



Charge transport and transfer processes in CuInS_2 nanocrystal-based hybrid solar cells

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Abstract

Colloidally synthesized CIS NCs are investigated in this work for their charge transport and charge transfer properties. By post-synthesis removal and replacement of the different types of ligands surrounding the CIS NCs, these properties can be enhanced - especially by a combination of successive solution-phase and post-deposition ligand exchanges -, which is derived from results obtained by measurements in combination with different polymers as active layer blends for BHJ solar cells. An investigation of the charge carrier transport in the CIS NCs by single carrier devices shows a three orders of magnitude larger hole than electron mobility. Regarding the polymers used for the CIS NCs blends, P3HT exhibits generally favorable properties compared to PCPDTBT, such as effective charge transfer processes and more efficient solar cell performances.

Kurzfassung

Kolloidal synthetisiert CIS NCs werden in dieser Arbeit für ihre Ladungstransport und Ladungstransfer -Eigenschaften untersucht. Durch die nach der Synthese Ausbau und Austausch der verschiedenen Arten von Liganden, um die CIS- NCs können diese Objekte gefunden verbessert werden - vor allem durch eine Kombination von aufeinander folgenden Lösungsphase und nach der Abscheidung Ligandenaustausch-, die aus den Ergebnissen von Messungen erhalten ableitet in Kombination mit verschiedenen Polymeren als aktive Schicht Mischungen für BHJ -Solarzellen. Eine Untersuchung der Ladungsträgertransport in der CIS- NCs durch einzelne Trägervorrichtungen zeigt eine drei Größenordnungen größeres Loch als Elektronenmobilität. In Bezug auf die für die CIS- NCs Mischungen verwendeten Polymere zeigt P3HT allgemein günstige Eigenschaften im Vergleich zu PCPDTBT wie effektive Ladungstransferprozesse und effizientere Solarzellen- Performances.

For my family

My little angels, Rizka & Annisa

He is the Lord of the two easts and the Lord of the two wests. Then which of the Blessings of your Lord will you both deny?. He has let loosed the two seas meeting together. Between them is a barrier which none of them can transgress. Then which of the Blessings of your Lord will you both deny?.

(Holy Quran, QS. 55:17-21)

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Chapter 1

Introduction

1.1 Background and motivation

The research and development on different kinds of solar cells can be divided into three generations: (i) the p-n junction solar cells, (ii) the thin films solar cells, and (iii) the solution-processed solar cells. The first generation of p-n junction solar cells exhibit high efficiencies but suffer from high production cost. The second generation of thin film solar cells, on the other hand, is more cost-effective but has lower efficiencies than the first generation. Here, the third generation of solution-processed solar cells combines the advantages of p-n junction with those of the thin-film solar cells, namely high efficiencies as well as low production costs (for example with the rapid roll-to-roll printing method).

One example for solution-processed solar cells are organic bulk heterojunction (BHJ) solar cells, of which three types of polymer-based solar cells exist: (i) polymer-fullerene blends, (ii) polymer-polymer blends, and (iii) polymer-nanocrystal blends. Polymer-fullerenes BHJ solar cells have easily tuneable bandgaps but poor absorption in the solar spectrum range. Solution-processed polymer-nanocrystal BHJ solar cells - better known as hybrid solar cells - have gained much attention in the scientific research because of their unique combination of polymer, organic semiconductor as well as inorganic

semiconducting colloidal nanocrystal properties. Here, colloidal nanocrystals offer advantages concerning the stability, a higher dielectric constant, a wider optical absorption range (extending into the near infrared (NIR) region), a good processability in solution as well as a possibility of combination with organic semiconductors, such as conjugated polymers. Hence, both the inorganic and the organic materials can be processed from the same solvent for the fabrication of hybrid BHJ solar cells.

A wide variety of organic/inorganic solar cells based on colloidal nanocrystals (NCs), such as CdS [17–22], CdSe [23–32], CdTe [33–35], PbS [36–41], PbSe [42], TiO₂ [43–46], and ZnO [13, 47–54], have been fabricated. In combination with conjugated polymers, Dayal *et al.* [24] reported a high power conversion efficiency (PCE) of 3.13% in the CdSe nanotetrapods in combination with a low band gap polymer. Most recently, the highest PCE of BHJ solar cells based on CdSe was reported to be 4.7% [31]. With alloys of PbS and PbSe, PCEs up to 5.5% have been achieved [42]. A major drawback of the Cd- and Pb-based material systems, which currently achieve the largest efficiencies, however, is their toxicity, which motivates research on more environmentally friendly (Cd- and Pb-free) materials. Here, one of the candidates is nanocrystalline copper indium disulfide (CuInS₂, CIS), which is already in use as absorber materials for thin film solar cells [55]. A recent study by Chen *et al.* [56] points to a high chemical stability and low cytotoxicity of colloidal CIS NCs. CIS NCs are used in combination with a semiconducting polymer in the absorber layer of hybrid bulk heterojunction (BHJ) solar cells, in order to form the so-called donor/acceptor system [32, 57, 58]. Several studies on hybrid solar cells with CIS NCs synthesized using a colloidal approach report comparable PCE of 0.1% to 0.6% [55, 59–62]. A better device performance with a PCE of up to 2.8% was achieved with CIS/polymer hybrid solar cells, where the CIS phase was synthesized via an in situ process in the polymer without using additional organic ligands [63]. Despite the better performance of this solar cells, the nanoparticle synthesis in this approach is dependent on the polymer, which adds difficulties in control over the size and shape of the CIS NCs as well as that of the morphology of the blends. These issues limit the applicability of a nanoparticle synthesis by the in situ approach, as the performance of excitonic solar cells is among others critically influenced by the charge transport, charge generation and the transfer at donor/acceptor interfaces, which are in turn influenced by the sizes and shapes of the CIS NCs as well as the morphologies of the blends used for the setup.

In hybrid solar cell devices, the surfaces of the nanocrystals play a highly influential role on the charge transfer from polymer to nanocrystals, and thus the power conversion

efficiencies of the solar cells. The surface of a nanocrystal is typically capped by organic ligands which ensures solubility and passivates the surface electronically. These organic ligands surrounding the nanocrystal play an important role both during the synthesis of nanoparticles and alternating contact between nanocrystals and polymer in hybrid solar cells. Hence it is possible to control the charge transfer between polymer and nanocrystal, and from nanocrystal to nanocrystal by the careful selection of ligands [64]. Therefore, one major strategy for improving the performance of hybrid solar cells is the surface modification of nanocrystals [65–71].

1.2 Outline of the thesis

In this work, the charge transport and transfer processes in hybrid solar cells based on colloidally synthesized CIS NCs and different organic semiconducting polymers are investigated. The kind of organic ligands surrounding the CIS NCs after the synthesis as well as their removal and replacement by other ligands are investigated for a discussion of the effect of the ligand capping on the transfer processes.

The fundamental research on hybrid solar cells based on colloidal nanocrystals and semiconducting polymers is reviewed in Chapter 2. Furthermore, the basics of solar cells including light absorption processes are presented as well as fundamental concepts of bulk heterojunction (BHJ) solar cells and the current-voltage characteristics. An introduction to the principle of light harvesting of hybrid solar cells is given along with the theory for the determination of charge transport properties and the photophysical processes included in the charge and energy transfers of hybrid systems.

Chapter 3 gives the details of the characterization methods used in this work as well as the materials used for the active layers of the BHJ solar cells and the device preparation.

In Chapter 4 the ligand shells of the as-prepared CIS NCs as well as those of the CIS NCs after solution ligand exchange with two different ligands, namely hexanethiol and pyridine are discussed based on simultaneous TGA/DSC and gas phase FTIR measurements.

Chapter 5 investigates the charge transport characteristics in thin films of CIS NCs by using single carrier device structures, namely hole-only (HO) and electron-only (EO) devices. A comparison to HO devices based on P3HT is drawn.

A systematic study of charge transfer as an elemental step involved in the energy conversion process of CIS NCs-based solar cells is presented in Chapter 6. Here, the excited state properties and the processes of charge transfer in CIS NCs/polymer composites are studied by quasi-steady state photoinduced absorption (PIA) and steady state as well as time-resolved photoluminescence (PL) spectroscopy. The two investigated composites are CIS NCs in combination with poly(3-hexylthiophene) (P3HT) and poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT), respectively.

The effect of the CIS NCs ligand shell and subsequent ligand exchanges on charge transfer processes in CIS NCs/P3HT-based solar cells is discussed in Chapter 7. Here, CIS NCs are investigated after two different kinds of ligand exchange processes, namely solution phase-ligand and post-deposition ligand exchange. For the latter process the results obtained for ligand exchange with 1,4-benzenedithiol is also discussed. The effect of combined solution-phase and post-deposition ligand exchange by pyridine and 1,4-benzenedithiol on the solar cell performances and charge transfer are studied.

Furthermore, the charge separation and transfer processes before and after post-deposition ligand exchange in a PbS/P3HT blend are discussed for a general comparison.

Chapter 8 summarizes the major findings of this work in combination with a conclusion and recommendations for possible future work on this topic.

Chapter 2

Fundamentals

This chapter offers a brief introduction for bulk heterojunction solar cells and their current-voltage characteristics. The basic principle of light harvesting by hybrid solar cells will be reviewed as well as the theoretical background for the determination of charge transport properties and photophysical processes included in the charge and energy transfers in hybrid systems.

2.1 Bulk heterojunction solar cells

The two types of heterojunctions mainly used in the research and development of organic and hybrid solar cells are (i) multilayer structures and (ii) bulk heterojunction. Whereas, multilayer structures are fabricated by layer by layer deposition of the semiconductor material, bulk heterojunctions are obtained by mixing two semiconducting materials in the common solvents and subsequently depositing the mixture on top of a conductive glass substrate, such as indium tin oxide (ITO). The latter method provides the advantage that the mixing of the two semiconducting materials in the same solvent results in a reduction of the electron pathways between those two materials.

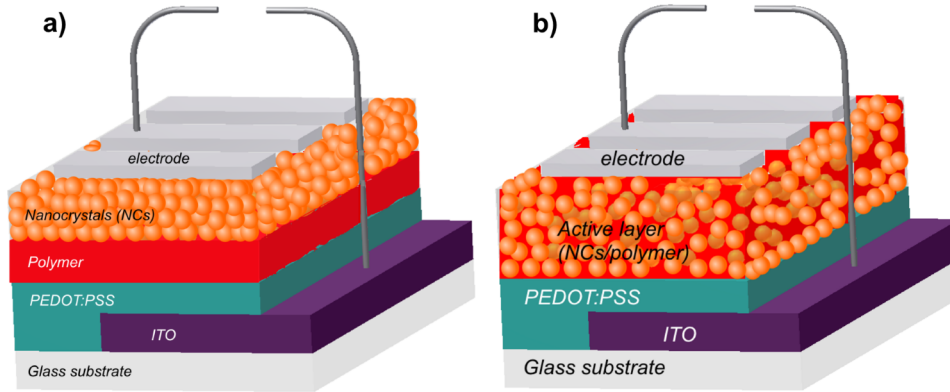


Figure 2.1: Schemes of (a) multilayer structure and (b) bulk heterojunction hybrid solar cell devices

The principle of light harvesting in BHJ hybrid solar cells after photon absorption in the NCs is depicted schematically in Fig. 2.2. (the photon absorption of polymers is neglected for clarity).

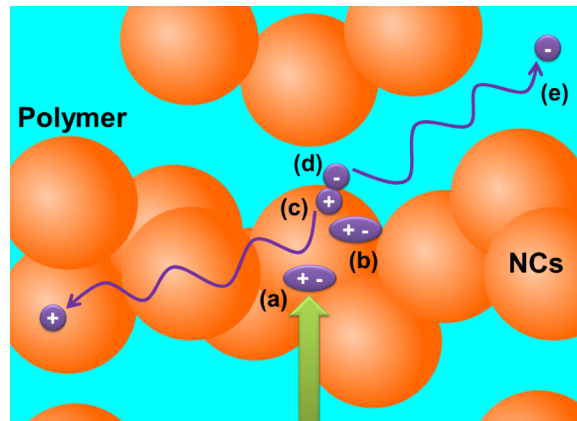


Figure 2.2: Schematic illustration of the consecutive light harvesting processes inside the active layers of BHJ hybrid solar cells: (a) Exciton generation by light absorption; (b) exciton diffusion; (c) charge transfer at the NCs/polymer interface; (d) dissociation and separation of the charge carrier pair and (e) charge carrier transport to electrode.

In the active layer of the solar cells six successive processes take place: (a) the absorption of a photon resulting in the creation of an exciton (i.e., a bound electron-hole pair); for a sufficient creation of excitons the absorption energy has to be well-matched with the solar spectrum; (b) exciton diffusion to NCs/polymer interfaces; (c) charge transfer from

NCs to the polymer interface; the charge transfer (CT) state is created when excitons arrive at the donor-acceptor interface within the exciton diffusion length; in the CT state a geminate recombination of excitons is possible, which has a crucial influence on the performance of solar cells [40]; (d) the dissociation of the exciton and the separation of the carrier pair into free charge carriers; the energy levels of the NCs and the polymer have to be properly aligned for the electron and hole to overcome their binding energy and be able to separate; (e) charge carrier transport to the corresponding electrodes percolating pathways; (f) collection of the charge carriers by the electrodes. A possibility, however, is that the charge carriers might decay via non-geminate recombination during their transport to the electrodes.

2.2 Characterization of solar cells

2.2.1 Space charge-limited current (SCLC)

One method for determining the charge carrier mobility in NCs is by measuring the current-voltage (J - V) characteristic of single carrier devices in the absence of light illumination. In these devices, the dielectric layer is sandwiched between two electrodes. In general, by a proper selection of the electrode materials (depending on their work functions) the device can be built to be a hole-only (HO), electron-only (EO) or bipolar device. The HO devices are basically built of a semiconductor film placed between high work function electrodes as illustrated in Fig. 2.3(a). The purpose is that only the holes in the HOMO (or valence band) are transported to the electrode, whereas the electron transport is suppressed. EO devices (see Fig. 2.3(b)), on the other hand, are constructed by sandwiching the semiconductor film between low work function electrodes, so that only electrons in the LUMO (conduction band) are transported in the device and the hole transport is suppressed. The space charge region is formed by the injection of charge carriers from the electrode resulting in a non-uniform charge density along the film thickness. The space charge-limited current is obtained due to the presence of the space charge region.

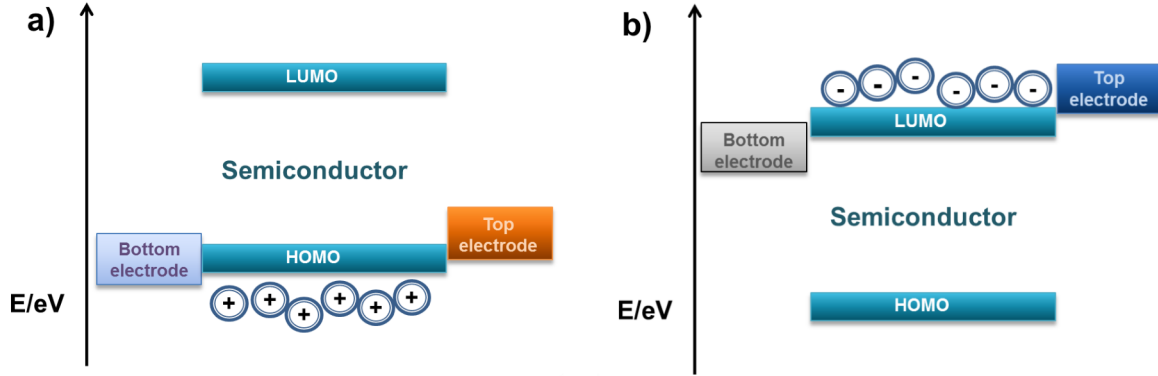


Figure 2.3: Energy diagram scheme of HOMO and LUMO levels of semiconductor and work function of the electrodes used in (a) HO and (b) EO devices.

In general, the charge transport in bulk-limited devices can be described by theories of space charge-limited currents (SCLC), such as the Mott-Gurney model [72] and Murgatroyd's model [1]. The space charge-limited current model to describe the current-voltage relation for a metal-insulator-metal system was first introduced by Mott and Gurney. The Mott-Gurney model describes space charge-limited currents with field-independent mobility. In that case, the current density depends on the voltage as described by the following relationship:

$$J_{SCLC} = \frac{9}{8} \epsilon_0 \epsilon_r \mu \frac{V^2}{d^3} \quad (2.1)$$

with the vacuum and the relative permittivity of the dielectric ϵ_0 and ϵ_r the charge carrier mobility μ , the voltage V , and the film thickness d . For the devices with different work functions of the electrodes, the applied voltage (V_{appl}) needs to be corrected by the built-in voltage V_{bi} , and the voltage drop across the series resistance of the substates V_{RS} [73–75].

$$V = V_{appl} - V_{bi} - V_{RS} \quad (2.2)$$

In the presence of the electric field effect, the Mott-Gurney model was later modified by including the Poole-Frenkel model. This model describes the effect of a decrease of the Coulombic potential barrier resulting from an interaction with the electric field (see Fig.

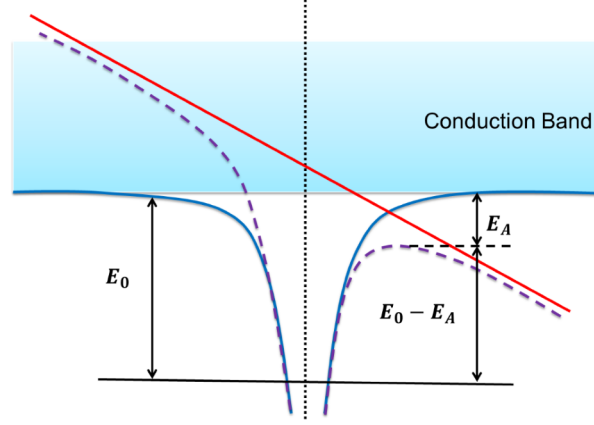


Figure 2.4: Illustration of the Poole-Frenkel effect, reproduced after [1]

2.4). In the presence of the electric field, the Coulomb barrier, E_0 , is decreased by E_A (the so-called Poole-Frenkel effect).

