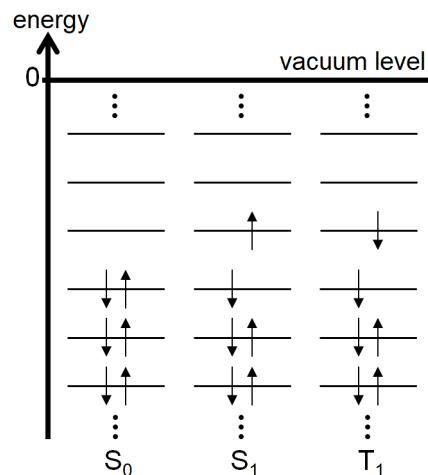The representation of the transitions between these states is referred to the

Abbildung 1.2: Figure 1.2: Orbital diagram of the dominant orbital occupations of the singlet states S_0 , S_1 and the triplet state T_1 [inspired by 4].

Jablonski-scheme and can be seen in Figure 1.3 for the system considered in this experiment. In addition to the vertically drawn absorptions, the transition of the intersystem crossing (ISC), which is spin-forbidden in the dipole approximation, is also shown. This transition is only partially permitted by sufficiently large spin-orbit coupling. Transitions in the vibrational levels of the states are called internal conversion (IC). Another illustration introducing further terms is shown in Figure 1.4. [4] The radiative transition from an excited singlet state to the ground state is called fluorescence; that from an excited triplet state is called phosphorescence. [2]
Question: What are the magnitudes of fluorescence and phosphorescence and
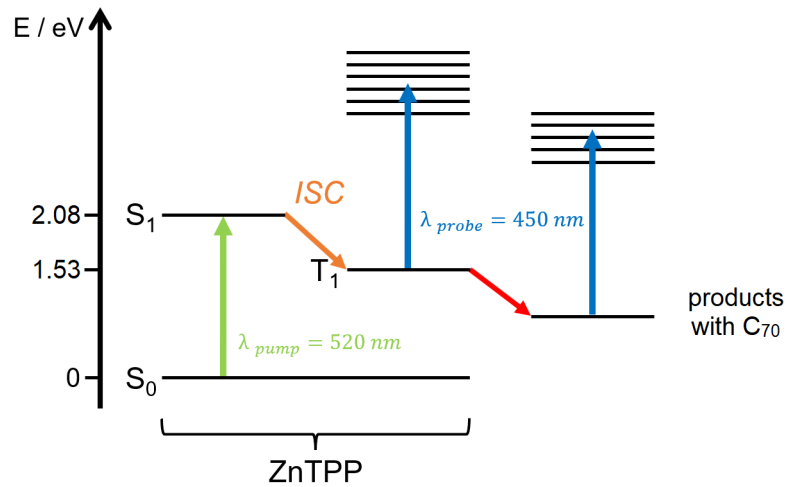
why?

Abbildung 1.3: Jablonski scheme of the system under investigation; ZnTPP-C_{70}.

Determining the lifetime of the excited triplet state from which the phosphorescence originates is an essential object of this experiment. Here, the lifetime τ is defined by the radiative and non-radiative decay rates k_r and k_{nr}: [2,4]

$$\tau = \frac{1}{k_r + k_{nr}} \tag{1.3}$$

The determination is achieved by a pump-probe experiment. The excited singlet state is occupied by stimulation by an excitation pulse (pump laser). With a fast ISC, the molecules in the triplet state can be further excited by an second excitation pulse (probe laser). The absorption of this second pulse is proportional to the occupation of the triplet state. By varying the time interval between the two pulses, a time-resolved TA spectrum can be obtained. [5]
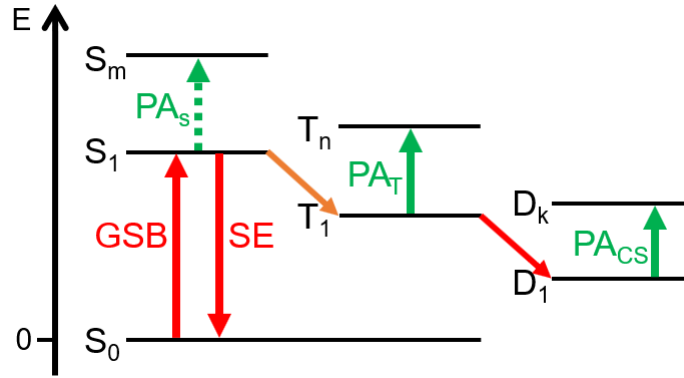
Abbildung 1.4: Ground state bleaching (GSB), Stimulated emission (SE) and Photo-induced absorption (PA) of different states in an energy diagram. [inspired by 4]

