

Determination of triplet energies and decay times of light-emitting layers

S. Brüninghoff, Merck KGaA, Dept SO-ACP-7, Darmstadt, Germany (April 2015)



Application Note

1. Introduction

Organic light-emitting diodes (OLEDs) are opto-electronic components, which can be manufactured as monochrome (red, green, blue) as well as by a mixing e.g. as white components. Additionally, these materials can be applied as amorphous layers onto any substrate, which, due to non-existent lattice strains, leads to a mechanical flexibility. Apart from these mechanical properties the superior optical properties are of interest for the display industry.

As the OLED materials age and lose their efficiency at different rates, it is important to understand the internal processes in the materials in order to improve them.

Unlike inorganic semiconductor systems, in which the properties are influenced e.g. by dopings, in organic materials the properties are modified directly via the structure of the molecule.

2. Nature of the problem

Layers with different functions are needed in the production process of organic LEDs. Depending on the function, these layers must have different optical properties. The optimization of the physical properties of the individual layers can improve the efficiency of the overall OLED system. By knowing the properties of the individual layers, the layer system to be used can be optimized and the efficiency of the overall OLED system can be improved.

The decay time of the fluorescence and the phosphorescence as well as the positioning of the S1 and T1 level have to be mentioned as important properties of the OLED materials respectively the overall OLED system.

At Merck KGaA in Darmstadt (department OLED research) a measurement system for the determination of triplet energy and decay times of light-emitting layers has been set up in order to optimize the efficiency of the materials for the different layers and the overall OLED system. The aim of the set-up is to measure the T1 level at low temperatures and likewise with the same measuring station the temporal course of the T1 level is recorded and evaluated.

From the data obtained, conclusions on the path and velocity of diffusion as well as on different interactions between different energy levels of the excitons can be drawn.

Moreover, with this test unit the thermal behavior of the OLED materials resp. the overall OLED system is tested.

3. Measurement setup

As a principle, the measurement setup consists of the following structural components:

- Laser (Crylas FQSS 266-200)
- Cryostat (Oxford Instruments Optistat DN-V2)
- Spectrograph (Andor SR-303i-A)
- Camera (Andor ICCD iStar DH320T-18F-03)

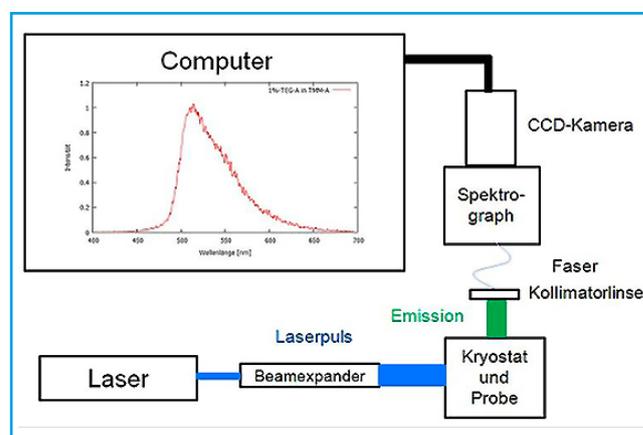


Illustration 1 - Schematic structure of the measuring station

The laser of the company Crylas FQSS 266-200 is a threefold doubled pulsed ND:YAG laser with a wavelength of 266 nm. The pulse energy of the laser is 200 μ J at a pulse width of 1.5 ns.

As the punctual high energy would destroy the layers that have to be examined, a beam expander was installed between the laser and the sample chamber for the expansion of the beam.

The sample chamber consists of the Oxford Instrument Optistat DN-V2, which is cooled with liquid nitrogen and placed under vacuum for thermal isolation. At the lower end of the cryostat is a sample chamber with four windows through which the sample is irradiated with the excitation light and the emission is taken with a collimating lens into a glass fiber.

The glass fiber transmits the light to spectrograph Andor SR-303i-A, which splits the emitted light and displays the set wavelength range onto camera Andor ICCD iStar 320.