Murgatroyd's model includes the dependency of the SCLC on the electric field as a result of the Poole-Frenkel effect in the device. Equation (2.3) describes the current density according to Murgatroyd's model [1]:

$$J_{SCLC} = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{d^3} \exp \left(0.891 \gamma \sqrt{\frac{V}{d}} \right) \quad (2.3)$$

with the field activation factor γ and the zero-field mobility μ_0 . The field-dependent mobility $\mu(F)$ is then given by:

$$\mu(F) = \mu_0 \exp \left(\gamma \sqrt{F} \right) \quad (2.4)$$

with $F = V/d$. According to Ref. [1] γ can be analytically be expressed as $\gamma = \left\{ \frac{1}{kT} \left(\frac{q^3}{\pi \varepsilon_0 \varepsilon_r} \right)^{\frac{1}{2}} \right\}$, so that Eq. (2.3) becomes:

$$J_{SCLC} = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{d^3} \exp \left\{ \frac{0.891}{kT} \left(\frac{q^3 V}{\pi \varepsilon_0 \varepsilon_r d} \right)^{\frac{1}{2}} \right\} \quad (2.5)$$

2.2.2 Electrical characterization under illumination

The characteristics of the performance of the solar cells are determined by performing a current-voltage measurement in dark and under illumination. Figure 2.5 shows the typical current-voltage (J - V) characteristics of a solar cell in the dark and under illumination.

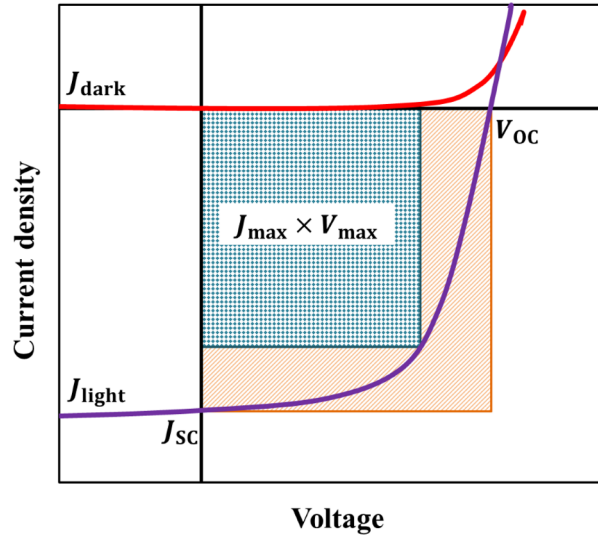


Figure 2.5: J-V characteristics of bulk heterojunction solar cell in the dark and under illumination conditions.

The dark current shows the diode characteristic of a solar cells. On the other hand, under illumination, the open circuit voltage (V_{oc}) and the short circuit current (J_{sc}) are available when the photovoltage and the photocurrent reached when the terminals are isolated or connected together. The power density of the solar cells can be determined by:

$$P = J \times V \quad (2.6)$$

With the maximum power: $P_{max} = J_{max} \times V_{max}$. The fill factor (FF) of the solar cell is defined as the ratio between the maximum power and the cells power density

$$FF = \frac{J_{max} \times V_{max}}{J_{sc} \times V_{oc}} \quad (2.7)$$

The power conversion efficiency (PCE, η) of the solar cells, which is defined as the percentage of input power converted to maximum output power, as follow

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \quad (2.8)$$

2.3 Photophysical process

Optical probes, such as time-resolved spectroscopy and in particular pump-probe spectroscopy, are very powerful tools for the study of charge generation and recombination dynamics as well as that of the general picture of the photophysical processes.

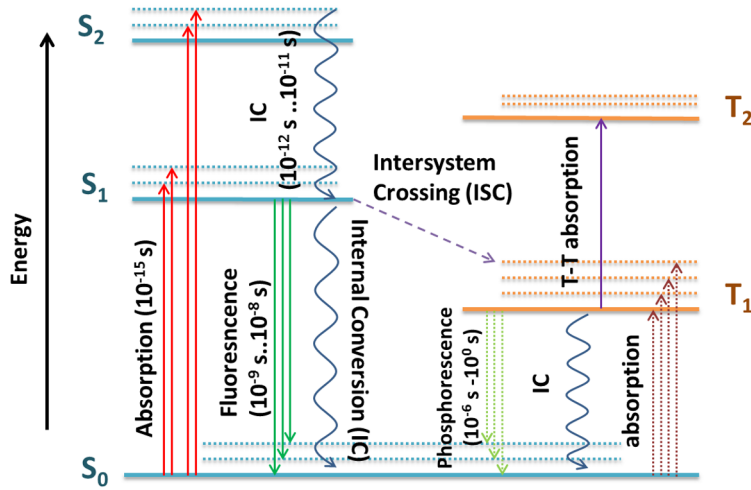


Figure 2.6: Jablonski diagram with singlet (S) and triplet (T) manifolds. Solid arrows: optical transition, dashed arrows: intersystem crossing (ISC), squiggly arrows: internal conversion (IC). Scheme redrawn after [2].

Upon photon absorption, electrons are excited to an unoccupied excited state, which can result in different effects and processes on different energy levels and time scales. Upon excitation by electrons, bound electron-hole pairs - the so-called excitons - are formed. These excitons are localized on one molecule with a binding energy of about 0.3 eV to 1 eV. The energy levels of excited states and the possible transitions are depicted in the Jablonski diagram shown in Fig. 2.6. In general, the ground state (S_0) has fully occupied

orbitals, and thus a multiplicity of 1 with a total spin of zero. The excited states are classified as either singlets (S) or triplets (T) by their respective multiplicities. The triplet state has a multiplicity of 3 with a total spin of one. In Fig. 2.6, the red arrows represent the absorption of photons, which result in the electron excitation from the S_0 to an excited state (S_1 , S_2 , ...). Subsequently, light is emitted in the form of radiative (fluorescence, $S_1 \rightarrow S_0 + h\nu_F$, green arrows) or non-radiative transition (internal conversion (IC), squiggly arrows) [2]. The first excited state (S_1) has a typical lifetime in the range of 1-10 ns. As the triplet states usually have lower energies than the singlet excited states, electrons can move from the singlet to the triplet states via intersystem crossing (ISC). Because this so-called singlet-triplet transition is spin-forbidden, the probability of an ISC caused by spin-orbital coupling is small. The typical lifetime of electrons in the triplet states is in the range of μ s-ms. Here, the relaxation to the ground state can take place either via radiative (phosphorescence, $T_1 \rightarrow S_0 + h\nu_P$, dotted green arrows) and/or via non-radiative decay (IC, squiggly arrows). The IC from the higher singlet to lower singlet excited states, or higher triplet to lower triplet states takes place in a time scale of fs to tens of ps. The binding energy of singlet excitons is about 0.3 eV to 0.5 eV, whereas those of triplet excitons are larger, which is due to the the same spin orientations and thus an attraction interaction.

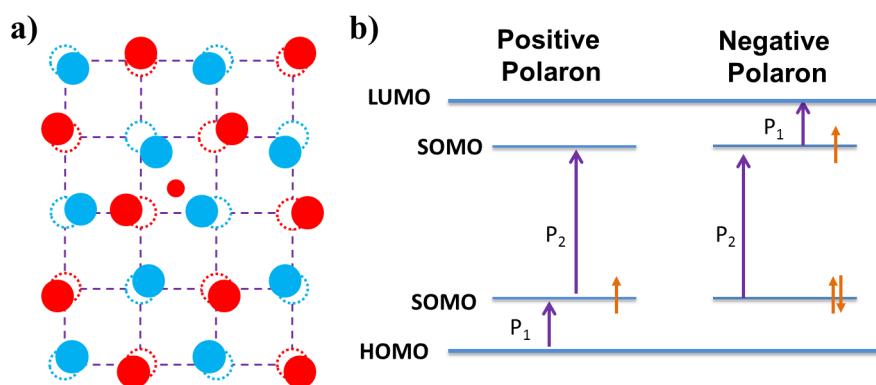


Figure 2.7: (a) Schematic illustration of a polaron: a negatively charged particle attracts positive ions (blue circles) and repels negative ions (red circles), which leads to displacements of the surroundings in the structure lattice; (b) energy level diagram of the electronic transitions in polarons [3–5].

In a donor-acceptor system, the excitons in the first excited state (S_1) can undergo transformation to the CT state. A dissociation of CT states results in the creation of

free charges (i.e., a free electron and/or hole), which in turn leads to a distortion of the surrounding geometry. This distortion of the surrounding geometry together with the electron (or hole) forms a quasi-particle, the so-called polarons (see schematic illustration in Fig. 2.7(a)). In organic semiconductors, the energy levels of polarons (known as single occupied molecular orbitals (SOMO)) are positioned between the organic HOMO and LUMO levels (see energy diagram in Fig. 2.7(b)) [3–5].

2.4 Energy and charge transfer

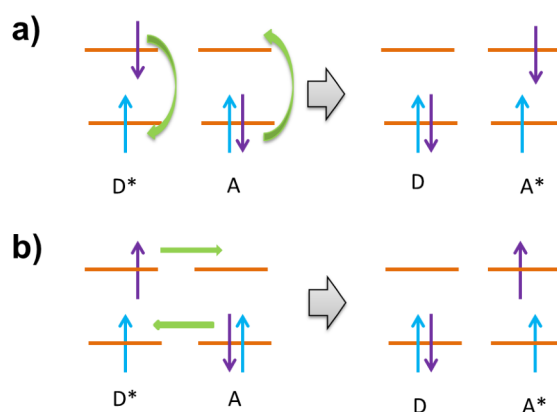


Figure 2.8: Scheme of (a) Förster and (b) Dexter energy transfer

In donor-acceptor systems, energy transfers can be classified by two models, namely the Förster (dipole-dipole) and the Dexter (electron exchange) mechanisms, which are schematically depicted in Fig. 2.8. The Förster energy transfer (see Fig. 2.8(a)), also known as Förster resonance energy transfer (FRET), is an energy transfer process between a donor and an acceptor by non-radiative dipole-dipole coupling. In donors, this process results in the relaxation of an electron from an excited state back to the ground state in donor, whereas in acceptors, the excitation of an electron to an excited state takes place. Therefore, for the FRET mechanism to take place an overlap between the acceptor absorption wavelength and the donor emission wavelength is required. The FRET model is often used to describe singlet energy transfers. However, the electron in the triplet state can also undergo relaxation to the ground state via phosphorescence by the FRET mechanism. The other energy transfer mechanism according to the Dexter

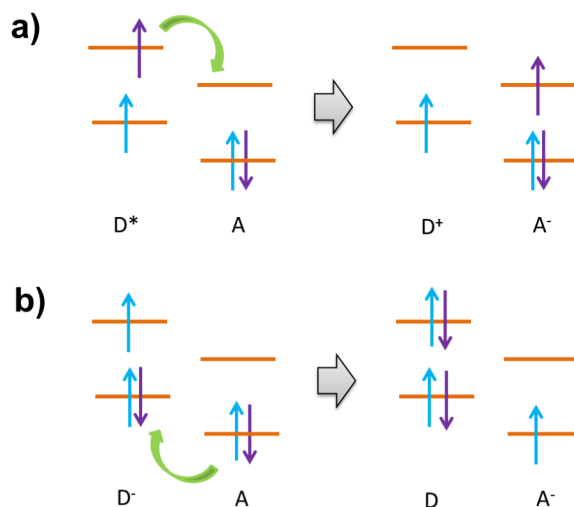


Figure 2.9: Scheme of (a) electron and (b) hole transfer

energy transfer model is usually found for triplet-triplet energy transfers. As shown in Fig. 2.8(b) this energy transfer mechanism involves an exchange of electrons between donor and acceptor.

For the charge transfer processes to take place the energy levels of the donors and acceptors have to be well-aligned (see Fig. 2.9). An electron transfer is possible, when the LUMO energy of the donor is higher than the LUMO of the acceptor (see Fig. 2.9(a)). Hole transfers, on the other hand, (see Fig. 2.9(b)) can occur, when the HOMO energy of the donor is higher than the HOMO of the acceptor. Whereas there is a possibility for the occurrence electron transfers in type I as well as type II heterojunction solar cells, hole transfers can only take place in type II heterojunction solar cells.

2.5 Detection of photophysical processes

The optical transitions in the excited states of donor-acceptor system can be studied by various spectroscopic techniques.

2.5.1 Steady state and time-resolved photoluminescence

Steady state and time-resolved photoluminescence (PL) spectroscopy is a powerful technique to study the electronic properties of the excited states in various materials, e.g., in our case in the blend films of solar cell active layers. The steady state PL spectroscopy detects the population of allowed transition energy states after electronic excitation of the material. In donor-acceptor systems, the energy and charge transfers from donors to acceptors compete with the different relaxation processes, which results in the quenching of the PL. There are two possible mechanism of PL quenching, namely static and dynamic quenching. The respective type and the quenching rate can be estimated by the Stern-Volmer plot. Recently, the so-called super-quenching phenomena were observed in polymer/NCs blends [76, 77], which show that Stern-Volmer plots follow linear behavior at low concentrations and become exponential at high concentrations. The linear behavior at low concentration can be fitted as [2, 77]:

$$\frac{PL_0}{PL} = 1 + K_{D,S} [Q] \quad (2.9)$$

Where $[Q]$ is the concentration of the quencher (or NCs), $K_{D,S}$ is quenching rate as contribution of dynamic and static quenching. (PL_0) is the luminescence intensity without quencher (or pristine polymer, in the polymer/NCs blend case) and (PL) with quencher (in the presence of NCs). Moreover, at high concentration of the quencher, Goutam *et al.* [77] suggested the exponential dependency of the PL quenching as

$$\frac{PL_0}{PL} = 1 + \alpha [Q] + \beta \exp(\gamma) [Q] \quad (2.10)$$

2.5.2 Quasi steady state photoinduced absorption

Quasi steady state photoinduced absorption (PIA) is a direct technique to investigate the photoinduced charge transfer between donor and acceptor. These technique detect the photogenerated species in the μ s-ms time domain. PIA utilizes the structural relaxation of the molecular species upon excitation, thus created localized and relaxed polaron states and generated the new optical transitions. The pump beam excites the electron from ground state to excited states. Here, the pump beam is frequency modulates, which

is creating modulation of the density of the photoexcited species. The continuous wave (cw) white light probe changes the transmittance of the samples, so that information about the change of the population density in the excited states (including the allowed optical transition from the states) can be taken from the fractional change in transmission ($\Delta T/(T)$) of the sample. The fractional change of the transmission ($\Delta T/(T)$) in the sample can be calculated as:

$$\frac{\Delta T}{T} = 1 - e^{-\sigma n I} \approx \sigma n I \quad (2.11)$$

Note that $\sigma n I \ll 1$, with, σ medium of extinction coefficient, n the concentration, and I the intensity of pump beam. The lifetime of the photoexcited states species can be estimate by measuring the frequency dependence of PIA intensity. For monomolecular recombination, the fractional change of the transmission ($\Delta T/(T)$) is propotional to [78–80]

$$\frac{\Delta T}{T} \propto \frac{g I \tau}{\sqrt{1 + (\omega \tau)^2}} \quad (2.12)$$

with the generation efficiency g , the excitation light modulation frequency ω , the intensity of the laser I and the lifetime of long-lived species τ . The PIA signal for monomolecular recombination shows a linear, chopping frequency-independent behavior for $\omega \tau \gg 1$ and $\omega \tau \ll 1$.

Dispersive recombinations, which include trapping and de-trapping processes in the system can be described as [79–81]

$$\frac{\Delta T}{T} \propto \sqrt{\frac{g I}{\beta}} \frac{\alpha \tanh \alpha}{\alpha + \tanh \alpha} \quad (2.13)$$

with $a = \pi/(\omega \tau)$ and $\tau = (g I \beta)^{-0.5}$. β is the bimolecular decay constant. Dispersive recombination which takes into account the trapping and de-trapping process in the system can be described as [79–82]

$$\frac{\Delta T}{T} = \frac{(\Delta T/T)_0}{1 + (\omega \tau)^\gamma} \quad (2.14)$$

with the dispersive parameter γ and the PIA signal intensity at the limit of zero frequency $(\Delta T/T)_0$

Chapter 3

Materials, device preparation and experiment techniques

This chapter provides an overview of the colloidal synthesis CuInS₂ nanocrystals (CIS NCs) as well as their optical and physical properties. Furthermore, the preparation of bulk heterojunction solar cell samples and single carrier devices is presented. Subsequent to the description of the ligand exchange procedure the experimental techniques used in this work are introduced.

3.1 Materials

3.1.1 Synthesis of CuInS₂ NCs and their properties

For the synthesis of colloidal CuInS₂ nanocrystals (CIS NCs) copper (I) acetate (CuAc, 97%), trioctylphosphine oxide (TOPO, technical grade 90%), dodecanethiol (1-DDT, 98+%) and *tert*-dodecanethiol (*t*-DDT, 98.5%, mixture of isomers) were purchased from

Sigma Aldrich. Indium (III) acetate (InAc_3 , 99.99%, metal basis) was delivered by Alfa Aesar and oleylamine (OLAM, C18-content 80–90%) was purchased from Acros Organics. All chemicals were of the highest purity available and were used without further purification. The hot injection method used for the synthesis is described in detail in ref [83]. The experimental setup is shown in Fig. 3.1(a). Here, a 100 mL three-neck flask is connected to a thermometer and a nitrogen flow from a standard Schlenk line in order to avoid contamination with oxygen. The flask is immersed in a heating mantle for temperature control. For the synthesis, a mixture of 0.5 mmol 1-DDT and 0.25 mmol *t*-DDT is injected at 220°C into a solution of 1 mmol CuAc , 1 mmol InAc_3 and 1 mmol TOPO in 10 ml OLAM. After 1 h of stirring at 240°C, the reaction is stopped by cooling the mixture to room temperature. Subsequently, the product is purified by three cycles of precipitation with ethanol and dissolution with chlorobenzene. In this synthesis, OLAM serves as solvent, regulator of the monomer activities as well as stabilizing agent of the particles, i.e., as a ligand. The mixture containing 1-DDT and *t*-DDT acts as sulfur resource and controls the reactivity of the copper monomers. TOPO is used to decrease the reactivity of the indium precursor and stabilize the particles, i.e., is another ligand. Figure 3.1 (b) depicts a transmission electron microscopy (TEM) image of the as-prepared CIS NCs, which exhibit well defined pyramidal shapes. A high-resolution TEM (HRTEM) image is shown in the inset of Fig. 3.1(b). Figure 3.1(c) displays the size distribution of the as-synthesized CIS NCs results in an average diameter of about 9.2 ± 1.6 nm.

