The technological potential offered by organic semiconductors including compatibility with low-cost, large-scale and high throughput deposition methods, as well as a possibility to tune their optical and electronic properties through a chemical synthesis attracts an increasing amount of attention. Organic optoelectronic devices, such as organic light emitting diodes (OLEDs), organic light emitting transistors (OLETs) organic solar cells (OSCs) and sensors, have been extensively studied during the last decades. A number of devices (e.g. OLEDs) is already available on the market and more to be commercialized in the near future, however, there are still many challenges as well as novel materials and device concepts, which require further investigation. Here, timeresolved photoluminescence spectroscopy may be particularly useful as it is a robust technique sensitive to various internal and external factors affecting organic semiconductors. In this thesis, time-resolved photoluminescence spectroscopy measurements are used to study properties and various processes occurring in organic materials and devices.

Time-resolved photoluminescence spectroscopy in combination with exciton diffusion-based Monte Carlo simulations is used to study degradation mechanisms occurring in N,N-di-1-naphthalenyl-N,N-diphenyl [1,1':4',1"'-quaterphenyl]-4,4"'-diamine (4P-NPD) thin films. It is shown that the degradation caused by photo-induced oxidation of 4P-NPD leads to a formation of defect states, which act as fluorescence quenchers. The degradation progress is characterized by means of time-resolved photoluminescence measurements. Monte Carlo simulations based on experimental results show that the defect formation rate decreases as the degradation progresses. This self-inhibiting behavior indicates that the photo-induced oxidation occurs through the excited state of 4P-NPD.

Degradation studies are extended to characterization of 4P-NPD based field-effect transistors. Electrical measurements showed that the photo-induced oxidation of 4P-NPD results in a substantial drop of the transistor performance. It was found that the field-effect hole mobility, the saturation source-drain current and the threshold voltage depends on the photo-induced defect concentration in the similar fashion. Performed studies suggest that the defect states are traps located above the level of the highest occupied molecular orbital. Time-resolved photoluminescence spectroscopy together with electrical measurements is used to investigate the impact of long-lasting electrical stress. It was found that the drop in the transistors performance is caused by the charge trapping, which is caused by charge accumulation rather that charge transport.

Finally, systematic studies on temporal fluorescence characteristics of *para*-hexaphenylene nanofibers grown on three different substrates: muscovite mica, gold and platinum thin films, under various conditions are performed. The substrate strongly affects the fluorescence lifetime as it determines the formation of various fibers polymorphs. The fluorescence lifetime was found to decrease for growth temperatures close to the critical temperature, which indicates cease of the fibers growth. For fibers grown on mica and gold, the lifetime exhibit increases with the nominal film thickness. However, the fibers grown on platinum exhibit a shorter lifetime as the increasing film thickness leads to formation of new polymorphs. Furthermore, it is demonstrated that the transfer process, which is commonly used for integrating the fibers in optoelectronic devices, has no influence on their fluorescence lifetime. The presented results have a great importance for fabrication of nanofibers-based devices. The influence of protective diamond-like coating with on plasmonic interactions in organic-plasmonic hybrid systems (organic nanofibers on top of the gold nanosquare arrays) is studied for various coating thicknesses. Time-resolved photoluminescence spectroscopy is used to investigate exciton-to-plasmon coupling, which can be considered as an additional loss channels for photoluminescence from organic nanofibers.

Preservation of a plasmonic field-enhancement induced by gold nanosquare arrays is, then, characterized by means of Finite-Difference Time-Domain simulations and second harmonic mapping. Performed measurements reveal that plasmonic interactions are preserved for film thicknesses up to 55 nm.