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Illustration 2 - The measurement setup

With this measurement setup, the measurement is started by the laser, which on the one hand emits the laser impulse and on the other hand transmits an electrical trigger signal to the camera. In our measurement setup, the signal propagation delay of this trigger signal is 72 ns. For the measurement, this means that the first exposure and the resultant emission are not measured. However, for the synchronization of the further measurements, the software of the camera factors this signal propagation delay in.

Another point crucial for the procurement of the used components was, that a Labview Software Developer Kit is available to program an own software that can control all components. For the measurement of the emission and the decay times the "kinetic mode" of the camera is used. At this, at certain points in time emission spectra are recorded and by choice of a suitable delay time, the camera is instructed to open the measuring window continuously later. By this a temporal course of the emission is obtained. To get a signal-to-noise ratio, multiple measurements are performed.

4. Results

In Illustration 3 an emission spectrum of an OLED material is visualized. The evaluation of the T1 level is effected by finding the first maximum (here at 474 nm).

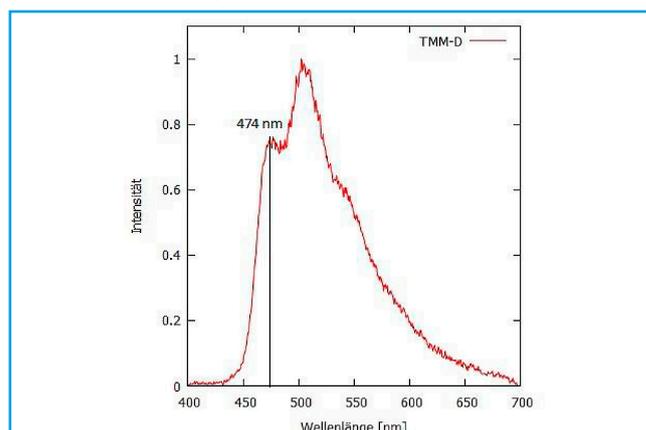


Illustration 3 - Emission spectrum of an OLED material

With the read-out mode "kinetic mode" emission spectra with a time offset are recorded. By recording the intensity at 474 nm over the time the Illustration 4 is achieved, which represents the time dependent course of the intensity of the emission light originating from the recombination of excitons with T1 levels. Since fluorescence and phosphorescence are overlapping and as we are interested in the time dependent course of the phosphorescence, in the following the section marked in Illustration 5 in blue is discussed.

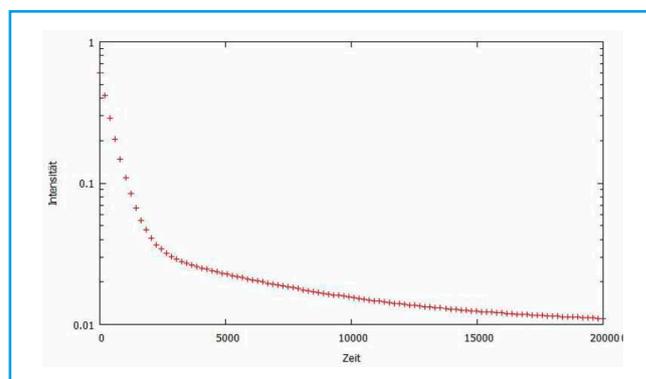


Illustration 4 - Measurement of a sample's decay time

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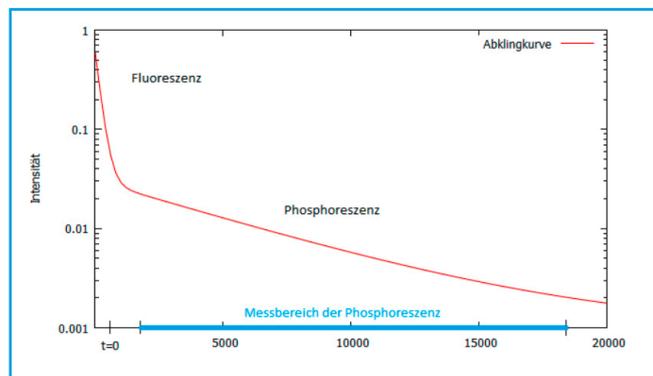


Illustration 5 - Time range of the phosphorescence

The property of the triplet-triplet-annihilation (TTA) of the OLED materials can be determined with a mathematical model from the time dependent course of the phosphorescence. For this, with a fit of the time dependent course of the phosphorescence the impact of the TTA can be determined (see Illustration 6).