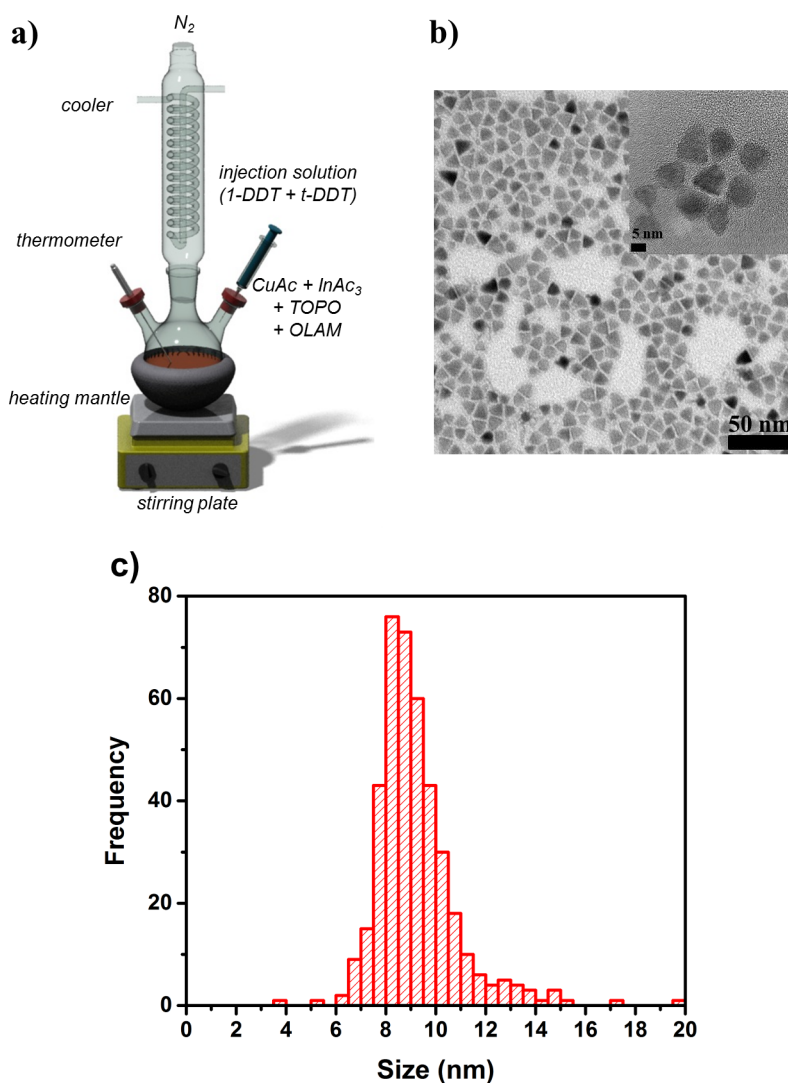


Figure 3.1: (a) Scheme of the experimental setup for the synthesis of colloidal CIS NCs by a hot injection synthesis as well as (b) TEM and HRTEM (inset) images and (c) the size distribution of the as-synthesized CIS NCs.

Figure 3.2(a) shows the XRD pattern of CIS NCs with the Rietveld refinement fit. The diffraction analysis revealed a wurtzite crystal structure of CIS NCs with mean domain sizes of 14.3 nm and 12.0 nm along the a and c axes, respectively. The lattice parameters are $a = (3.906 \pm 0.002) \text{ \AA}$ and $c = (6.429 \pm 0.003) \text{ \AA}$. The UV-Vis absorption data of the CIS NCs dissolved in chlorobenzene (see Fig. 3.2(b)) shows the wide absorption range of the CIS NCs extending up to about 800 nm.

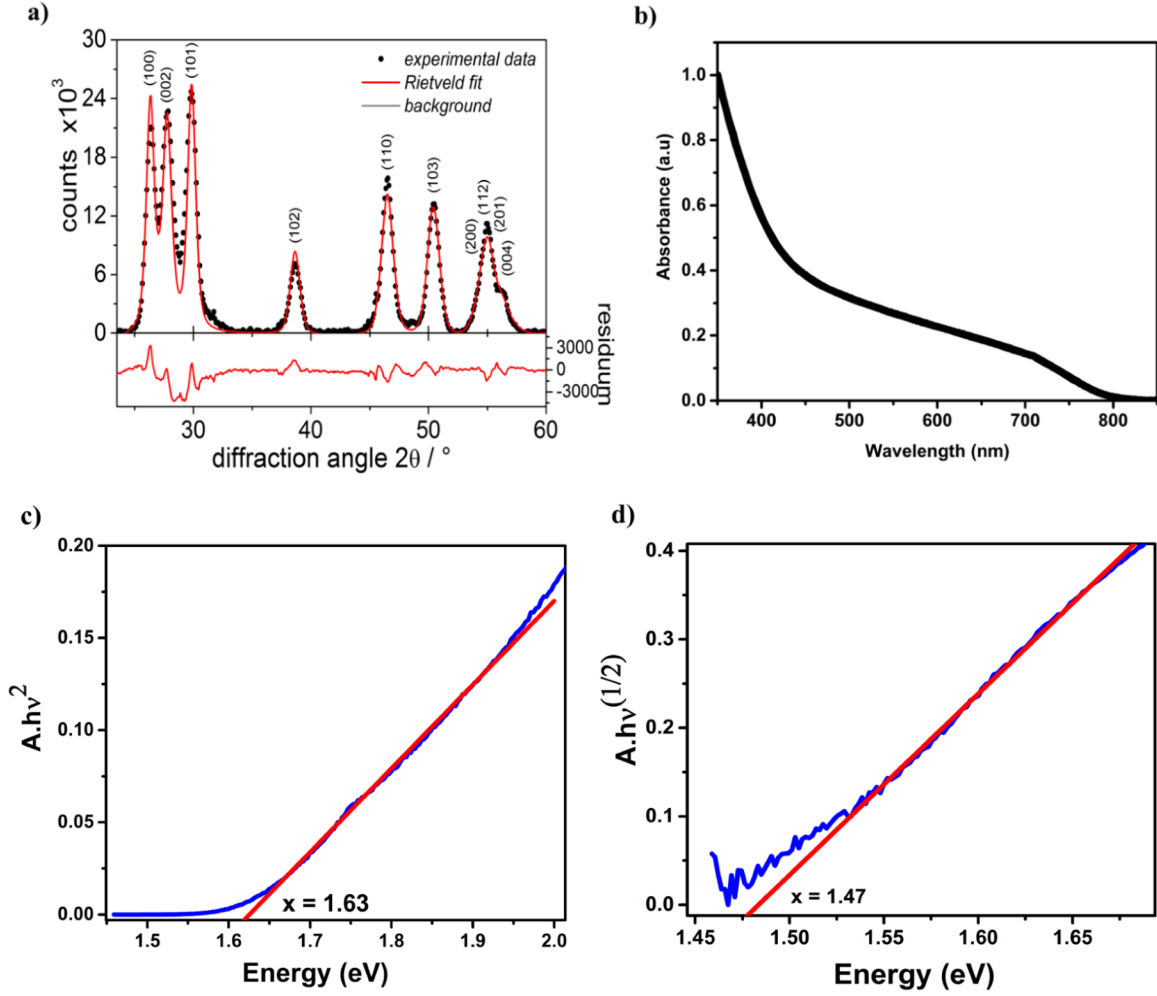


Figure 3.2: (a) XRD pattern of the as-synthesized CIS NCs including the Rietveld refinement and (b) the UV-Vis spectrum of a colloidal emulsion of the as-synthesized CIS NCs as well as Tauc plots of (c) $(Ah\nu)^2$ vs. $h\nu$ and (d) $(Ah\nu)^{(1/2)}$ vs. $h\nu$ used for estimating the direct and indirect energy gap, respectively.

The energy gap was analyzed by Tauc plots, for which two cases have to be distinguished: (i) for direct semiconductors the quantity $(Ah\nu)^2$ (with the absorbance A , the Planck's constant h and the frequency ν) is plotted against the photon energy E (see Fig. 3.2(c)), whereas (ii) for indirect semiconductors the quantity $(Ah\nu)^{(1/2)}$ is plotted (see Fig. 3.2(d)). From a least-squares fit of the linear part of the curve the energy gap can be obtained as the intercept with the energy axis [84–86]. As observed in Figs. 3.2(c) and (d) two different energy gaps are obtained, namely a direct and an indirect

energy gap. The energy gaps of the CIS NCs estimated from the fittings are about 1.63 eV for the direct transition and 1.47 eV for the indirect transition. The observation of two optical transitions is in agreement with a previous report on similar CIS NCs [10], in which the absolute positions of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) with respect to the vacuum of comparable CIS NCs were determined by cyclic voltammetry (CV) to be about -4.7 eV and -3.3 eV, respectively. A comparison of the energy gap of the CIS NCs obtained by the Tauc plot results to CV measurements (1.4 eV) suggested the CIS NCs to be indirect semiconductors. The slight difference between the optical and electrochemical band gap is probably due to the uncertainty of the CV measurements [10].

3.1.2 PbS quantum dots (QDs) and their properties

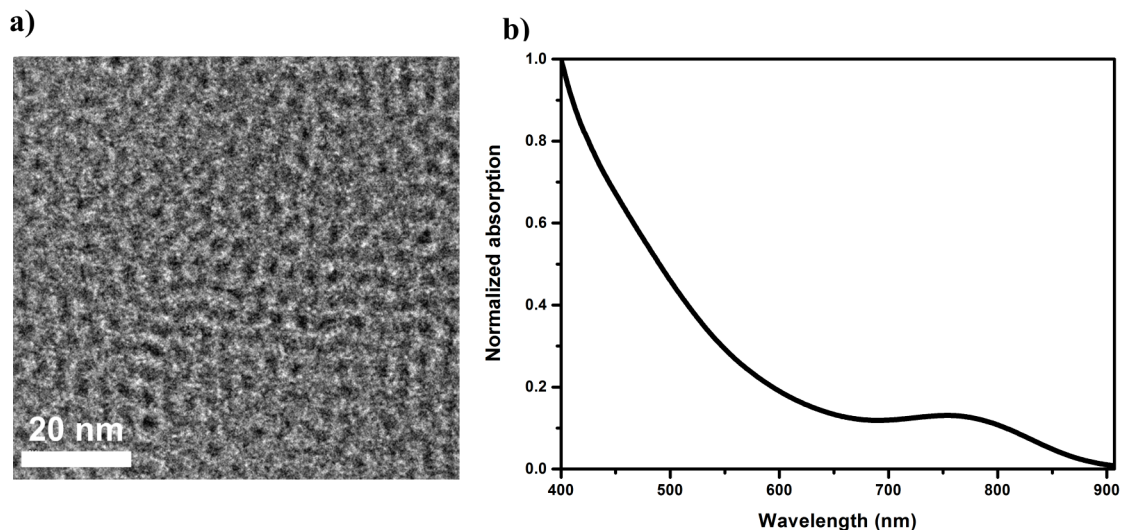


Figure 3.3: (a) TEM image of PbS QDs and (b) the UV-Vis spectrum of a colloidal PbS QDs solution.

Colloidal PbS quantum dots (QDs) with core diameters of approximately 2.4 nm, which are capped by oleic acid (OLA) were purchased from Evident Technologies (Troy, NY). Figure 3.3 displays a TEM image of the PbS QDs as well as a UV-Vis spectrum of PbS QDs dispersed in chlorobenzene. The passivation of the PbS QDs by oleic acid expands

the absorption to the NIR region with an exciton peak at 760 nm and an energy gap of about 1.63 eV [37].

3.1.3 Conjugated polymers

All polymers in this study were used without further purification. The two kinds of polymers investigated are poly(3-hexylthiophene) (P3HT) and poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT). P3HT was purchased from Rieke Metals, Inc (MW = 50,000-70,000, regioregularity (RR) = 91-94%), PCPDTBT from Sigma Aldrich (MW = 7,000-20,000) and poly(3,4-ethylene dioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, formulation Clevios P VP AI 4083) from Heraeus Precious Metal GmbH & Co. KG. The structures of the polymers used in this work are shown in Fig. 3.4. The experiments for Chapter 5 were conducted with P3HT concentrations (dissolved in chlorobenzene) of 25 mg/mL and 30 mg/mL. For the investigations presented in Chapter 6 constant polymer concentrations (P3HT and PCPDTBT in [name of the solvent], respectively) of 10 mg/mL were used. The experiments were conducted by dissolving the required amount of CIS nanoparticles chlorobenzene before mixing with the respective polymer solution, so that the resulting CIS percentages in the polymer were 0%, 30%, 45%, 60%, 75%, and 90% by weight, respectively.

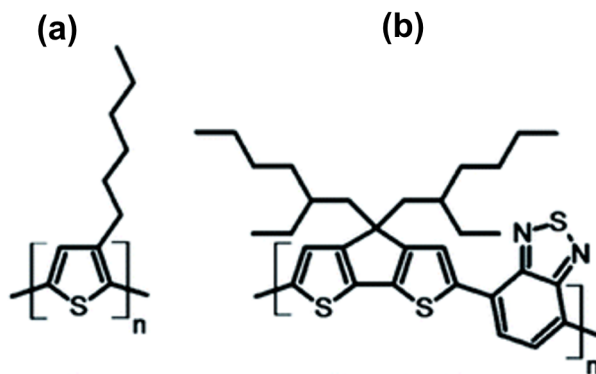


Figure 3.4: The structure of (a) poly(3-hexylthiophene) (P3HT) and poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)- alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT).

The P3HT/PbS QDs blends investigated in Chapter 7 were dissolved in chloroform with total concentrations in the range of 20-38 mg/mL and varied PbS QDs loadings of 60wt%, 75wt% and 90wt%. The P3HT used for these blends was purchased from Rieke Metals (Sepiolid P200, $M_n = 13.9$ kg/mol, $RR > 96\%$).

3.2 Sample preparation

3.2.1 Preparation of bulk heterojunction solar cells

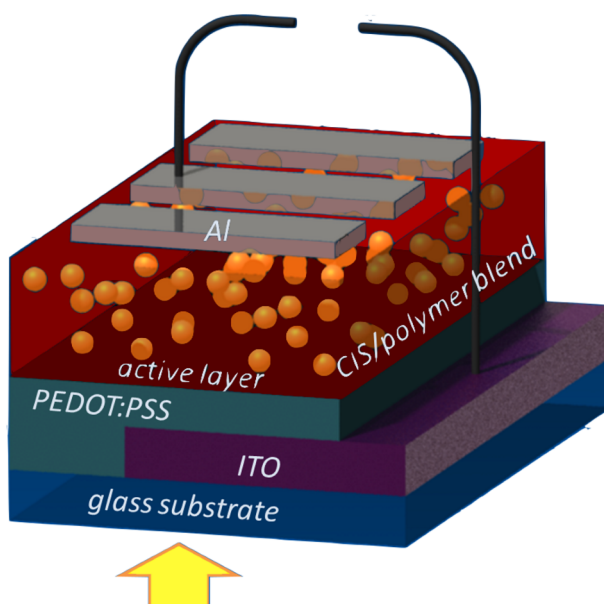


Figure 3.5: Schematic illustration of a BHJ solar cell.

Figure 3.5 shows the basic structure of bulk heterojunction (BHJ) solar cells, as they were used in this work. The hybrid BHJ solar cells were prepared on top of indium tin oxide (ITO)-coated glass substrates. Prior to the sample preparations, the substrates were cleaned in an ultrasonic bath with deionized water, acetone and isopropanol. The clean ITO substrates were subsequently plasma-etched for 10 min, onto which PEDOT:PSS was spin-coated for 30 s with 3500 rpm, which was followed by an annealing process at 180°C for 15 min, which resulted in a sample thickness of ~ 40 nm. The polymer and CIS

NCs were mixed and dissolved in chlorobenzene solution with well-defined concentrations as described in the previous section. Subsequently, the solution was spin-coated for 80 s with 1000 rpm and annealed at 150°C for 15 min. Finally, a 120 nm Al layer was evaporated onto the active layer.

3.2.2 Preparation of single carrier devices

In order to study the hole and electron transport in CIS NCs, single carrier devices were fabricated. These were prepared by sandwiching CIS NCs between top and bottom electrodes with different work functions. The device structure used in this work is depicted schematically in Fig 3.6. All the device preparations were performed in a glove box in nitrogen atmosphere. For this preparation, the CIS NCs were dissolved in chlorobenzene and filtered through a 0.45 μm PTFE (Polytetrafluorethylene) filter. The prepared solution was subsequently spin-coated with 1000 rpm on the top of cleaned ITO substrates. Finally, a Au top electrode with 120 nm thickness was vapor-deposited through a shadow mask, resulting in three 0.1 cm^2 pixels on one substrate.

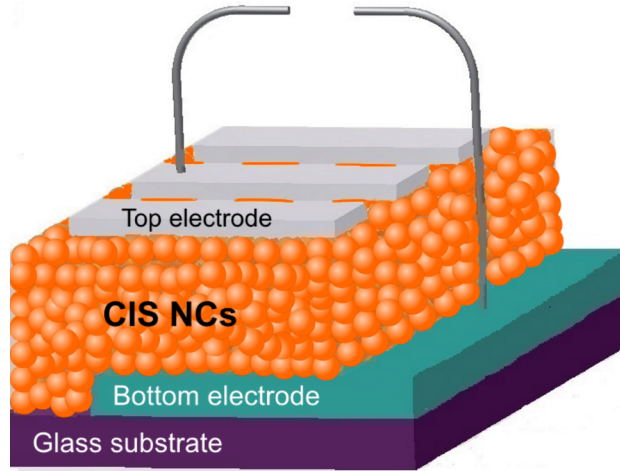


Figure 3.6: Schematic illustration of a single carrier device.

Additionally, HO devices with P3HT were prepared for comparison. The device structure was similar to that of the HO devices with CIS NCs, except for a thin interlayer of PEDOT:PSS, which was placed between the ITO substrate and the P3HT layer.

The PEDOT:PSS layer was deposited by spin-coating with 3500 rpm for 30 s and subsequently annealed at 180°C for 15 min. The P3HT layer was deposited on top by spin-coating from a solution of P3HT in chlorobenzene and annealed at 150°C for 15 min.

The bottom electrodes of the electron-only (EO) devices were prepared by consecutive deposition of a thin Cr layer (in order to improve the adhesion of the next layer), a thick Al layer (100 nm) and a thin (protective) Cr layer onto glass substrates. Subsequently, a Ca layer (120 nm) was deposited as top contact. The CIS NPs layer was prepared the same way as for the HO devices.

3.2.3 Ligand exchange

Two kinds of ligand exchange processes were performed in this work in order to replace the long-chain ligand capping the CIS NCs with the shorter chain ligands which could improve the charge transport or transfer in the solar cell.