The kinetics of the decay of this triplet state is described by the following differential equation, where $C_T(t)$ denotes the concentration of the triplet and $C_G(t)$ the concentration of the ground state. The relaxation into the ground state is described by the reaction rate k_1 and various bimolecular deactivation processes by the rates k_2 and k_3.

$$-\frac{dC_T(t)}{dt} = k_1\,C_T(t)\,+\,k_2\,(C_T(t))^2\,+\,k_3\,C_T(t)\,C_G(t) \tag{1.4}$$

$$\overset{C_T(t)\ll C_G(t)}{\Longleftrightarrow}\quad -\frac{dC_T(t)}{dt} = k_1\,C_T(t)\,+\,k_3\,C_T(t)\,C_G(t) \tag{1.5}$$

$$\overset{C_G(t)=C_G=const.}{\Longleftrightarrow}\quad -\frac{dC_T(t)}{dt} = C_T(t)\,(k_1\,+\,k_3\,C_G) \tag{1.6}$$

$$\overset{k_0:=C_G=const.}{\Longleftrightarrow}\quad -\frac{dC_T(t)}{dt} = C_T(t)\,k_0 \tag{1.7}$$

$$\Longrightarrow\ C_T(t) = C_T(0)\,\exp(-k_0\,t) \tag{1.8}$$

The lifetime can be reduced by additional decay paths (quenching). These are provided in the experiment by the acceptor component, the fullerene C_{70}, with the concentration C_q. Correspondingly, the kinetics are obtained by describing the quenching process with the reaction rate k_q:

$$-\frac{dC_T(t)}{dt} = C_T(t)\,(k_0\,+\,k_q\,C_q) \tag{1.9}$$

$$\overset{k_{app}:=k_0+k_q\,C_q}{\Longleftrightarrow}\quad -\frac{dC_T(t)}{dt} = C_T(t)\,k_{app} \tag{1.10}$$

$$\Longrightarrow\ C_T(t) = C_T(0)\,\exp(-k_{app}\,t) \tag{1.11}$$

2 Questions for preparation

1.) What would an experimental setup for investigating the wavelength dependence of the triplet state population decay look like?

2.) Before the triplet state of the investigated complex ZnTPP is occupied, its excited singlet state is occupied. Can this process be identified in the TA signal?

3.) What effect does the use of a lens with a focal length of 75 mm instead of 60 mm in the beam path of the probe beam have on the measurement procedure and the measurement result?

4.) Explain the phenomenon of anisotropy in relation to luminescence phenomena! Do they expect anistropic behaviour in the examined materials (in the preparation state used)?

5.) Airtight (or inert gas assisted) and dark storage can extend the shelf life of the solutions used in the experiment with regard to their optical properties. Explain the underlying processes and those to be avoided!

6.) P3HT is a polymer. How should the concentration of 1 mM be understood here?

7.) Comprehend and explain the assumptions in the kinetics of triplet decay!

8.) What is the significance of a negative or positive transient absorption? What are the underlying processes in each case?

