Summary

Charge transfer plays a central role in many photoinduced processes in physics, chemistry, and biology. It is also key to the photon-to-charge conversion process in organic photovoltaic (OPV) systems, which find more and more widespread use. Unlike their conventional inorganic counterparts, this class of photovoltaic systems compulsorily includes organic conjugated conductive molecules. The conjugated materials, usually used as an active layer in OPVs, are chemical structures which are coupled through the π-orbitals leading to a delocalization of charges over the bonds participating in the conjugation. Usage of the organic materials determines the strong and weak points of the OPVs. The main advantages of using organic molecules are potentially low production cost in large volumes and solution processability. In addition, OPVs are relatively flexible and lightweight, and are thus very convenient for portable applications. On the other hand, the main weakness concerns mainly the relatively low conversion efficiency (up-to-date around 12%), and limited photostability in comparison to their inorganic analogues. In this work, we present a number of studies dedicated to charge photogeneration and charge transfer processes in novel conjugated systems. We focus on revealing the charge photogeneration efficiency and clarifying the intermolecular (between different molecules) and intramolecular (within one molecule) charge transfer processes that form the crucial initial steps in the energy conversion process in OPV devices.

Since charge transfer occurs on an ultrafast timescale, \textit{i.e.} faster than $10^{-10}$ s, it requires an experimental tool suitable to monitor the relevant processes with an adequate time resolution. In our studies the dynamics of generation and recombination of photoinduced charges are studied using ultrafast visible-pump – IR-probe photo induced absorption (PIA) spectroscopy, which allows monitoring the time evolution of photoinduced charges. The method is based on the fact that photoinduced charge (a hole) created on a polymer molecule creates absorption bands in the IR range in the polymer bandgap. In the PIA technique, two pulses are applied: the first one photogenerates the charges and the second one probes the charge concentration by monitoring induced IR absorption that is proportional to the amount of holes at the conjugated molecule. This technique is applied to a
variety of blends of conjugated polymers and organic acceptors, which represent different classes of conjugated systems.

Our investigations start with a study of the charge recombination dynamics in ground state charge-transfer complexes (CTCs) formed between an archetypical conjugated polymer donor MEH-PPV and a family of small molecular acceptors (Chapter 2). One of the reasons why the polymer-based ground state CTCs are important is that they can be beneficial for the OPVs. CTCs (which energy is within the polymer band gap) can extend the spectral absorption range up to 1 µm, thereby improving the absorption overlap with the solar spectrum. In addition it has been shown that their presence leads to an increased photooxidation stability of OPV devices. To reveal which parameters govern the charge recombination rates for CTC forming donor-acceptor systems, we vary the electron affinities (EAs) of fluorine based acceptors by changing the attached functional electron withdrawing groups (cyano, nitro, and carbonyl), thereby systematically modifying the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) energies of the acceptors. Clear signatures of CTC formation in the polymer-acceptor blends have been found in both the optical absorption spectra of the blends, which showed the formation of a clear wing red-shifted relative to the polymer main HOMO-LUMO transition, as well as in vibrational Raman spectroscopy. Acceptor-to-polymer recombination rates, obtained from ultrafast Visible-IR PIA spectroscopy, exhibit an exponential scaling with the acceptor EA with parameters that are similar to those reported earlier for small-molecule CTCs. From the ultrafast studies presented we arrive at the following conclusion: It is well established that increasing the acceptor EA increases the driving force for efficient exciton dissociation. Inevitably, however, increasing the acceptor EA simultaneously enhances unwanted recombination due to formation of the CTCs. Therefore, in order to improve the efficiency of photovoltaic devices, one should carefully balance these two competing processes.

Continuing the topic of the ground-state CTCs, in Chapter 3 we perform studies of push-pull polymers which recently attracted considerable attention as acceptor polymers in OPV applications. These polymers feature the formation of a state which one could call an intramolecular (intrapolymer) ground-state CTC. Even though relatively high efficiencies have been demonstrated for devices based on these push-pull polymers, little knowledge exists on the initial steps of charge generation in these materials. To extend our knowledge in this direction we
perform a set of experiments aiming to elucidate the intermolecular and intramolecular charge transfer processes following photon absorption. For this, we use blends of phenyl-C71-butyric-acid-methyl ester ([70]PCBM) with two contemporary push-pull polymers: poly[N-9”-heptadecanyl-2,7-carbazole-alt-5,5-(4’,7’-di-2-thienyl-2’,1’,3’-benzothiadiazole)] (PCDTBT) and benzo-[1,2-b:3,4-b’:5,6-d”] trithiophene-diketopyrrolopyrrole (BTT-DPP). These particular model systems are chosen for their different donor-acceptor LUMO energy level offsets in order to separate the intermolecular and intramolecular charge transfer processes. The results presented in this work demonstrate that the interplay between the intramolecular (i.e. within the polymer) and intermolecular (i.e. between the polymer and fullerene) charge transfer processes, is governed by the value of the LUMO energy offset. Hence, in a broader context, our findings show the importance of an effective intermolecular charge transfer process for efficient photogeneration of charges in OPVs, in line with the in the literature reported power conversion efficiencies (PCE) of the studied systems.

In Chapter 4 we focus on excited state CTCs, and in particular on the role of the so-called “hot” states in charge generation in OPV blends. The influence of the driving energy and the degree of delocalization of interfacial charge transfer states on the charge separation process in OPVs are studied in this chapter. For this investigation we use a variety of well-known conjugated macromolecules as electron donors and/or acceptors. In addition to the normal PIA experiments as used in the previous chapters, we also use a novel optical pump-push-probe experiment. The main difference of this method is the application of an additional push pulse in between the pump and probe. This pulse excites the interfacial charge transfer state created by the initial pump pulse, thereby deliberately generating a hot state which subsequentially may charge separate into free charges. In addition, we use a further modification of this technique, where the probe pulse was replaced by a measurement of the optically induced changes in the photocurrent as function of the delay between pump and push pulses. The main advantage of the latter technique, which is performed on actual OPV devices, is that it allows for a direct measurement of the photo-induced current, which is one of the main parameters of OPV device efficiency. Our results demonstrate that delocalised band states are critical for long-range charge separation in organic photovoltaic cells. Even though these are typically short-lived (<1 ps), they enable charges to overcome the otherwise dominant Coulomb interaction, and hence
make the charge separation process more efficient. Therefore, we conclude that the delocalization of the hot state plays an important role in the charge separation efficiency in the OPVs.

Finally, Chapter 5 is dedicated to the study of the charge transfer dynamics in donor:acceptor blends based on another class of novel conjugated systems, small star-shaped molecules. These molecules have a great potential for small molecule based OPVs, where it is possible to combine the advantages of polymer solar cells with all the benefits of small molecules. We study several star-shaped donors, which differ from each other by the length of the alkyl end group and by the length of the conjugated arms. Our findings show that the star-shaped small molecules indeed provide long-lived charge separation in the blends with [70]PCBM, which makes them perspective materials for use as a donor counterpart in organic solar cells.

Using a variety of ground- and excited-state spectroscopies we reveal and study a diversity of important physical phenomena occurring during the photon-to-charge conversion process in OPV materials. The results described in this thesis provide a detailed insight into some of the key parameters determining the efficiency of the conversion process and may serve as guidance for further optimization of the efficiency of OPV devices.