3.2.3.1 Solution-phase ligand exchange

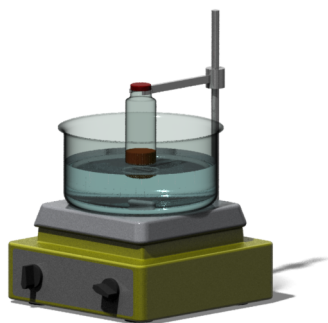


Figure 3.7: Apparatus for solution-phase ligand exchange.

Two different ligands were used for solution-phase ligand exchange, hexanethiol and pyridine. Both of the ligands are widely applied for the removal of phosphonic acid and TOPO ligands [67, 87]. The schematic illustration of the solution-phase ligand exchange is shown in Fig. 3.7. For this, as-prepared CIS NCs were dissolved ~ 6 ml hexanethiol

or pyridine. These solutions were subsequently heated in an oil bath and stirred at 80°C for about 24 h. The ligand exchanged product was then precipitated with ethanol. The nanocrystals were kept in chlorobenzene solution.

3.2.3.2 Post deposition ligand exchange

The post-deposition ligand exchanges are performed on spin-coated film of P3HT/CIS NCs blend. The films were spin coated onto ITO/PEDOT:PSS layer at 1000 rpm for 80 s. Here, 1,4-benzenedithiol (BDT) ligand is used for the studied on P3HT/CIS NCs films in Chapter 7. The ligand solutions were prepared by dissolving the ligand in acetonitrile with concentration of 0.1 M. The thin films of P3HT/CIS NCs blend were then dipping into the solution for 60 s. At last, to remove the rest of the ligand, the film was rinsed with pure acetonitrile for 60 s. The films were then annealed at 150°C for 15 minutes.

For P3HT/PbS QDs, the ligand exchange were carried out by dripped the ligand solution until it covers the active layers for 60 s and continued by spin coated for 60 s at 1500 rpm. For removing the rest of the solution, pure acetonitrile were dripped and spin coated at 1500 rpm for 60 s. Afterwards, the films were annealed at 150°C for 10 minutes. The 1,4 benzenedithiol (BDT), octylamine (Oam) and octanethiol (OT) ligands were used in P3HT/PbS QDs post-deposition ligand exchanges.

3.3 Optical, structural and device Characterization

3.3.1 UV-Vis Spectroscopy

The absorption spectra of the CIS NCs were recorded with a Varian Cary 100 Scan UV-Vis-spectrometer. The spectrometer measures the transmission, T , and the absorbance is calculated by Beer's law neglecting reflection losses. Figure 3.8 (a) shows the illustration of the Beer's law in the films. The intensity transmitted through the film I_{trans} , can be describe as:

$$I_{trans} = I_0 \cdot \exp(-OD) \quad (3.1)$$

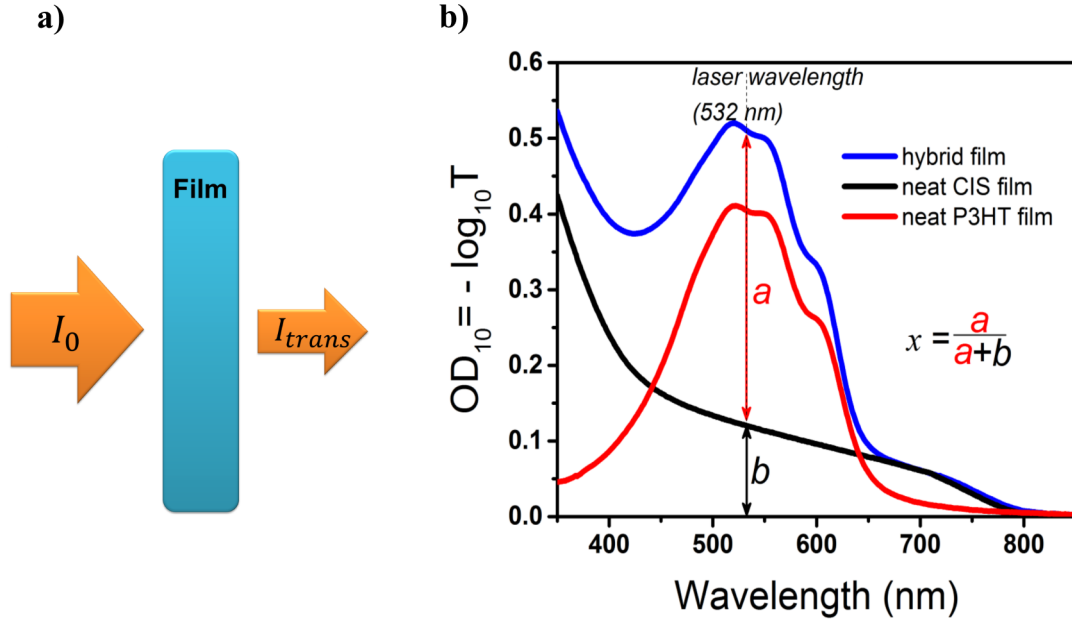


Figure 3.8: (a) Illustration of Beer's law for the film. (b) Exemplary UV-VIS spectra for determining the absorption of the polymer.

with the incident intensity, I_0 , and the optical density of the film, OD . The absorbance, or optical density, OD_{10} is calculated neglecting reflection as:

$$OD_{10} = -\log_{10}(I_{trans}/I_0) = -\log_{10}(T) \quad (3.2)$$

The absorption, A , with neglecting the reflection, can be calculated as:

$$A \approx 1 - T = 1 - 10^{-OD_{10}} \quad (3.3)$$

For estimation of the absorption of light in blend hybrid films, the absorbance can describe as a sum of the absorbance of polymer and nanocrystals:

$$OD_{blend} = OD_{Polymer} + OD_{NCs} \quad (3.4)$$

with OD_{Polymer} and OD_{NCs} denoting the contributions of the polymer and nanocrystal. The absorption of the blend, A_{blend} , can be calculated as

$$A_{\text{blend}} \approx 1 - T_{\text{blend}} = 1 - 10^{-OD_{10,\text{blend}}} \quad (3.5)$$

Figure 3.8(b) show the exemplary of UV-Vis spectra and the estimation of the individual contributions. With x denoting the fraction of the absorbance attributed to the polymer, the absorption by the polymer, A_{polymer} , can finally be calculated as follows:

$$A_{\text{Polymer}} \approx 1 - T_{\text{Polymer}} = 1 - 10^{-x \cdot OD_{10,\text{blend}}} \quad (3.6)$$

3.3.2 Transmission electron microscopy (TEM)

Transmission electron micrographs were measured with a Zeiss EM 902A microscope. The samples were prepared on top of copper grids and letting the samples dry at room temperature. High resolution transmission electron microscopy (HRTEM) measurements were carried out on a JEOL JEM2100F microscope. Drops of solution were prepared onto a nickel grid and dried at room temperature.

3.3.3 X-ray diffraction (XRD)

The samples were prepared by dissolving CIS NCs in chlorobenzene and then drop casted onto silicon substrates. The samples were dried at 50°C to remove the excess of the solutions. A PANalytical X'Pert PRO MPD diffractometer operating with Cu K α radiation, Bragg-Brentano θ -2 θ geometry, a goniometer radius of 240 mm, was used. The XRD data were then analyzed by using the X'Pert HighScore Plus software and the pattern refined by applying Rietveld refinement with the program MAUD [88].

3.3.4 Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)¹

Thermogravimetric analysis (TGA) is a technique for determining the organic and inorganic content of various materials by measuring the weight loss of a material as a function of temperature. The technique usually accompanying TGA is differential scanning calorimetry (DSC) which can be used to study enthalpy changes associated with the cleavage of bonds between ligands and the nanoparticle surface. The TGA/DSC setup were connected to the FTIR measurement, which detected the decomposed compound in the gas phase. The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed by using a Netzsch STA 449 F3 Jupiter thermoanalysis system connected to FTIR-spectrometer. The samples were deposited in Al_2O_3 crucibles and heated from 35°C to 600°C with a heating rate of 2 K/min in an O_2/Ar (1:2) and an Ar gas flow of 40 mL/min, respectively. The gas phases of evaporated materials were detected by MCT detector.



Figure 3.9: TGA/DSC Setup connected to the FTIR setup. Taken from [6].

3.3.5 Determination of the Dielectric Constants

The dielectric constant of the films was estimated using an established method [89] by measuring the capacitance and the thickness of the films placed between two parallel electrodes. To measure the capacitance, the films were connected in an RC circuit in series with a resistor (100 Ω), a signal generator (100 kHz), and a LeCroy 9400A digital

¹The TGA/DSC as well as the FTIR measurement were carried out by J. Neumann and D. Fenske at Fraunhofer Institute for Manufacturing Technology and Advanced Materials (IFAM) Oldenburg.

oscilloscope. The relative dielectric constant of the film, ϵ_r , was then estimated according to the parallel plate capacitance equation, $\epsilon_r = C_d/(\epsilon_0 A)$, where C is the capacitance, ϵ_0 is the permittivity of vacuum, A is the area of the plates and d is the film thickness.

3.3.6 Electrical characterization

Current density-voltage measurements for single carrier device were performed under dark condition inside the glovebox with a Keithley 2400 source measurement unit. For the solar cell performance, the current-density measurements were recorded with a Keithley 4200 source measure unit. The solar cells were illuminated with a Photo Emission Tech. solar simulator (simulated AM 1.5G spectrum), adjusted to an intensity of 100 mW/cm².

3.3.7 Quasi steady state Photoinduced Absorption (PIA) & Steady state Photoluminescence (PL)

The quasi-steady state PIA and PL measurements were performed in the same setup as shown in Figure 3.10. For both measurements, an incident laser beam with excitation wavelengths of 532 nm and 660 nm were used for P3HT and PCPDTBT, respectively. Round sapphire substrates with a diameter of about 1 cm was used in this experiment. The substrates were rinsed with Helmanex solution, distilled water, acetone, and isopropanol prior to the application. The films were spincoated from chlorobenzene solution onto the substrates at 1000 rpm for 80 s (the experiment with different conditions will be specified later in the section). The prepared samples were mounted into a nitrogen flow cryostat and kept under vacuum conditions. The temperature was either at 80 K or room temperature.

The samples were excited by a continuous wave solid state laser, equipped with an optical chopper for photomodulation and probed with a white light halogen lamp. The pump power incident on the sample is 15 mW with a beam diameter of 2 mm. The frequency of the modulation time was kept at 80 Hz unless otherwise specified. Both light sources were focused onto the same point of the sample. Misalignment of the beam is result in reducing or undetectable PIA signal. The mechanically chopped pump beam will induced PIA signal fluctuation and changing the pump modulation frequency will

change the induced PIA population. The modulated pump provides an AC signal with the same frequency of the strobing rate. The frequency controller sent the information to the lock-in amplifier. The frequency information was then used to recover the AC component of the detector input. A white light halogen lamp used to probe source for scanning across measurement frequency range. To avoid the probe beam creating new electronic levels in the measurement, the intensity of probe beam set in lower intensity than pump beam. A triple grating monochromator were used for restricting the wavelength range of the scanning of the incident light on the sample. The intensity of the light passed through the monochromotar can be adjusted by altering the entrance and exit slits. Appropriate filters were used in front of the monochromator to suppress the second order interference effect. The signals were detected by two types of detectors based on the wavelength (550-1100 nm by silicon detector and 1100-5550 nm by InSb detector). Lastly, the laser induced changes in transmission of the white light source were measured by lock-in detection.

The PIA spectrum was measured in three steps. First, the transmittance (T) of the systems during illumination of the samples with the white light only, second the photoluminescence (PL) of the sample and finally the transmission measured with both, the white light and the laser on (PA). The fractional change in the sample is then calculated with

$$-\frac{\Delta T}{T} = -\frac{(PA - PL)}{T} \quad (3.7)$$

The resulting spectrum shows the function of the fractional changes of transmission as a function of energy probed. The negative signal is called photobleaching band (PB band), due to the depletion of the ground state of the material. In contrast, new optical transitions show up as positive signals in the PIA spectra.

To enable a quantitative comparison of films with different nanocrystal content, the steady state PL and PIA spectra were normalized to the absorption by the polymer component in the films at the respective excitation wavelength (i.e., at 532 nm for P3HT and 660 nm for PCPDTBT) as described in 3.3.1.

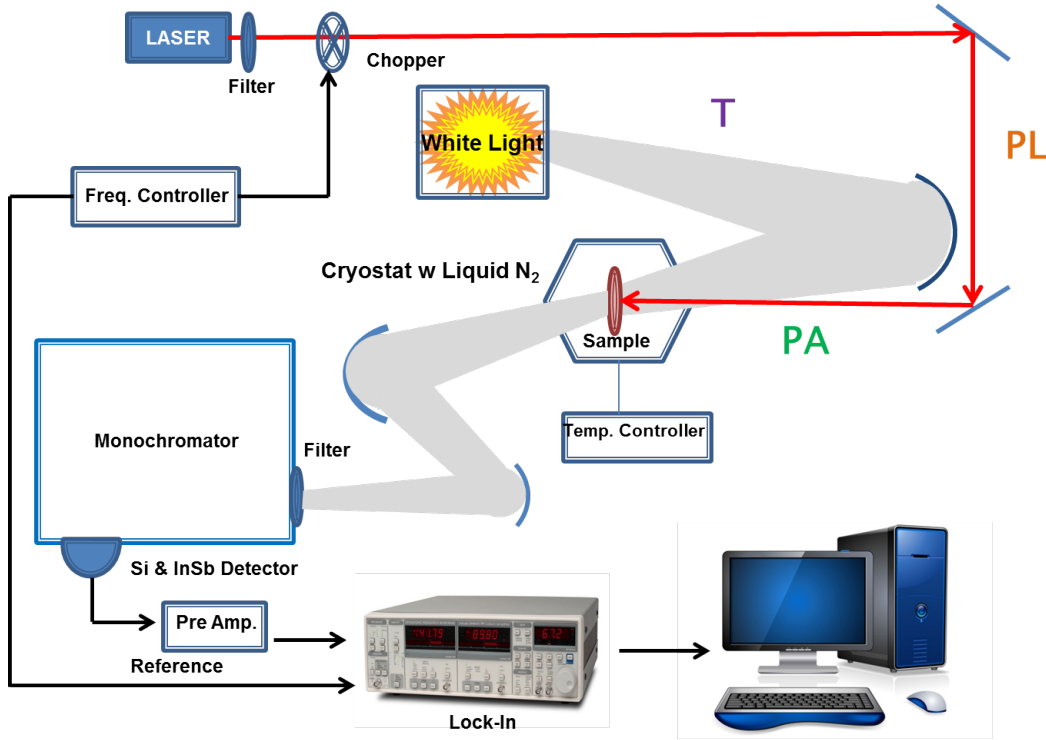


Figure 3.10: Photoinduced absorption setup.

3.3.8 Time-resolved Photoluminescence (TRPL) Spectroscopy.²

The time-resolved properties and excited state dynamics of our systems were studied using the time-correlated single photon counting (TCSPC) technique [90]. The TCSPC setup [91], as illustrated in Fig. 3.10, consists of a Tsunami Ti:Sapphire laser (Spectra Physics) pumped by a Millennia XS CW-laser (Spectra Physics), resulting in pulsed laser light, which is tuneable between 760 and 1100 nm, with a repetition rate of 81 MHz. Using a pulse picker (GWU) the repetition rate could be decreased to 8.1 MHz. The frequency of the light is doubled with a flexible harmonic generator (GWU-FHG from GWU Lasertechnik). Emission from the sample was detected with a cooled R3809U-51 MCP-PMT detector from Hamamatsu after passing through with a polarizer at the magic angle (54.7°) and a subtractive monochromator. The signals were processed using an SPC 430 (Becker & Hickl GmbH) computer card. The instrument response function

²The TRPL measurements were carried out within collaboration by Y. Firdaus, Y. Baeten, E. Fron, and M. Van der Auweraer at the KU Leuven (Belgium).

(IRF) was recorded using a LUDOX scattering solution, and its Full Width at Medium Height (FWHM) amounted to 20-30 ps.

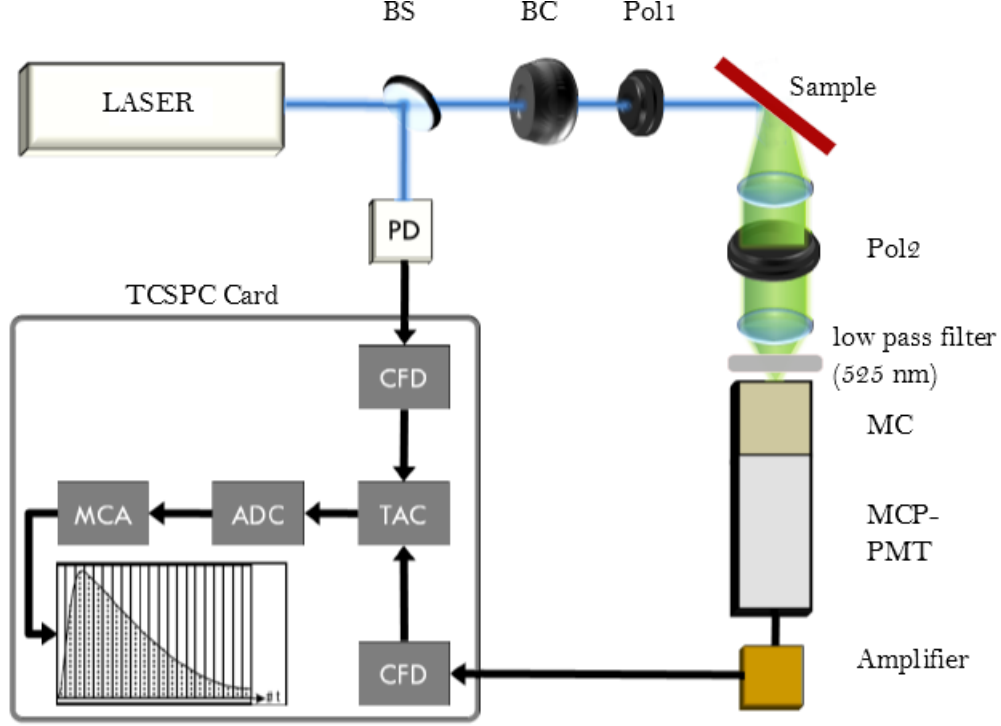


Figure 3.11: Operation principle of TCSPC setup. BS:Beam splitter; BC:Berek compensator; Pol:polarizer; PD: photodiode; MC:monochromator. Taken from [7]

The photoluminescence decay curves were analysed by fitting the data to a convolution of the instrumental response function with a decay function for a δ -pulse. The fitting was done with the TRFA Global Analysis Program [92] based on a Marquardt-Levenberg minimization algorithm and a Gaussian-weighted nonlinear least-square fitting. The quality of each fit was assessed by the random distribution of the residuals, their autocorrelation function and the value of the reduced chi-square parameter (χ^2) [93, 94], which was around 1.1. All decays were fitted with the function:

$$I_{PL}(t) = \sum A_n \cdot \exp\left(-\left(\frac{t}{\tau_n}\right)\right) \quad (3.8)$$

where A_n and τ_n are fitting parameters describing the amplitude and decay-time of the

n-th decay component, respectively. The relative contribution P_n of the n-th component to the stationary PL can be calculated as

$$P_n = \frac{A_n \tau_n}{A_j \tau_j} \quad (3.9)$$

so that $\sum_j P_j = 1$. The amplitude-weighted average decay time constant is obtained as [2, 95]:

$$\langle \tau \rangle = \frac{\sum_j A_j \tau_j}{\sum_j A_j} \quad (3.10)$$

Chapter 4

Ligand shell analysis of CuInS₂ nanoparticles

Ligand shells surrounding nanocrystals (NCs) play an important role during the colloidal synthesis and subsequently in the performance of the devices. During the synthesis ligands not only act as stabilizing agents but also facilitate the dispersion of the NCs in the solvents. The presence of capping ligands can affect the film morphologies and the phase separation as well as the charge transport and solar cell performances. In this chapter, the ligand shells surrounding the CuInS₂ (CIS) NCs are investigated by combined thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) as well as Fourier transform infrared spectroscopy (FTIR). Furthermore, changes in the ligand shell of the particles by solution-phase ligand exchange processes with hexanethiol and pyridine are analyzed.¹

¹Parts of this chapter have been published in: C. Krause, **R. Miranti**, F. Witt, J. Neumann, D. Fenske, J. Parisi, and H. Borchert, Sol. Energy Mater. Sol. Cells 124, 241 (2014).