3 Experimental section

3.1 Used chemicals and safety instructions

ZnTPP
5,10,15,20-Tetraphenyl-21H,23H-porphinzink(II)
M = 678,11 g/mol

Zn4PP
5,10,15,20-Tetrakis-(4-pyridyl)-21H,23H-porphinzink(II)
M = 682,06 g/mol

ZnOEP
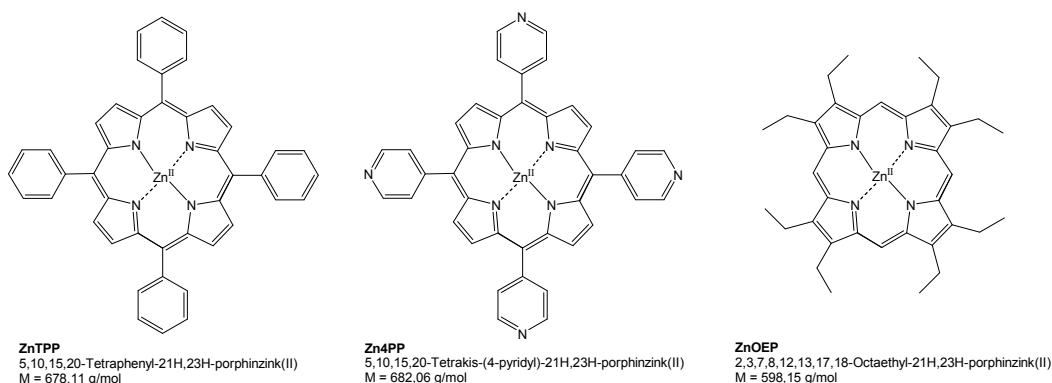2,3,7,8,12,13,17,18-Octaethyl-21H,23H-porphinzink(II)
M = 598,15 g/mol

Abbildung 3.1: These organometallic complex compounds are investigated in the experiment

n this experiment, solutions of the metalorganic zinc complexes shown in Figure 3.1 are used in benzonitrile (PhCN) and in toluene (PhMe) and a solution (already prepared) of the polymer P3HT in toluene. The fullerene C_{70} is also added to the ZnTPP solutions.

The handling of opened containers of organic solvents takes place exclusively in the fume hood. However, the perception of an almond-like odor, characteristic of benzonitrile, cannot be completely avoided. Work quickly, but not hectically! While working in the chemistry laboratory, make sure to wear appropriate personal protective equipment, i.e. gloves, safety glasses and lab coat. The toxicity of the complexes used has not been scientifically investigated. However, by working cleanly, contamination can be almost completely ruled out. The general safety regulations for laboratories (no working alone, neither eating nor drinking, disposal regulations, etc.) must always be observed!

3.2 Sample preparation

The preparation is carried out in the chemistry laboratory. Only the solutions to be examined in sealed cuvettes are transported to the measuring laboratories in the sample holder.

Table 3.1 ists all samples to be prepared. Start with the preparation of the following solutions:

(A) ZnTPP in benzonitrile, 0.8 mM (approx. 10 mL)

(B) ZnTPP in toluene, 0.8 mM (approx. 2 mL)

(C) C_{70} in benzonitrile, 0.8 mM (approx. 4 mL)

The solutions in benzonitrile are treated for twenty minutes in an ultrasonic bath. A 1.5 mM solution of P3HT in toluene is also available. Starting from these stock solutions, the starting materials and the appropriate solvents, prepare the required solutions (2 mL for TRAS, 1 mL for UV-VIS). Sample vessels with a volume of 1 mL, 4 mL, 10 mL and 20 mL are available. Think about your procedure before starting the experiment! For the transient absorption spectroscopy (samples 1 to 12), cuvettes from Thorlabs with a filling volume of approx. 550 μL are used, for the UV-VIS spectroscopy (samples 13 to 17) 1mm quartz cuvettes with a filling volume of approx. 400 μL.

Tabelle 3.1: Samples for TRAS and UV-VIS spectroscopy.

Sample number	Description
1	ZnTPP in benzonitrile, 0.8 mM
2	ZnTPP in benzonitrile, 0.6 mM
3	ZnTPP in benzonitrile, 0.4 mM
4	ZnTPP in benzonitrile, 0.2 mM
5	ZnTPP : C_{70} in benzonitrile, 1:0.1
6	ZnTPP : C_{70} in benzonitrile, 1:0.2
7	ZnTPP : C_{70} in benzonitrile, 1:0.3
8	ZnTPP in toluene, 0.8mM
9	P3HT in toluene, 1.5 mM
10	P3HT in toluene, 0.75 mM
11	Zn4PP in benzonitrile, 0.8 mM
12	ZnOEP in benzonitrile, 0.8 mM
13	ZnTPP in benzonitrile, 0.016 mM
14	ZnTPP in toluene, 0.016 mM
15	ZnOEP in benzonitrile, 0.08 mM
16	Zn4PP in benzonitrile, 0.016 mM
17	P3HT in **Toluol**, 0.15 mM

