1 Introduction

Nanotechnology is the exciting field of research dealing with objects smaller than approximately 100 nm. On this scale, matter can display phenomena not encountered on a macroscopic scale. Many such aspects involve the electronic properties of materials and their interaction with light. Photophysics describes the investigation of these interactions.

This thesis is separated into five chapters of experimental work. To allow for properly understanding them, the relevant material classes carbon nanotubes (CNTs), colloidal quantum dots (CQDs) and conjugated polymers will be introduced in Chapter 2. The two former are prime examples for nanoscale objects, in which the limited size confines the free motion of charge carriers and thereby leads to the emergence of surprising features. In colloidal quantum dots, for example, carriers are confined in all three spatial dimensions, which is why these objects are often referred to as zero-dimensional. Assembling such CQDs in films can give rise to matter with remarkable properties: optically behaving like isolated CQDs and electrically almost like a bulk crystal.

In CNTs, charge carriers move freely in one direction, but are confined in the remaining two. These objects are consequently referred to as being one-dimensional. This, again, has a profound effect on the properties of the material. Carriers encounter hardly any resistance when moving longitudinally to the tube axis, but are confined within the narrow diameter of these tubes. One-dimensional semiconductors also give rise to narrow optical transitions, found in the near infrared spectral region, in case of CNTs.

Conjugated polymers and organic molecules attract considerable attention in the research community for applications in flexible electronics. Fabrication and eventual commercialisation of opto-electronic products, such as solar cells, photodetectors or light emitting devices, is one major aspect driving research on these three material classes. In order to successfully apply them, though, the photophysical processes occurring in single materials or in blends and at their interfaces need to be properly understood.

Their interaction is here investigated with several optical techniques – mostly in the infrared region of the electromagnetic spectrum. Chapter 3 is thus devoted to explaining basic concepts of these techniques, as well as the specific set-ups used in this thesis. Most prominently, photoluminescence- (PL) and photoinduced absorption (PIA) spectroscopy will be discussed, as these are the main tools of investigation. A special focus is devoted to the introduction of the Fourier
transform infrared (FTIR) spectrometer technique, since this method is rarely employed within this field of research. Often, spectroscopic studies are limited to the near infrared (NIR) spectral region, down to 1.1 or 0.55 eV, depending on the detector material. Using FTIR spectroscopy, processes at low energy (few tens of meV), in the mid infrared (MIR) spectral region, can easily be monitored and considerably improve the understanding of light-matter interaction in the systems discussed herein.

This MIR PIA technique is then used to more closely examine the spectral signatures of charge carriers in donor-acceptor polymers in Chapter 4. By comparing the similar polymers C-PCPDTBT and Si-PCPDTBT and their blends with PCBM, differences and similarities are investigated. Using density functional theory (DFT) simulations, it is shown that the PIA signatures in the MIR are due to positive polarons on the polymer. This examination adds to the previously existing literature on similar experiments for homopolymers. The concept of intra- and interchain delocalisation of polarons is finally invoked to explain the PIA at lowest energy, as previously observed for P3HT. It is shown, though, that instead of an extended crystallinity, the partial alignment of neighbouring chains already gives rise to these transitions.

In Chapter 5 the working mechanism of a ternary blend comprising two conjugated polymers with PC_{70}BM leading to a high power conversion efficiency (PCE) in solar cells is investigated. Contrary to the expectations from the bulk energy levels of the components, this system does not work as an energy cascade, but is governed by an efficient energy transfer from the crystalline wider band gap polythiophene to the narrow band gap donor-acceptor polymer. The energy transfer is observed \textit{via} a delayed maximum in PL intensity of the latter. It is furthermore observed that the former, despite its supposedly lower lying HOMO level, acts as the hole transporting polymer in the ternary blend.

Based on the discoveries reported in Chapters 4 and 5, the photophysical behaviour of polymer wrapped semiconducting single walled carbon nanotubes is investigated in Chapter 6. Even when exciting this composite material at an energy below the polymer band gap, polymer polarons can be monitored in the MIR spectral region. This surprising observation is a clear indication that the two materials act as a single hybrid. Additional quantum chemical calculations indeed reveal states to be partially shared between the polymers and the CNTs.

The excited states interaction of a narrow band gap polymer with lead sulphide colloidal quantum dots (CQDs) is investigated in Chapter 7. These materials exhibit a complementary absorption, thus seem to be prime candidates for hybrid photovoltaics. A favourable charge transfer interaction is observed if the long insulating ligands capping the CQDs after synthesis are exchanged for shorter entities. Despite this promising observation, fabricated solar cells, suffer from hampered charge carrier transport through an unfavourable microstructure and consequently exhibit a poor performance.
The last experimental Chapter is devoted to the investigation of trap states in PbS colloidal quantum dots. These nanocrystals exhibit two distinct trap distributions below 0.5 eV. Their energy increases for smaller CQDs but is shown to be independent of the surface ligands. The ligand exchange from native oleic acid to shorter entities, however, leads to a significant increase in PIA signal. Fano resonances are furthermore observed between the broad trap-related absorption bands and the vibrational modes associated with the surface ligands.

These investigations help to develop a deeper understanding of excited states and their interaction in different materials relevant for opto-electronic applications. The MIR PIA technique, in particular, allows for accessing information beyond reach for more commonly employed techniques. Its power is shown here by investigating vastly different aspects ranging from the identification of polymers through their vibrational fingerprints, deduction of information about the environment of charge carriers as well as polymer chain alignment or the monitoring of surface trap states in colloidal quantum dots. With its versatility proven, this thesis also aims at a popularisation of this technique.