4.1 Motivation

Hybrid bulk heterojunction (BHJ) solar cells were prepared by blending the conducting polymers and inorganic colloidal NCs. The performance of hybrid BHJ solar cells is highly dependent on the incorporation of colloidal NCs in the polymer matrix. Factors like shape, solubility and surface modification of the NCs are believed to affect their incorporation in the polymer matrix. Colloidal NCs are commonly synthesized in an environment of long alkyl chain ligands in order to control the nucleation and growth during the synthesis [96–98]. Colloidal semiconductor NCs are most commonly synthesized in insulating long-chain organic ligands [39, 69, 71]. A disadvantage of these organic ligands (used as stabilizing agents during the NCs synthesis and to prevent aggregation after the synthesis), is that they can act as an insulating layer and result in long hopping distances, thus impeding efficient charge transport and reducing charge separation at the polymer-NCs interfaces. Hence, they affect the performance of BHJ solar cells [65].

One strategy to improve the transport and transfer processes for a better solar cell performance is the modification of the ligand shell via ligand exchange procedures, i.e., replacing the long ligands with shorter ligands. Short ligands like, e.g., pyridine [23, 24, 67, 69, 99–107] as well as different short-chain amines [29, 36, 69], thiols [68] etc. are commonly used in solution-phase ligand exchange procedures. Here, especially the solution-phase ligand exchange with pyridine is of interest, because pyridine is shorter and more conductive than most of the capping ligands present after synthesis, which thus leads to a better solar cell performance. Recently, Dayal *et al.* reported the highest efficiency obtained for polymer/CdSe hybrid solar cells based on PCPDTBT and pyridine-treated CdSe tetrapods with efficiencies up to 3.2% [107]. A treatment with hexanethiol, on the other hand, was reported to result in better morphologies of the solar cells compared to those constructed after pyridine treatment [10].

In this chapter, the ligand shells of as-synthesized CIS NCs as well as those of CIS NCs subjected to solution-phase ligand exchanges with hexanethiol and pyridine are investigated.

4.2 The ligand analysis of as synthesized CuInS₂ nanoparticles

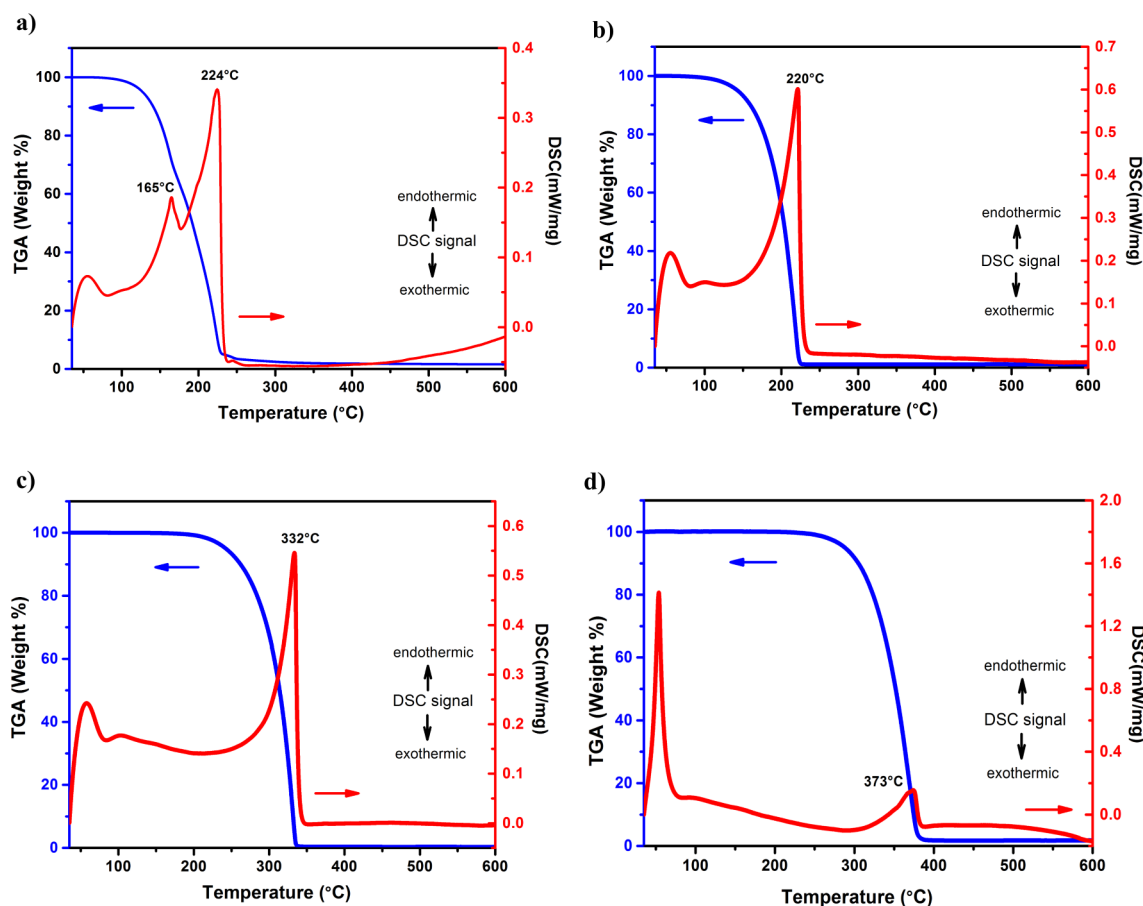


Figure 4.1: Representative TGA (blue/ DSC (red) measurements of liquid (a) 1-DDT, (b) *t*-DDT and (c) OLAM as well as (d) solid TOPO.

CIS NCs were synthesized using four different ligands, namely 1-dodecanethiol (1-DDT), tert-dodecanethiol (*t*-DDT), oleylamine (OLAM) and trioctylphosphine oxide (TOPO) (see Chapter 3, section 3.1.1 for details). In order to clarify, which of the above ligands are present on the CIS NCs surface after synthesis, combined TGA/DSC and gas phase FTIR measurements were carried out. Figure 4.1 shows the combined TGA and DSC analysis of the pure ligands. All measurements were recorded in a temperature range of 35-600°C with liquid samples of the ligands, excluding TOPO, which was solid at room

temperature. The DSC peaks visible at 55°C in all diagrams are caused by the experimental setup (see Fig. 4.1). All pure ligands except for 1-DDT show a one-step process in the TGA curve and a complete mass loss at the respective evaporation temperatures. On the other hand, the TGA measurement of 1-DDT exhibits two pronounced steps as shown in Fig. 4.1(a). Two endothermic peaks of 1-DDT are observed at 165°C and 224°C. The TGA/DSC curve of *t*-DDT in Fig. 4.1(b) shows a complete evaporation of the liquid at 220°C, which is also observed by the endothermic DSC peak at the same temperature. As *t*-DDT serves as sulfur source in the synthesis, it is expected to decompose at this temperature. The endothermic evaporation peaks of OLAM (Fig. 4.1(c)) and TOPO (Fig.4.1(d)) are found at higher temperatures of about 332°C and 373°C.

In order to obtain information about the compounds resulting, from ligand decomposition, the gas atmosphere leaving the TGA/DSC setup was examined by FTIR (see Fig. 4.2). In general, the FTIR spectra for all ligands show strong signals in the region of 3000-2800 cm⁻¹, which correspond to the symmetric and asymmetric CH₂ stretching modes and the asymmetric CH₃ stretching vibrations [99–104]. The signals observed for all ligands in the region of 1500-1350 cm⁻¹ arise from multiple IR bands assigned to $\nu(\text{C-C})$ stretch, $\nu(\text{C-O})$ stretch, and CH₂ deformation vibrations.

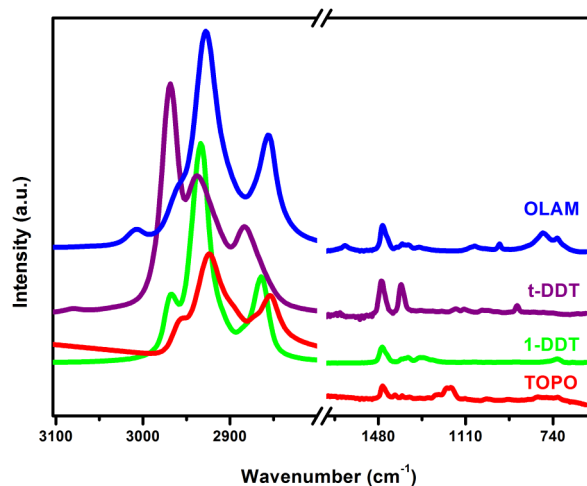


Figure 4.2: Representative gas phase FTIR spectra at respective boiling points of 1-DDT (green), *t*-DDT (purple), OLAM (blue) and TOPO (red).

The IR bands observed in the detection range of 4000-600 cm⁻¹ in Fig. 4.2, which are characteristic for the different ligands, are summarized in Table 4.1 with the respective

references. In the following, the discussion of the IR spectra will mainly focus on the signals assigned to the thiol, amine and phosphine oxide functional groups of the 1-DDT as well as *t*-DDT, OLAM and TOPO ligands, respectively.

Table 4.1: FTIR signals characteristic for the respective (pure) ligands (observed in Fig.4.2)

Ligand	Wavenumber (cm ⁻¹)	Vibrational modes ^{a)}	Ref.
1-DDT	1300, 1353, 1459	$\nu(\text{C-C})$, $\nu(\text{C-O})$, and $\delta(\text{CH}_3)$	[103, 104]
	2864, 2934, 2967	$\nu_s(\text{CH}_2)$, $\nu_{as}(\text{CH}_2)$, $\nu_{as}(\text{CH}_3)$	[99–104]
<i>t</i> -DDT	1034	$\nu(\text{C=S})$	[108]
	1379, 1464	$\nu(\text{C-C})$, $\nu(\text{C-O})$, and $\delta(\text{CH}_3)$	[103, 104]
	2882, 2936, 2969	$\nu_s(\text{CH}_2)$, $\nu_{as}(\text{CH}_2)$, $\nu_{as}(\text{CH}_3)$	[99–104]
OLAM	714,783 (broad peak)	NH ₂ wag, $\delta(\text{NH}_2)$	[103, 104]
	966	$\gamma(=\text{C-H})$	[103, 104]
	1069	$\nu_{as}(\text{C-O-C})$	[103, 104]
	1371, 1464	$\nu(\text{C-C})$, $\nu(\text{C-O})$, and $\delta(\text{CH}_3)$	[103, 104]
	2855, 2927	$\nu_s(\text{CH}_2)$, $\nu_{as}(\text{CH}_2)$	[99–104]
	3010	$\delta(=\text{C-H})$	[103, 104]
TOPO	1173	CH ₂ -O-P	[109]
	1459	$\delta(\text{CH}_3)$	[103, 104]
	2853, 2923, 2954	$\nu_s(\text{CH}_2)$, $\nu_{as}(\text{CH}_2)$, $\nu_{as}(\text{CH}_3)$	[99–104]

a) ν_s = symmetric stretching vibration; ν_{as} = asymmetric stretching vibration;
 δ = in plane deformation vibration; γ = out of plane deformation vibration.

Figure 4.3 depicts a combined plot of TGA/DSC measurement of an as-synthesized CIS NCs powder sample. The TGA data plot (blue line) shows a total mass loss of about 10%, which is complete at about 450°C. Three steps at about 150°C, 325°C and 400°C are observed in the TGA curve. The DSC analysis, however, suggests that at least four processes are involved at temperatures of 165°C, 261°C, 328°C and 420°C. The weak endothermic DSC peak around 165°C is accompanied by the first mass loss of 0.8%, which can be assigned to the loss of adsorbed water and was also observed for the measurements with 1-DDT ligand (see section 4.2). The most intense DSC peak observed at 220°C for pure 1-DDT, on the other hand is not visible for the CIS NCs. This suggests, that there is no free 1-DDT evaporating from the sample at 220°C, which is most probably due to ligand bonding to the nanocrystals' surface.

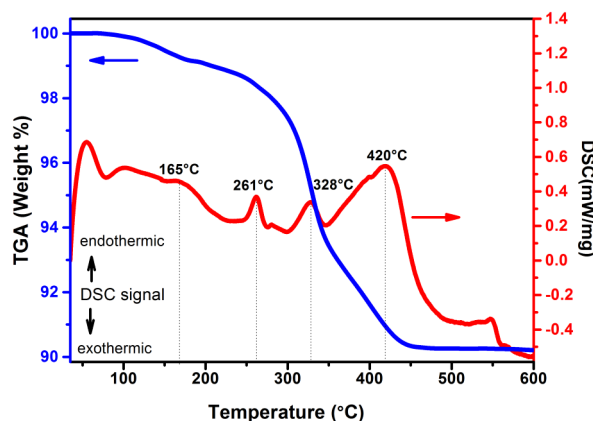


Figure 4.3: Representative TGA (blue) and DSC (red) measurements of a CIS NCs sample.

Further information about the compounds decomposing during the heating of the as-synthesized CIS NCs was obtained by FTIR measurements of the exhaust gas from the TGA/DSC unit in a region from 4000 cm^{-1} to 600 cm^{-1} . Figure 4.4 shows the gas phase FTIR spectra recorded at the sample heating temperatures of 172°C, 262°C, 327°C and 432°C, which correspond to the DSC signals observed in Fig. 4.3. The region between 4000-3550 cm^{-1} and 1900-1400 cm^{-1} contain the typical signals assigned to O-H vibrations of H₂O. The intense negative signal in the region between 2400 cm^{-1} and 2250 cm^{-1} is due to the O=C=O stretching mode of CO₂. The IR signals of both H₂O and CO₂ will not be discussed in this chapter, as their presence in the atmosphere of the spectrometer contributes to the detected signals, which therefore cannot be assigned unambiguously. The signal observed in the IR spectrum at $T = 172^\circ\text{C}$ (see black line in Fig. 4.4) at about 1300 cm^{-1} is assigned to $\nu(\text{C-O})$ vibrations, which indicates an at least partial oxidation of the 1-DDT carbon chain by oxygen from the gas atmosphere. On the other hand, no signals are observed in the C-H stretching region (around ~ 2950 cm^{-1}), which could provide evidence for the decomposition of 1-DDT to gaseous alkyl chain fragments. However, the appearance of a weak =C-H deformation signal about 967 cm^{-1} points to partially dehydrated (i.e., oxidized) alkyl fragments. Furthermore, the IR bands assigned to C-C and/or C-O stretching vibrations are observed at ~ 1370 cm^{-1} . Moreover, a weak IR band at 1030 cm^{-1} indicates a C=S stretching vibration of oxidized alkyl thiol groups (R-S-H). Hence, the TGA/DSC signal at 165°C is most probably due to water desorption from the sample and the decomposition of the alkyl chains of the 1-DDT ligands on the surface of the CIS NCs.

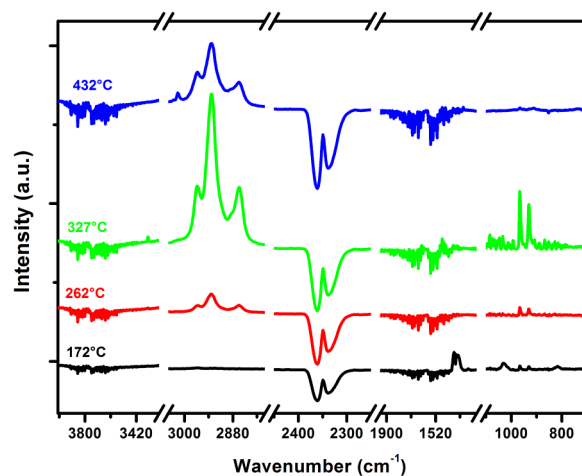


Figure 4.4: Representative gas phase FTIR spectra recorded during the heating of CIS NCs at 172°C (black), 262°C (red), 327°C (green) and 432°C (blue).

The second endothermic DSC peak observed at 261°C is accompanied by a further mass loss of about 1% (from 165°C to 261°C, see Fig. 4.3). The process corresponding to this signal is most likely the loss of the 1-DDT ligands bound to the nanoparticle surface. The bonding of the ligand to the nanoparticle surface provides an explanation for temperature shift to higher decomposition temperatures compared to that of pure 1-DDT (see Fig 4.1(a)). In the IR spectra recorded at 262°C (see red line in Fig. 4.4) neither C-C or C-O vibration signals in the region of about $\sim 1370\text{ cm}^{-1}$ nor C=S stretching vibration bands at about 1030 cm^{-1} are observed. On the other hand, the appearance of a signal of the C-H stretching in the region of $2800\text{--}3000\text{ cm}^{-1}$ indicates the decomposition of the carbon chain of 1-DDT with no or minor oxidation. This observation is in good agreement with the conclusion from the TGA data, that the 1-DDT bound to the CIS NCs surface is decomposing at the temperature of about 260°C. However, the absence of the C=S signal leads to the conclusion, that the thiol group (S-H) is still attached to the CIS NCs subsequent to the ligand decomposition.