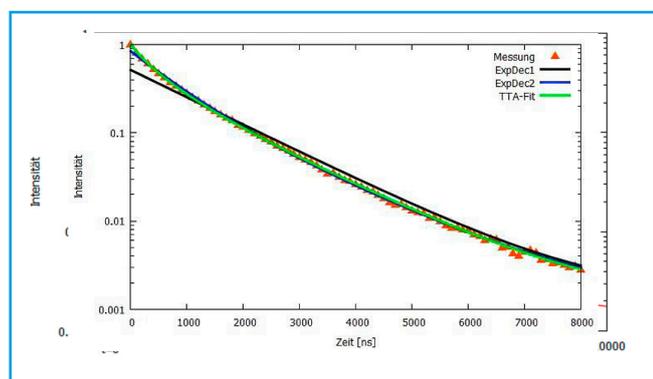


Illustration 6 - Determination of the triplet-triplet-annihilation

As the fluorescence has a disruptive effect on the result of the measurement of low phosphorescent OLED materials, the camera enables a "boxcar" mode, which enables a delay time, so that the quickly disappearing fluorescence is no longer recorded by the camera. After that, the sensor of the camera is exposed until the next laser impulse is present. By this, even spectra of very low phosphorescence can be recorded. Illustration 7 shows three spectra of an OLED material that has been recorded with different delays. The first spectrum (red) was recorded at the time of $t = 0$. It shows the typical fluorescence spectrum of the OLED material. If a delay is set and the spectrum is recorded at a later time of the decay curve, a second peak can be identified. This second peak is the phosphorescence.

However, apart from the phosphorescence a strong fluorescence is emitted, that shows a high decay time. The problem which arises for the measurement of the T1 level of this OLED material is, that the fluorescence spectrum and phosphorescence spectrum partially overlap. As a result of the delay time, in the measurement the intensity of the fluorescence has fallen to such a point that the low phosphorescence can be measured again.

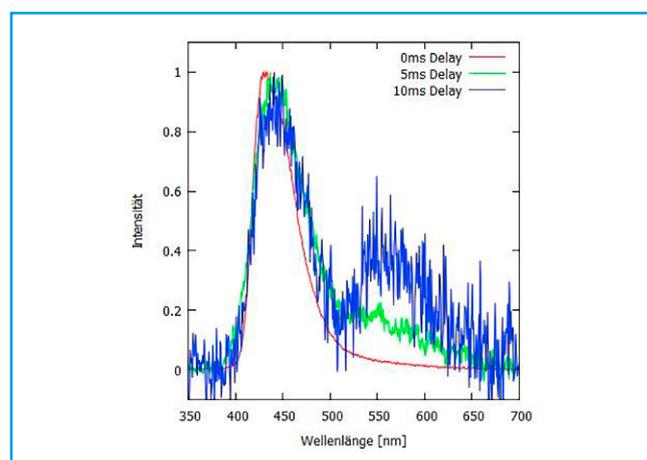


Illustration 7 - Recording of low phosphorescent OLED materials measured with the boxcar mode and different delay times (normalized spectra)

Summarized it can be stated, that the components of Andor can be used to achieve good results when recording emission spectra (even for low phosphorescent samples), decay times in the wavelength range of 350 - 700 nm and in time intervals of nanoseconds up to several seconds. The software puts you in the position to measure and show the temperature dependency of the decay times. In addition, the evaluation of the measured data enables the determination of properties of the OLED materials such as the triplet-triplet-annihilation.

Contact

Sven Brüninghoff
Merck KGaA
Dept. SO-ACP-7
64293 Darmstadt, Germany

Phone +49 6151 72 4719
E-mail sven.brueninghoff@merckgroup.com
www.merckgroup.com