3.3 UV-VIS spectroscopy

In the UV-VIS spectroscope, samples 13 to 17 are examined in a wavelength range between 300 nm and 700 nm. Steady-state absorption spectra are recorded. A baseline correction is carried out and the respective pure solvent is used as a reference. Care must be taken on ensuring the complete mapping of the signals. It may be necessary to use differently concentrated solutions.

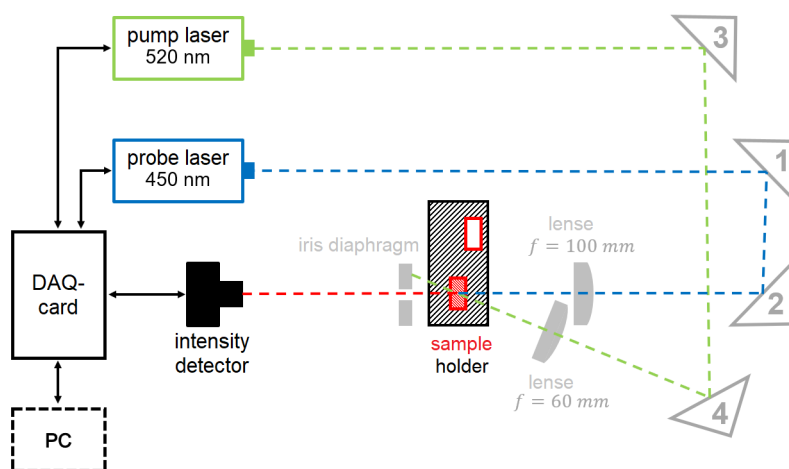## 3.4 Time-resolved absorption spectroscopy

Abbildung 3.2: Scheme of the TRAS measurement setup.

3.4.1 Adjustment of the setup

The optical setup shown schematically in Figure 3.2 has to be setted up and adjusted. The position of the lasers, the cuvette holder and the height adjustment of the mirrors must not be changed. The fluorescent adjustment aids and the adjustment card are used to adjust the beam path. The option Reduced Pump Frequency should be activated during the entire adjustment. The pulse widths of the lasers are turned to the minimum. The approximate position of the components can be taken from Figure 3.3.

After positioning mirror 1, the alignment of the beam to the desired row of holes using the adjustment aid is carried out, followed by the positioning of mirror 2. The mirror settings are now adjusted using both adjustment aids. The adjustment aid with crosshairs is located at the end of the row of holes on which the sample will be located and the one with a hole is located a few centimetres in front of the mirror. The beam should hit the centre of the crosshairs. The position on the first adjustment aid
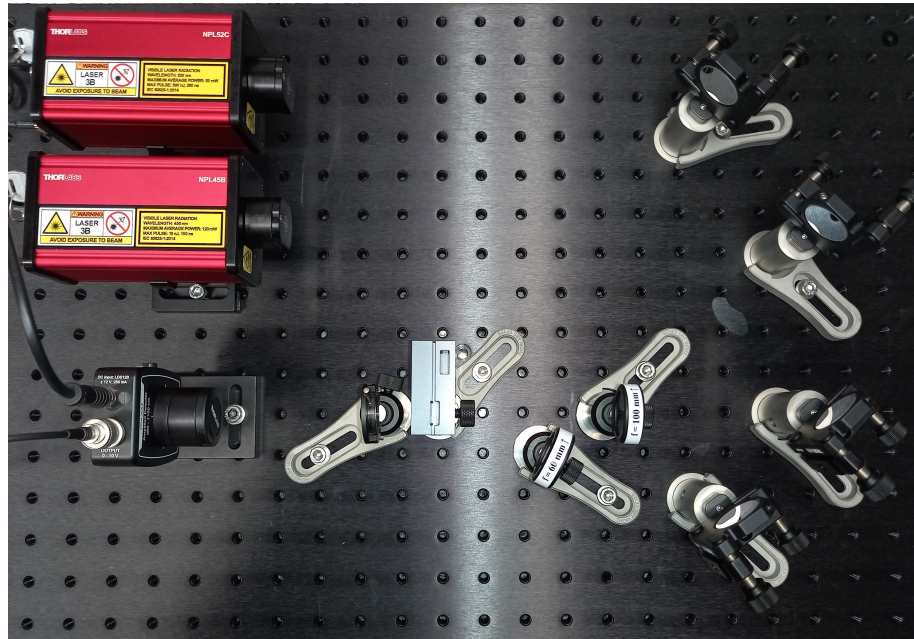
Abbildung 3.3: Picture of the adjusted setup (without computer and DAQ card).