The endothermic DSC peak observed at 328°C in combination with an additional mass loss of about 3% (see Fig. 4.3) was assigned to the evaporation of OLAM (compare the DSC peak at 332°C for pure OLAM (see Fig. 4.1(c)). In the IR spectra recorded at 327°C (see green line in Fig. 4.4) a signal assigned to the $\nu(\text{N-H})$ vibrational mode of the amine group is detected at 3332 cm^{-1} . Furthermore, the IR spectra show bands of the C-H stretching vibrations in the region of $2850\text{--}3000\text{ cm}^{-1}$ and more intense =C-H

deformation signals at 966 cm⁻¹ and 933 cm⁻¹ compared to those detected at 261°C, which are further indication for the evaporation of OLAM. Hence, the TGA/DSC signal observed at 328°C can be assigned to the evaporation of OLAM ligands from the powder sample, which are not bound to the CIS NCs.

The final broad DSC signal is observed at around 420°C with a simultaneous mass loss of 5% observed by TGA (see Fig. 4.3). This DSC peak is located at a higher temperature compared to those observed for the pure OLAM (see Fig. 4.1(c)) and TOPO ligands (see Fig. 4.1(d)). Whereas the desorption of OLAM is evidenced by the weak IR signal at 3012 cm⁻¹ (see blue line in Fig. 4.4), which is indicative of C=C double bonds in the (oleyl) hydrocarbon chain, neither phosphine oxide- nor amine-related signals are observed in the IR spectrum. In the case of TOPO, the absence of a phosphine oxide signal in the gas phase could be due to a strong bond of the functional group to the CIS NCs, so that the octyl groups are decomposed, whereas the phosphine oxide group might be fully oxidized. For OLAM, the absence of C-N and N-H signals could be due to a complete oxidation of the amine group to gaseous N₂, which is not detectable by IR. The TGA/DSC signal can therefore be assigned to the loss of the OLAM ligand and the decomposition of the TOPO ligand bound to the nanoparticle surface as well as the loss of this ligand's alkyl groups.

In conclusion, the combined TGA/DSC and FTIR analysis of the CIS NCs powder showed that the surface of the nanoparticles contains all three ligands, namely 1-DDT, OLAM and TOPO. Because long chain ligands can hinder the charge transport and transfer processes in the performance of BHJ solar cells, a ligand exchange with short ligands is a prerequisite for a better performance of these solar cells. One suitable ligand exchange method is the solution-process ligand exchange, which will be discussed in the following sections for the short-chain ligands hexanethiol and pyridine.

4.3 Hexanethiol ligand exchange

A TEM image and an UV-Vis spectrum of CIS NCs after a hexanethiol ligand exchange are depicted in Figs. 4.5(a) and (b). Here, no obvious changes in shape or size distribution as well as the absorption range of the NCs are observed, so that the properties of the nanoparticles do not seem to be influenced by this ligand exchange procedure (see discussion about the properties of as-synthesized CIS NCs in Chapter 3, section 3.1.1).

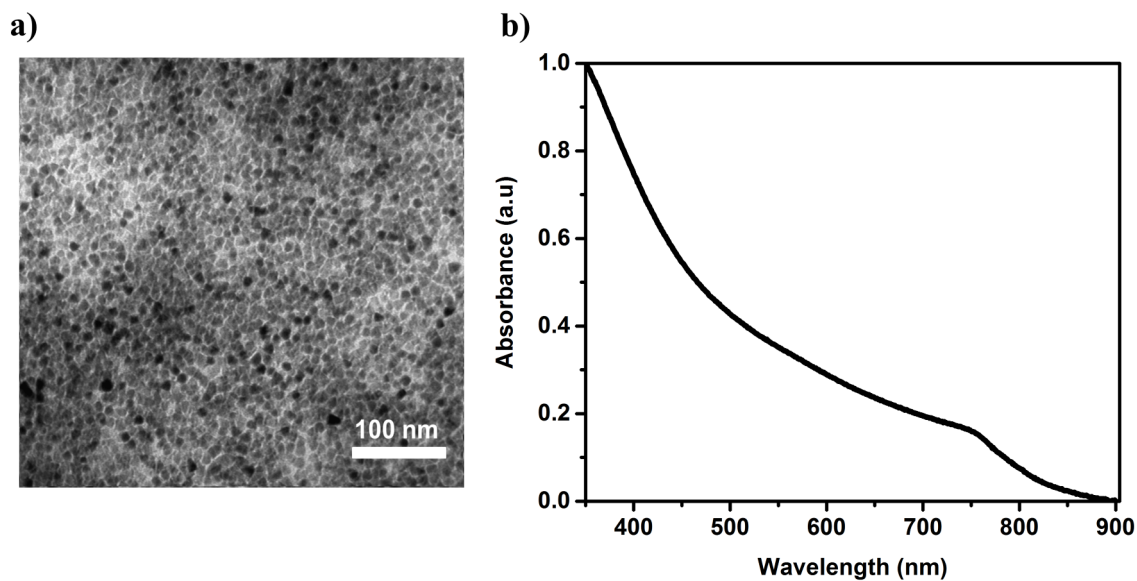


Figure 4.5: (a) TEM image and (b) UV-Vis spectrum of CIS NCs after hexanethiol ligand exchange.

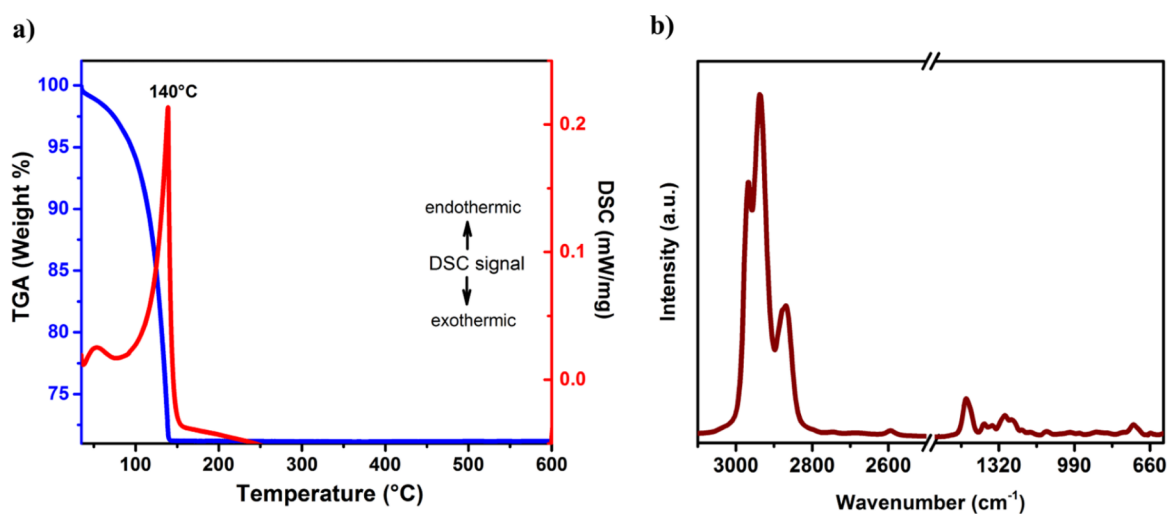


Figure 4.6: Representative (a) TGA (blue)/DSC (red) curves, and (b) FTIR spectrum of pure hexanethiol recorded at $T = 140^{\circ}\text{C}$.

For a comparison with the analysis results of the ligand shells of the CIS NCs after hexanethiol ligand exchange, pure hexanethiol was investigated by combined TGA/DSC and gas phase FTIR measurements (see Fig 4.6). The TGA/DSC measurement of pure

(liquid) hexanethiol in Fig. 4.6(a) shows the mass loss and an endothermic DSC peak at 140°C corresponding to the evaporation of hexanethiol.²

Figure 4.6(b) depicts the FTIR spectrum of pure hexanethiol recorded at 140°C. The characteristics IR bands for pure hexanethiol observed in Fig.4.6 are summarized in Table 4.2 with repective references. In the FTIR spectra of pure hexanethiol depicted in Fig.4.6(b) strong signals of C-H stretching vibrations are observed in the region from 3000 cm⁻¹ to 2800 cm⁻¹. The characteristic bands of the sulfur-containing molecules are visible at 2593 cm⁻¹ and 733 cm⁻¹, which are assigned to the $\nu(\text{S-H})$ stretching and $\nu(\text{C-S})$ stretching modes of hexanethiol (see Table 4.2).

Table 4.2: Assignments of the IR bands observed for hexanethiol (see Fig. 4.6(b))

Wavenumber (cm ⁻¹)	Vibrational modes ^{a)}	Ref.
2969, 2963, 2867	$\nu_s(\text{CH}_2)$, $\nu_{as}(\text{CH}_2)$, $\nu_{as}(\text{CH}_3)$	[103, 104]
2593	$\nu(\text{SH})$	[103, 104]
1463	$\delta(\text{CH}_3)$	[103, 104]
1381, 1347	$\nu(\text{C-C})$, $\nu(\text{C-O})$	[103, 104]
733	$\nu(\text{C-S})$	[103, 104]

a) ν_s = symmetric stretching vibration;

ν_{as} = asymmetric stretching vibration;

δ = bending vibration

In order to investigate the influence of the hexanethiol ligand exchange on the ligand shell surrounding the CIS NCs combined TGA/DSC and gas phase FTIR measurements of these particles (see Fig. 4.7) are discussed in the following in comparison to those of as-synthesized CIS NCs and pure hexanethiol (see Figs. 4.3, 4.4 and 4.6).

Figure 4.7(a) depicts respresentative TGA/DSC curves of CIS NCs subsequent to hexanethiol ligand exchange. The total mass loss of about 10% is comparable to that observed for the CIS NCs before ligand exchange (see Fig. 4.3). The TGA curve shows three steps of mass loss (located at about 200°C, 325°C and 400°C), which are accompanied by four endothermic DSC peaks (see Fig. 4.7(a)). These temperatures, at which the TGA/DSC signals are observed, are comparable to those for the CIS NCs before the

²The reason for ther mass loss detection of only 30% in Fig. 4.6(a) is most probably due to technical errors, which, however, do not affect the measurement.

ligand exchange (see Fig. 4.3) but show different amounts of sample weight loss in the different steps.

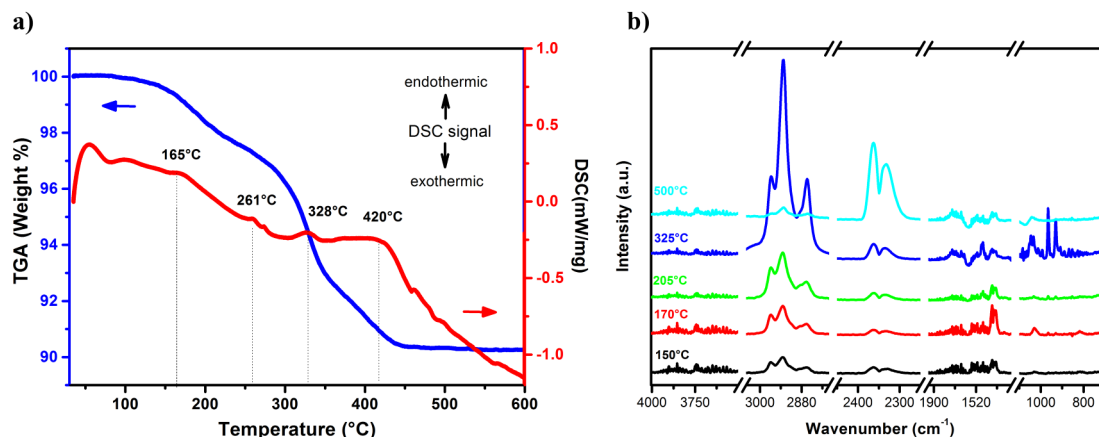


Figure 4.7: Representative (a) TGA (blue)/DSC (red) curves, and (b) gas phase FTIR spectra of a CIS NCs powder sample after the hexanethiol ligand exchange recorded at 150°C (black), 170°C (red), 205°C (green), 325°C (blue) and 500°C (cyan).

The TGA signal shows a mass loss of about 3% up to a temperature of 200°C (see Fig. 4.7(a)). As pure 1-DDT and hexanethiol evaporate at the temperatures of 140°C and 165°C, respectively, the mass loss can be ascribed to the evaporation of unbound 1-DDT and hexanethiol as well as water from the powder sample. In the gas phase FTIR spectra of a CIS NCs sample after hexanethiol ligand exchange shown in Fig. 4.7(b) characteristic C-H stretching vibrational bands are observed in the region of 3000-2850 cm⁻¹ at a comparably low temperature of 150°C (see black line in Fig. 4.7(b)), which derive from the evaporating hexanethiol ligands. The intensities of these signals increase with increasing temperature up to 205°C (see green line in Fig. 4.7(b)). The intensity increase of the C=S vibrational band at 1030 cm⁻¹ – already visible at 150°C – up to 170°C supports the TGA/DSC results showing an evaporation of the unbound hexanethiol and 1-DDT ligands in this temperature range.

The ligand exchange treatment resulted in an increase of the mass losses to about 5% detected in TGA (compared to the mass loss of initial CIS NCs of about 3% observed in Fig. 4.3). This mass loss occurs simultaneously to the detection of DSC peaks at temperatures of 261°C and 328°C, which were previously assigned to the decomposition of bound 1-DDT (and can also be assigned to hexanethiol due to the same functional

group) and unbound OLAM. The loss of OLAM at the latter temperature is further indicated by the IR spectrum recorded at 325°C, where signals of C-H stretching vibrations in the region of 3000-2850 cm⁻¹ as well as =C-H deformation bands at 966 cm⁻¹ and 933 cm⁻¹. These results are comparable to those obtained for the CIS NCs before hexanethiol ligand exchange (compare for Fig. 4.4), so that only evidence for a partial replacement of 1-DDT ligands by hexanethiol could be obtained.

The final mass loss of 3% assigned to the decomposition of the OLAM and TOPO ligands bound to the nanocrystals is comparable to that observed for the as-synthesized CIS NCs (see discussion of Fig. 4.3). This indicates, that the ligand exchange did not lead to a replacement of the OLAM and TOPO ligands by hexanethiol. Hence, the hexanethiol ligand exchange was only successful in a partial replacement of the 1-DDT ligands from the as-synthesized CIS NCs. Therefore, another replacement ligand, namely pyridine was chosen to remove and replace the 1-DDT, OLAM and TOPO ligands present after the colloidal synthesis.

4.4 Pyridine ligand exchange

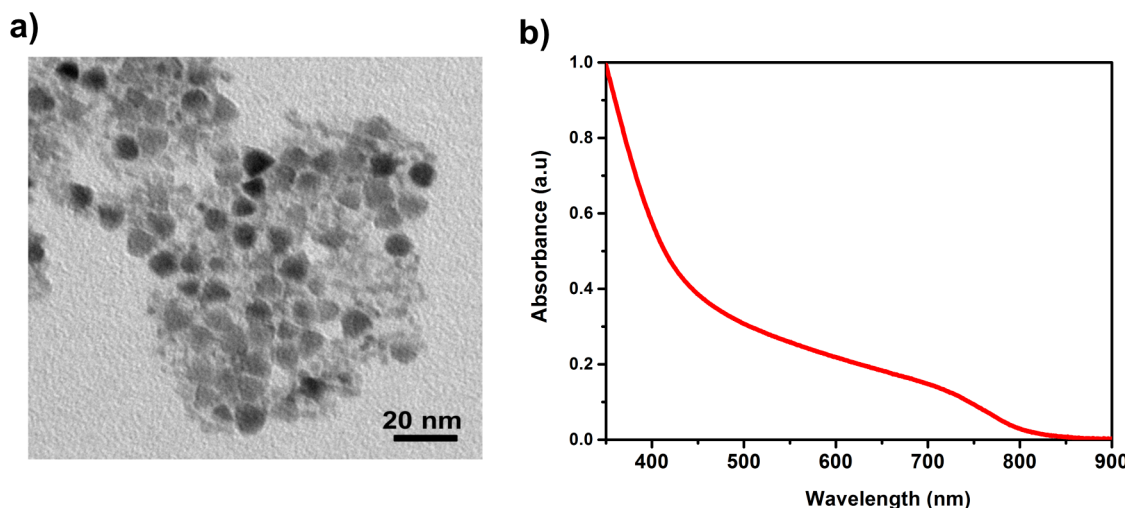


Figure 4.8: (a) TEM image and (b) UV-Vis spectrum of CIS NCs after pyridine ligand exchange.

The pyridine ligand exchange was carried out by a solution-phase ligand exchange method as described in Chapter 3 in order to replace the 1-DDT, OLAM and TOPO

ligands present on the as-synthesized CIS NCs, which could not be completely achieved with hexanethiol. Figure 4.8 shows a TEM image and the UV-Vis of the CIS NCs after pyridine ligand exchange.

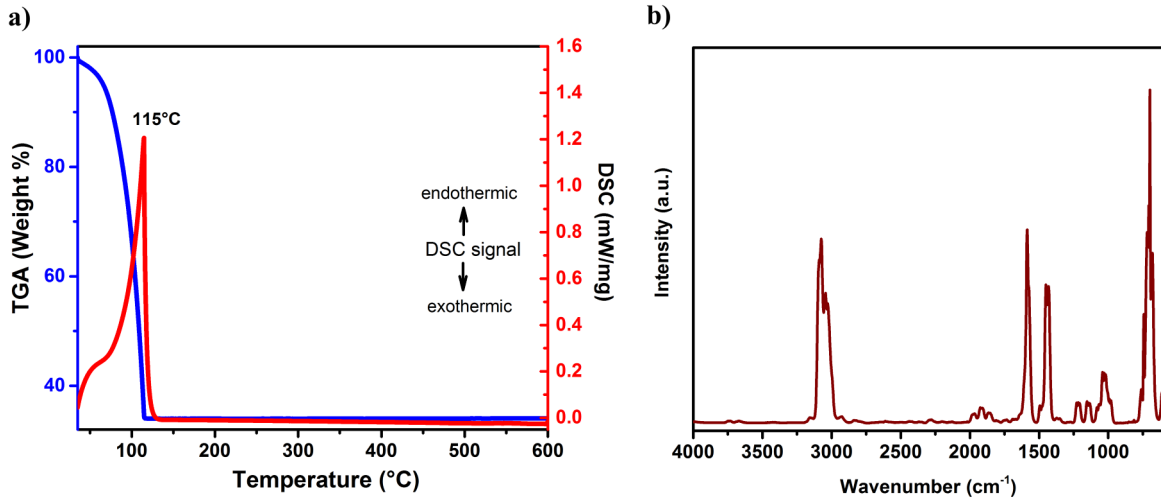


Figure 4.9: (a) TEM image and (b) UV-Vis spectrum of CIS NCs after pyridine ligand exchange.

Table 4.3: IR vibrational assignment of pyridine molecule (from Fig. 4.9(b))

Wavenumber (cm ⁻¹)	Vibrational modes ^{a)}	Ref.
3075, 3044	Aromatic ν_s (CH ₂), ν_{as} (CH ₂)	[103, 104]
1975, 1920, 1858	Aromatic (CH) overtones	[110]
1584	sym, ring wag-stretching	[111]
1443	In-plane C-H wagging	[103, 104]

a) ν_s = symmetric stretching vibration;

ν_{as} = asymmetric stretching vibration;

For a comparison with the analysis results of the ligand shells of the CIS NCs after pyridine ligand exchange, pure pyridine was investigated by combined TGA/DSC and FTIR measurements (see Fig. 4.9). The TGA of the pure (liquid) pyridine exhibits a mass loss at 115°C as shown in Fig. 4.9(a).³

³The reason for the mass loss detection of about 65% in Fig. 4.6(a) is most probably due to technical errors, which, however, do not affect the measurement.

The corresponding FTIR spectrum of pure pyridine recorded at 115°C is shown in Fig. 4.9(b). A list of characteristic IR bands observed for pyridine is given in Table 4.3 with respective references.

In order to investigate the influence of the pyridine ligand exchange on the ligand shell surrounding the CIS NCs, the combined TGA/DSC and gas phase FTIR measurements of these particles given in Fig. 4.10 are discussed by comparison to those of as-synthesized CIS NCs and pure pyridine (see Figs. 4.3, 4.4 and 4.9, respectively).

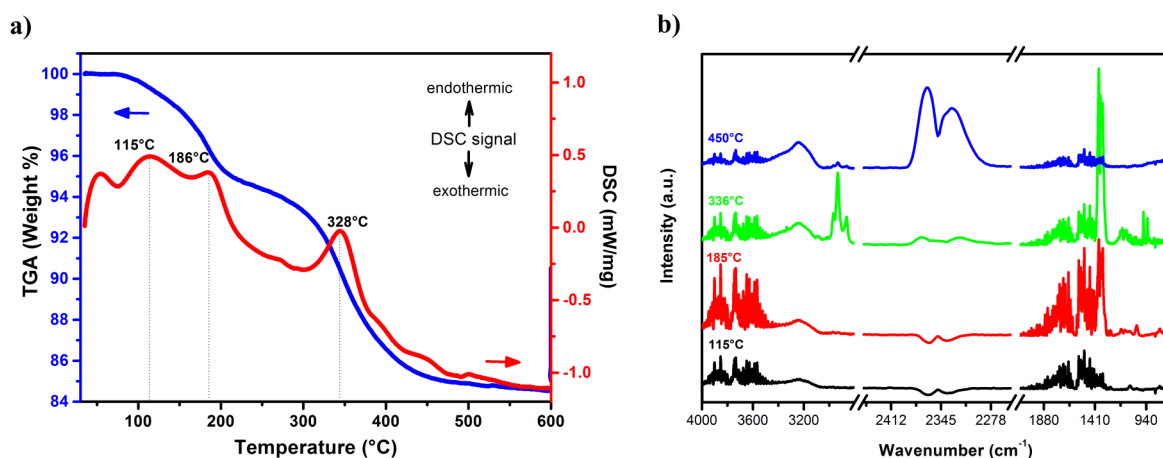


Figure 4.10: Representative (a) TGA (blue)/DSC (red) curves and (b) FTIR spectra of CIS NCs powder after pyridine ligand exchange at 115°C (black), 317°C (red), 336°C (green), and at 450°C (blue).

The combined TGA/DSC curves of CIS NCs after the pyridine ligand exchange are depicted in Fig. 4.10(a). The TGA shows a total mass loss of about 15% up to a temperature of about 450°C. Two steps of mass loss are observed in the TGA curves at about 200°C and 400°C. A mass loss of about 5% taking place up to a temperature of 200°C is accompanied by two DSC peaks at 115°C and 186°C. The low temperature signal occurs at the boiling temperature of pyridine at 115°C, so that it can be assigned to pyridine molecules not bound to the CIS NCs' surface, whereas the second DSC signal at 186°C is most probably due to the decomposition of bound pyridine ligands. The temperature shift can be explained by a stabilization of the molecules by the bonding to the particle surface. The FTIR spectra of the CIS NCs after pyridine ligand exchange recorded at different temperatures are shown in Fig. 4.10(b). The IR spectrum recorded at a temperature of 185°C (see red line in Fig. 4.10(b)), i.e., slightly above the decomposition

temperature of 1-DDT as discussed for Figs. 4.3 and 4.4), does not exhibit any band of C-H stretching vibrations in the region of $3000\text{--}2850\text{ cm}^{-1}$, which points to a removal of 1-DDT ligands from the CIS NCs surface by pyridine.

A third endothermic DSC signal observed at 328°C is accompanied by a mass loss of 10% up to 400°C (see Fig. 4.10(a)). The bands observed in the IR spectrum recorded at 336°C (see green line in Fig. 4.10(b)) in the region of $3000\text{--}2850\text{ cm}^{-1}$ confirm the presence of gaseous alkyl chains and thus a decomposition of OLAM. This means, the OLAM ligand is still present on the CIS NCs' surfaces, i.e., cannot be removed by pyridine ligand exchange. The IR spectra recorded at higher temperatures are in good agreement to the TGA/DSC measurements (see Fig. 4.10) as both show no evidence of the presence of TOPO ligands on the particles' surfaces, i.e., no mass loss/DSC signal or alkyl signals in the gas phase IR spectrum at temperatures around 450°C . Hence, the pyridine ligand exchange resulted in successful removal of the 1-DDT and TOPO ligands, whereas the OLAM ligands were still found to remain bound to the surface of the CIS NCs by gas phase IR.

4.5 Conclusion

The ligand shells of the CIS NCs before and after solution-process ligand exchange were investigated by combined TGA/DSC and FTIR measurements. The ligand shell of the as-synthesized CIS NCs were found to consist of three different compounds, namely 1-DDT, OLAM and TOPO. The solution-ligand exchange with hexanethiol as the replacement ligand only resulted in a partial removal of the 1-DDT ligands, so that subsequently the ligand shell of the CIS NCs was composed of hexanethiol, 1-DDT, OLAM and TOPO. The pyridine ligand exchange, on the other hand, led to a successful removal of the 1-DDT and TOPO ligands, whereas OLAM could not be replaced by pyridine. Here, the ligand shell of the pyridine-treated CIS NCs consisted of a mixture of pyridine and OLAM.

As the solution ligand exchanges with hexanethiol and pyridine were not able to remove all long-chain ligands from the in CIS NCs, further improvements have to be carried out for the ligand exchange regarding different kinds of replacement ligands and/or different ligand exchange procedures.

As mentioned before, long-chain ligands can affect the charge transport processes in nanoparticles. Therefore, the charge transport properties of the CIS NCs will be discussed in the next chapter.

Chapter 5

Charge transport through thin films made of colloidal CuInS_2 nanocrystals

Charge transport is one of important issue in BHJ solar cell. Charge transport in the thin films made of colloidal nanocrystals strongly affected by the ligand shell. In this chapter the charge transport characteristics in thin films of CIS NCs were investigated employing single carrier device structures, namely hole-only (HO) and electron-only (EO) devices.¹

5.1 Motivation

In the previous chapter the ligand shells surrounding the CIS NCs have been investigated. The charge transport properties of thin films made of these colloidal CIS NCs are

¹Parts of this chapter have been published in: **R. Miranti**, C. Krause, J. Parisi and H. Borchert, Mater. Res. Express 2, 066401 (2015)

discussed in this chapter based on measurements with single carrier devices. By a careful selection of the electrode materials (depending on their work functions) the devices can be built to be hole-only (HO), electron-only (EO) or bipolar devices. HO devices basically consist of a semiconductor film placed between high work function electrodes. In this configuration the work functions of both electrodes are close to the HOMO level of the CIS NCs, thus forming an Ohmic contact for hole injection, whereas a large barrier exists for the injection of electrons, so that electron conductivity is suppressed. For EO devices, electrode materials enabling electron injection but suppressing the injection of holes are required. Here, a systematic study of the charge carrier mobility in CIS NCs films is presented, which also includes a comparison to the charge carrier mobility in organic P3HT films.

5.2 Hole only P3HT

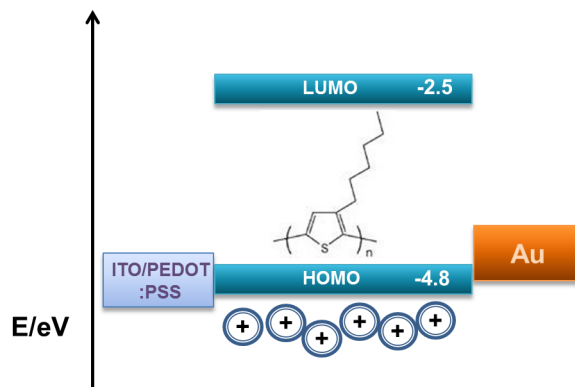


Figure 5.1: Energy diagram of the HOMO and LUMO levels of P3HT as well as the work functions of the electrode materials used in the HO device.

The space charge-limited current (SCLC) method was originally developed for organic semiconductors like P3HT. Here, the charge transport properties of P3HT used in this work as comparison material were investigated by applying the SCLC method. The HO devices with P3HT as dielectric layer were built by depositing the polymer on top of ITO/PEDOT:PSS. PEDOT:PSS was used as bottom contact because of the good alignment of the work function of PEDOT:PSS (about 5.2 eV [112]) with the HOMO

level of P3HT and its functionality as a hole-collecting interlayer [113]. As top contact, gold with a work function of about 5.1 eV was evaporated. An energy diagram of the materials used in this setup is depicted in Fig. 5.1.

Figure 5.2 shows representative J - V characteristics of a HO device with P3HT as well as the J - V plot on a double logarithmic scale. The J - V curve exhibits a poor rectification, which is caused by nearly symmetrical configuration of the device (see Fig. 5.1). For a correction of the applied voltage (V_{appl}), the voltage loss due to the series resistance (V_r) was subtracted. A series resistance (R_s) of around 4-6 Ω was determined from the obtained J - V curves of the reference devices without a P3HT layer (ITO/PEDOT:PSS/Au). The corrected data are shown in the inset of Fig. 5.2(b). At low voltages smaller than $V_{appl} - V_r = 0.2$ V the current exhibits an approximately linear development with $V_{appl} - V_r$ and follows Ohm's law (see the magenta fitting curve in the inset in Fig. 5.2(b)):

$$J_{Ohm} = qn\mu \frac{V}{d} \quad (5.1)$$

with the charge carrier density n , the mobility of the charge carriers μ and the thickness of the dielectric film d . In the ohmic regime, the current is limited by injection of charge carriers from the metal contacts.

At higher voltages ($V_{appl} - V_r = 0.2 - 2.7$ V), the J - V plot shows a transition to the SCLC regime. As mentioned in Chapter 2, the devices with different work functions should be corrected by the built-in voltages (V_{bi}). In order to obtain the built-in voltage (V_{bi}), the measured J - V data were fitted to Mott-Gurney model in the SCLC region as given below:

$$J_{SCLC} = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{d^3} \quad (5.2)$$

with the corrected voltage V ($V = V_{appl} - V_r - V_{bi}$) where V_{bi} is a fitting parameter. The measurements were furthermore carried out with samples of different thicknesses (see Fig. 5.2(c)) to confirm that the current is space charge-limited. The best fit was obtained for corrected voltages above $V_{appl} - V_r = 0.5$ V with $V_{bi} = 0.38 \pm 0.10$ V. This result for the V_{bi} is in good agreement with various literature reports [74, 75, 114], where the built-in voltage was calculated from the difference between the work

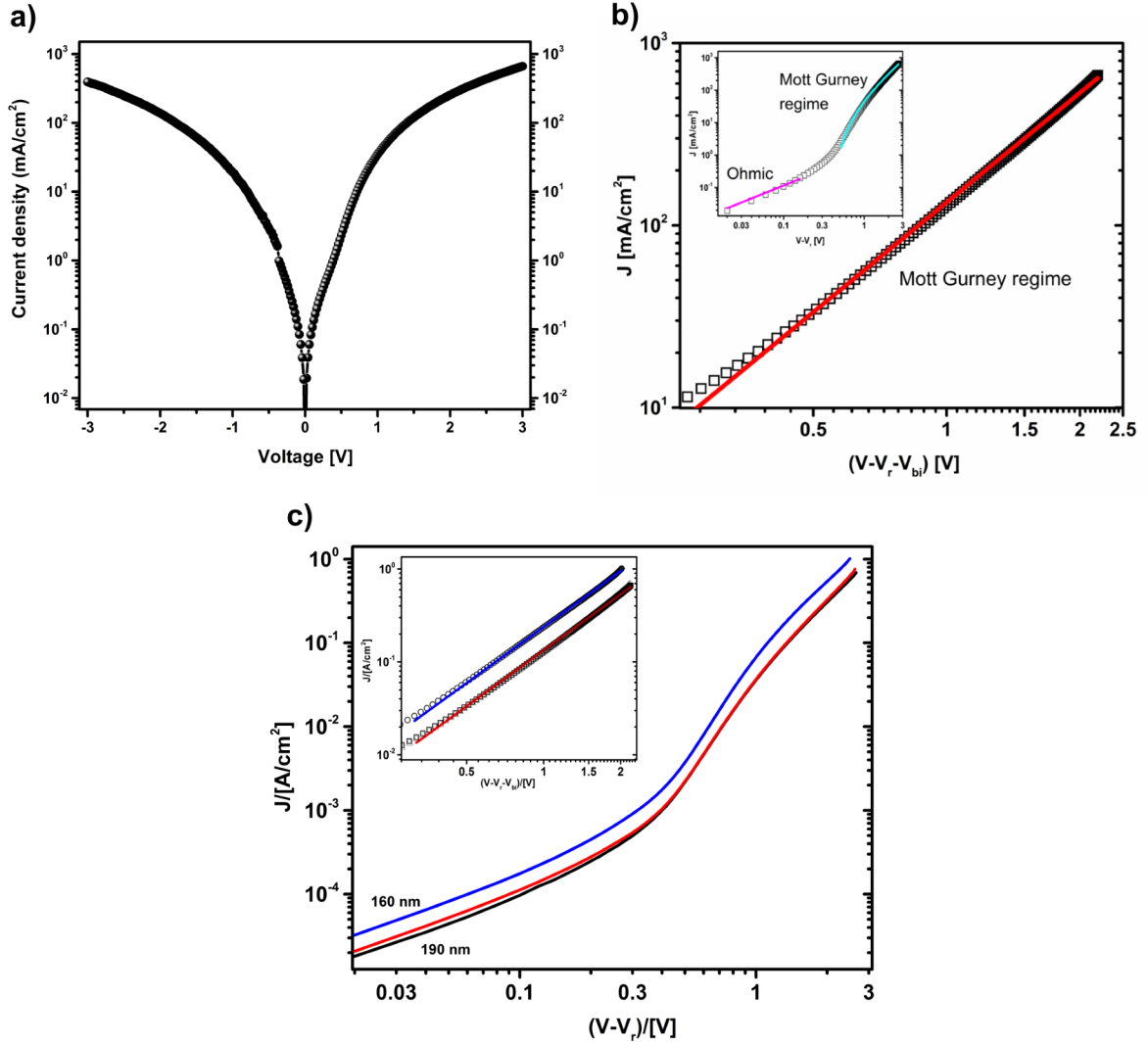


Figure 5.2: (a) The current density-voltage (J - V) characteristics for the HO devices with P3HT as well as (b) the corresponding J - V plot on a double logarithmic scale (after correction of the voltage for series resistance and the built-in voltage); in (b) the experimental data (black squares) as well as the fitting curve according to the Mott-Gurney model (red line) are shown; inset in (b): J - V plot before built-in voltage correction (experimental data (black squares) as well as fits according to Ohm's law at low voltage (magenta line) and the Mott-Gurney law at higher voltage (cyan line)); (c) J - V plots for HO devices with P3HT with different thicknesses.

function of the electrodes. The J - V data corrected by the built-in voltage and series resistance losses are shown in Fig. 5.2(b) including the SCLC fit. The data can be well fitted with Eq. (5.1), with $d = 190$ nm (for the selected sample shown in Fig. 5.2(b)) and the dielectric constant of P3HT ($\epsilon_r(\text{P3HT}) = 2.9$). The dielectric constant was calculated from measurements of the capacitance and the thickness of P3HT films placed between two parallel electrodes (see section 3.3.5) and is in good agreement with previous measurements using impedance spectroscopy [115]. As a result of the fitting procedure applied to all independent samples, we obtained a hole mobility for P3HT of $\mu_h(\text{P3HT}) = (3.9 \pm 1.01) \times 10^{-3} \text{ cm}^2/\text{Vs}$. This hole mobility is comparable to values reported elsewhere for regioregular P3HT [4, 73, 116–119]. Therefore, in the next section, the SCLC method and fitting procedure can be applied to the single carrier devices based on CIS NCs.

5.3 Charge transport in CIS NCs films

In this section, the charge transport properties of CIS NCs are investigated with HO and EO single carrier devices based on CIS NCs similar to those of P3HT in the previous section. Figure 5.3 shows the relative energy diagram of the LUMO and HOMO levels of CIS NCs in comparison to the work function (φ) of the electrodes used in the HO and EO devices. The HO devices were fabricated with ITO ($\varphi = 4.8$ eV) as bottom contact and gold (Au, $\varphi = 5.1$ eV) as top contact, which are commonly used electrode materials in HO devices [120, 121]. Furthermore the work functions of ITO and Au are well aligned with the HOMO level of the CIS NCs, which theoretically results in a good Ohmic contact and hence low contact resistance [122].

In the case of EO devices, Cr/Al/Cr and calcium (Ca) are used as bottom and top electrodes. Compared with HO devices, it is rather challenging to find suitable electrode materials to study the electron transport, because the electrode should have a low work function and a high chemical stability [123, 124]. Here, Ca is established as suitable top contact for electron injection due to its low work function ($\varphi = 2.8$ eV) [121, 125], which is close to the conduction band of the CIS NCs. For the bottom contacts, the stability of the electrodes is the main issue, because of possible reactions with the solvents during deposition of the electrode material layer, which was found for materials, such as low work function metals like Ca or Ba [126].