is optimised by means of mirror 1, that on the second by means of mirror 2. Now the detector can be positioned and its position checked by means of the unscrewable part of the adjustment aid with crosshairs. The TA signal should be between 0.6 V and 0.9 V, which can be achieved by the detector gain and the probe laser pulse width. The appropriate position of the lens (100 mm focal length) is found with the adjustment card inserted in the sample holder. The incident beam should be focused, i.e. appear as small as possible on the card.

The positioning and alignment of mirrors 3 and 4 is done in the same way as for mirrors 1 and 2, but the adjustment aid with crosshairs is placed between the detector and the probe laser. The lens (60 mm focal length) is also positioned in the same way. However, its position should be chosen so that the beam paths of the pump and sample lasers overlap on the adjustment card. Finally, the iris diaphragm is set up behind the cuvette holder so that the sample beam passes through it but the pump beam is intercepted by it.

3.4.2 Maximising the TA signal

To maximise the TA signal, the option Reduced Pump Frequency is deactivated and the pulse width of the pump laser is selected to the maximum. Sample 1 is used because of its high TA signal, approx. 40 mOD, and the cuvette should be refilled for later measurement. The delay between the pulses is set to 200 ns and the detection limit to a value 0.2 V below the maxima. With the help of the mirror 4, the TA signal can be improved by changing the beam overlap. Once a maximum is reached, the position of the 60mm lens is changed and the signal is optimised again using the mirror. By this method and decreasing shifts of the lens, a TA signal of approx. 40 mOD can be achieved. It is important to ensure that the signal hits the centre of the lens.

3.4.3 Carrying out the measurements

In the Measurement tab of the software, the start of the measurement is set to - 400 ns and the end to 5000 ns, with averaging over five measurements. With low TA signals, it may be useful to average over more than five measurements. The prepared samples 1 to 12 are fixed in the cuvette holder and measured. The measurement data should be saved as a .csv file. In addition, the influence of the pulse width of the pump laser is to be investigated by measuring sample 1 at four different pulse widths (-200 ns to 500 ns).

4 Evaluation

4.1 UV-VIS spectroscopy

Display the recorded spectra appropriately. Any de- tector jumps shown should be corrected. Discuss the observed bands using appropriate literature and compare the spectra of the ZnTPP samples. What is the origin of the signal shift that occurs?

4.2 Time resolved absorption spectroscopy

(1) Graphically represent the recorded measurement data. Six figures are to be created.

(2) Determine the lifetime of the triplet state by fitting a suitable function to the TA signal. Compare the lifetimes given the different sample compositions and discuss the trends that occur, also in relation to the expectations by the theory.

(3) From the lifetimes of samples 3 and 5 to 8, reaction rates can be determined. By plotting these against the concentration of C_{70} , the desired reaction rate of the quenching process k_q can be determined. Compare your result with a literature value.

(4) The TA signal of P3HT differs significantly from that of ZnTPP. What is the underlying process of P3HT?

(5) Explain the occurring (maximum) TA signals of the three zinc complexes (0.8 mM in benzonitrile) considering the UV-VIS spectra and the structures of the compounds.

(6) Discuss the influence of the pump laser pulse width on the TA signal.

5 Bibliography

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