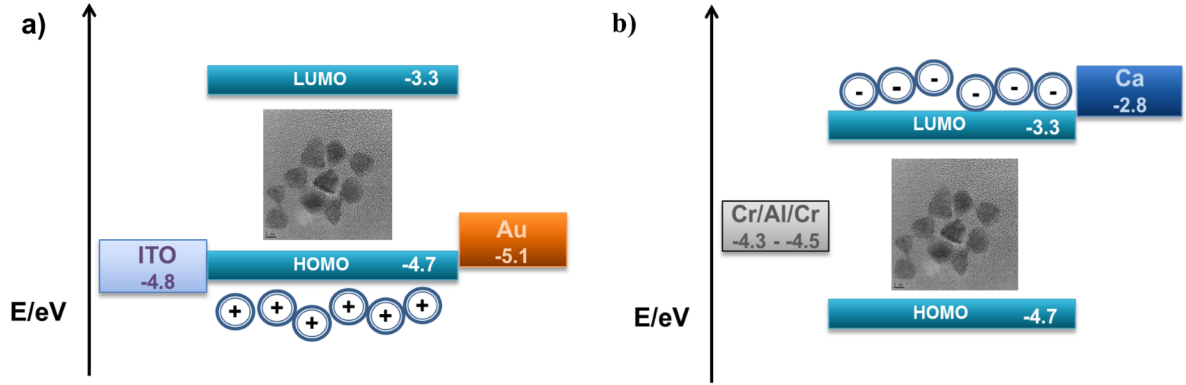


Figure 5.3: Energy diagram of the HOMO and LUMO levels of CIS NCs and work functions of the electrode materials used in (a) HO and (b) EO devices.

Cr/Al/Cr electrodes were chosen, because the work function of Al ($\varphi = 4.3$ eV) is in between the valence and conduction bands of CIS NCs. Several studies reported aluminum to be a good hole-blocking, but unfortunately a reactive bottom contact [123, 124]. Therefore, a thin protective Cr layer is used on the top of the Al layer to overcome the reactivity of Al from the solvent, as applied in case of inverted solar cells [127, 128]. However, the work function of such a composite metal electrode is not obvious. Pure Cr has a work function of $\varphi = 4.5$ eV, so the work function of the Cr/Al/Cr electrode should be in the range of 4.3-4.5 eV. As a consequence, the barrier for hole injection by this electrode is rather low, so that a significant contribution of the hole transport to the current in our devices with Cr/Al/Cr and Ca contacts cannot be excluded.

From the typical J - V curves of HO and EO devices with CIS NCs presented in Fig. 5.4 it is obvious that both devices show poor rectification characteristics. Although the EO device is expected to have a pronounced rectification ratio (based on the energy diagram presented in Fig. 5.3(b)), this is not observed in the experimental results. Figure 5.4 shows that the current density in the EO device is three orders of magnitude lower than that in the HO device. Since the conductivity is determined by the product of the charge carrier concentration and the charge carrier mobility, it is not directly evident, whether the higher hole current originates from a higher carrier concentration or a higher mobility. In the next section the charge transport properties in CIS NCs are investigated in more detail.

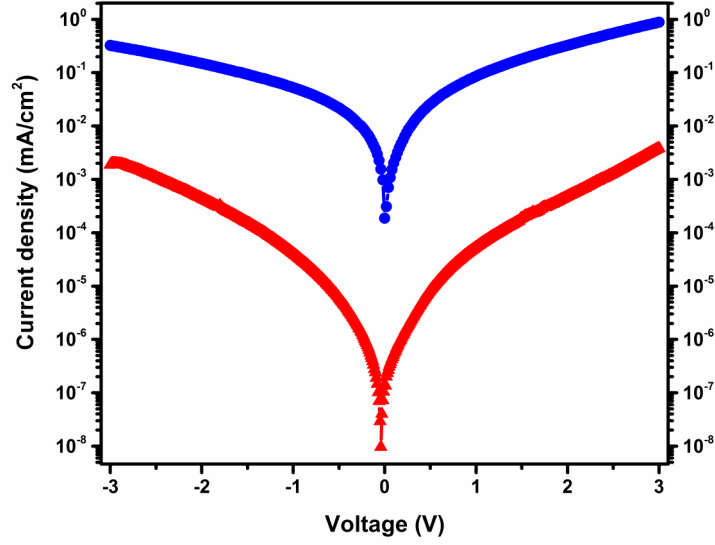


Figure 5.4: Representative current density-voltage (J - V) curves of HO (blue circles) and EO devices (red triangles) based on CIS NCs.

5.3.1 Hole transport in CIS NCs

Figure 5.5 shows the J - V plot of CIS NCs HO devices on a double logarithmic scale. After the voltage correction by the series resistance and built-in voltage (see description in section 5.2 as in the case of HO P3HT) it is found that in a fitting range of $V_{appl} - V_r = 0.5 - 5$ V the built-in voltage in HO devices of CIS NCs is $V_{bi} = 0.54 \pm 0.07$ V. A series resistance of $R_s = 3 - 4$ Ω was determined from the J - V curves of the ITO/Au reference device. The experiments were carried out with seventeen different samples, of which the thicknesses of the CIS NCs layer were measured individually. From the measured capacitance and the thickness of CIS NCs films placed between two parallel electrodes (see section 3.3.5) the dielectric constant of the CIS NCs was calculated to be ϵ_r (CIS NCs) = 5.4. Compared to the dielectric constant of bulk CIS ($\epsilon_r = 8 - 10$ [129, 130]), the value obtained for the CIS NCs is rather small. This, however, can be explained by considering that due to the measurement method, the obtained value for the CIS NCs' dielectric constant refers to a thin film of nanoparticles, which includes the space between the individual particles in the film. This is most likely the reason for the comparably low value of the dielectric constant and additionally shows that a simple application of values for bulk crystals would not be appropriate, as furthermore, size effects, differences in the crystal structure (chalcopyrite or wurtzite structure) and/or surrounding ligands

contribute to the differences.

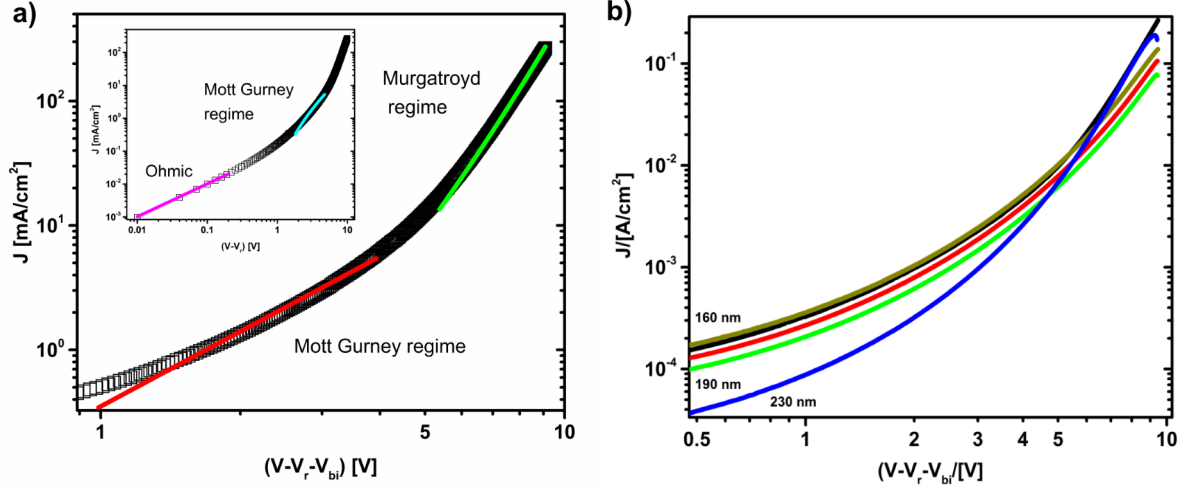


Figure 5.5: (a) The J - V plot for CIS NCs-based HO devices (black squares) on a double logarithmic scale including fits according to the Mott-Gurney model (red line) and Murgatroyd's model (green line); inset in (a): J - V plot before built-in voltage correction (experimental data (black squares) as well as fits according to Ohm's law at low voltages (magenta line) and the Mott-Gurney law at higher voltages (cyan line)); (b) J - V plots for different thicknesses of CIS NCs-based HO devices.

The J - V characteristics of the HO devices based on CIS NCs are shown in Fig. 5.4(a). In order to determine the hole mobility of CIS NCs the experimental data were fitted according to Eq. (5.1) (see red line in Fig. 5.4(a)). In comparison to the HO devices with P3HT, the fitting of the data obtained for CIS NCs-based HO devices using the Mott-Gurney model resulted in comparably high error values in the low voltage range ($V = V_{appl} - V_r - V_{bi} < 1$ V) (compare Fig. 5.2(b) and Fig. 5.4(a)). Furthermore, at voltages above 1 V, the data are not exactly linear in the double-logarithmic representation (see Fig. 5.4(a)), so that a fitting with the Mott-Gurney model can be applied only in a limited voltage range ($1 \text{ V} < V < 4 \text{ V}$) and thus can only be understood as a rough approximation to estimate the hole mobility of the CIS NC layer. Within this simple approximation, the hole mobility of $\mu_h(\text{CIS NCs}) = (2.5 \pm 0.3) \times 10^{-6} \text{ cm}^2/\text{Vs}$ was found to be three orders of magnitudes lower compared to that of P3HT. Deviations from the Mott-Gurney model might be related to the presence of a barrier caused by the charge carrier trap states, which are likely to occur in nanoparticle systems [106, 121]. In this

case, the presence of traps requires a consideration of the diffusion current in the fitting model, which is difficult in an analytical approximation [74, 131, 132].

At higher voltages (> 5 V), the experimental curve deviates strongly from the Mott-Gurney fit. Instead, the result in Fig. 5.5 can be fitted well with Murgatroyd's model, which shows the dependency of the SCLC on the electric field due to the Poole-Frenkel effect as given below (see section 2.2.1 for details):

$$J_{SCLC} = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{d^3} \exp \left\{ \frac{0.891}{kT} \left(\frac{q^3 V}{\pi \varepsilon_0 \varepsilon_r d} \right)^{\frac{1}{2}} \right\} \quad (5.3)$$

From the fitting according to Eq. (5.3) the zero-field mobility was calculated to be $\mu_0(\text{CIS NCs}) = (3.8 \pm 1) \times 10^{-9} \text{cm}^2/\text{Vs}$. For the voltage regime, where the Murgatroyd model is applicable, a representative mobility value was calculated at $V = V_{\text{appl}} - V_r - V_{bi} = 9$ V to be $\mu_h(\text{CIS NCs}, 9 \text{ V}) = (3.8 \pm 0.8) \times 10^{-6} \text{cm}^2/\text{Vs}$, i.e., an even higher value was obtained than in the Mott-Gurney regime.

5.3.2 Electron transport in CIS NCs

The electron transport properties were investigated using EO devices consisting of a CIS NCs layer sandwiched between Cr/Al/Cr and Ca contacts. In Fig. 5.6 the experimental J - V characteristics of the EO devices with a series resistance of $R_s = 3 - 5 \Omega$ are shown together with the fitting functions according to the models applied in this work. The electron current in these devices is by three orders of magnitude lower than the hole current in the HO devices (compare Fig. 5.4). Although for such small currents the series resistance plays a nearly negligible role, it was nevertheless considered in the calculations. At low voltages $V_{\text{appl}} < 0.3$ V the J - V characteristics were found to be of Ohmic nature (see inset in Fig. 5.6). In the range of $V_{\text{appl}} = 0.3 - 1.5$ V, the curve can roughly be approximated by the Mott-Gurney law, although the data is not exactly linear in the double-logarithmic representation (see Fig. 5.6). Fitting with Eq. (5.2) in this voltage range yields a value of $\mu_e(\text{CIS NCs}) = (3.2 \pm 1.5) \times 10^{-9} \text{cm}^2/\text{Vs}$ as a rough estimation of the electron mobility with a built-in voltage of $V_{bi} = 0.48 \pm 0.13$ V.

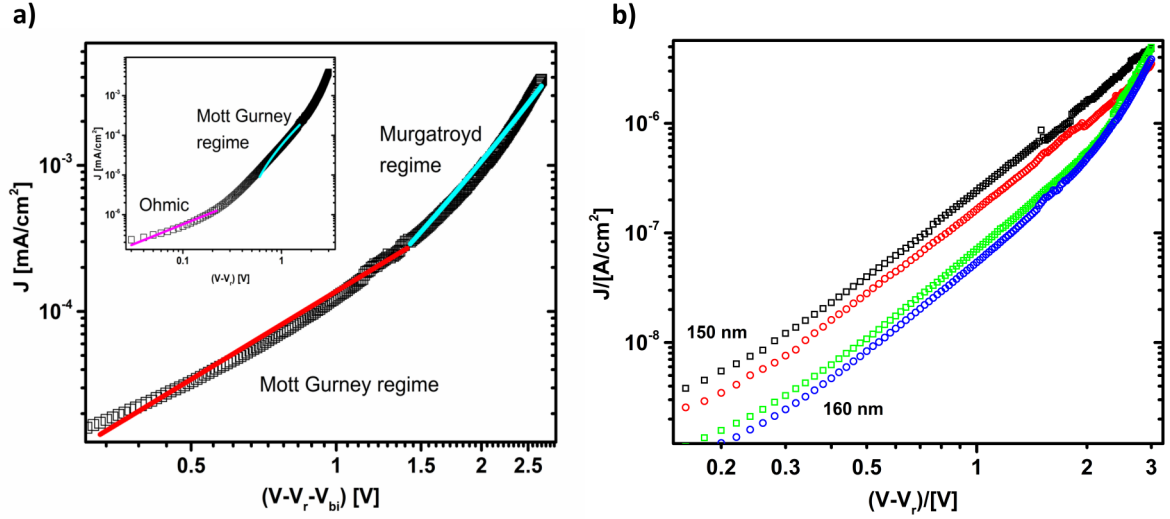


Figure 5.6: (a) The J - V plot for CIS NCs-based EO devices (black squares) on a double logarithmic scale including fits according to the Mott-Gurney model (red line) and Murgatroyd's model (cyan line); inset: J - V plot before built-in voltage correction (black squares) as well as fits according to Ohm's law at low voltages (magenta line) and the Mott-Gurney law at higher voltages (cyan line)); (b) J - V plots for different thicknesses of CIS NCs-based EO devices.

With an increase of the voltage beyond 1.5 V, the current increases faster than predicted by the Mott-Gurney model. However, taking into account a possible field-dependence of the mobility (Murgatroyd model) also does not give reasonable fitting results (see corresponding fitting attempt in Fig. 5.6(a)), so that the mechanism of electron transport seems to involve more factors than the ones taken into consideration by the trap-free SCLC models applied here. Furthermore, the behavior at voltages above 3 V could unfortunately not be studied, because the devices broke down under these conditions.

5.4 Conclusion

The charge transport in CIS NCs was analyzed by studying the J - V characteristics of CIS NCs-based single carrier devices. It was found that the charge transport in films of the prepared CIS NCs is hole-dominated. In order to understand the charge transport

in CIS NCs, a comparison to the characteristics of HO devices of P3HT was drawn. As a well-known semiconducting polymer, P3HT showed the space charge-limited current properties at voltages higher than 0.5 V (value corrected for the series resistance and built-in voltage). The fitting result with the Mott-Gurney model revealed a hole mobility of about $4 \times 10^{-3} \text{cm}^2/\text{Vs}$, which is comparable to values reported in recent literature. Since the J - V characteristics of HO devices with P3HT could be described well by the Mott-Gurney model, these devices are most likely free of trap states, so that the mobility does not depend on the electric field in the range studied. Contrary to this, the results of the HO devices based on CIS NCs exhibited an only approximate accordance to the theoretical description by the Mott-Gurney model in a limited voltage range. At higher voltages, good results were obtained by a fitting with the field-dependent Murgatroyd model. The hole mobility values for the CIS NCs films were in the order of $3 \times 10^{-6} \text{cm}^2/\text{Vs}$, i.e., rather low in comparison to those of the conductive polymer P3HT. Concerning the EO devices with CIS NCs, the models considered in the present work are only suitable as rough estimations for the electron mobility, with values being as low as $3 \times 10^{-9} \text{cm}^2/\text{Vs}$, i.e., an about 3 orders of magnitude lower electron than hole mobility in the CIS NCs films. Deviations between the rather simple theoretical models and experimental data might derive from charge carrier trap states, possibly related to the surface of the nanoparticles. A further development and application of more sophisticated models is necessary to obtain deeper insight into the charge transport through the nanocrystal films. However, the mobility of the CIS NCs films is expected to depend on the functionalization of nanocrystal surfaces with different organic ligand molecules. Therefore, surface modifications have a great potential to improve the charge transport in nanoparticle films.

Chapter 6

Photoinduced charge transfer in hybrid systems of CuInS₂ nanocrystals and conductive polymer

In this chapter a detailed investigation of the charge transfer as elemental processes involved in the mechanism of energy conversion is discussed. The photoinduced excited states and the processes of charge transfer in CuInS₂ (CIS) nanocrystal/polymer composites are studied with quasi-steady state photoinduced absorption (PIA) and steady state photoluminescence (PL) as well as time-resolved photoluminescence (TRPL) spectroscopy. The two different composites examined are CIS combined with poly(3-hexylthiophene) (P3HT) and CIS combined with poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT).¹

¹R. Miranti, Y.Firdaus, E.Fron, M. Van der Auweraer, J. Parisi, H. Borchert. J. Phys. Chem. C, 2015, 119, 22669–22680

6.1 Motivation

The performance of an excitonic solar cell is among others critically influenced by the charge generation and transfer at the donor/acceptor interfaces. Many studies have been conducted to investigate the fate of long-lived excited states in P3HT as well as the charge transfer from P3HT to organic fullerene acceptors [133, 134]. Another polymer frequently used in photovoltaics is the low bandgap polymer, PCPDTBT. This polymer is often used because of its smaller optical bandgap of $E_g = \sim 1.4$ eV, its broad absorption band, and its structure of alternating electron-rich and electron-deficient units. P3HT and PCPDTBT are well established bench mark materials for BHJ solar cells in combination with Phenyl-C61-butyric acid methyl ester (PCBM) [16, 135, 136]. Whereas the photoinduced charge carrier generation and transfer process in these blends are well studied [40, 137–141], corresponding studies on polymer/nanoparticle blends are rare [142–144]. In the case of polymer/CIS systems, only a few studies exist [145].

In this chapter, a comprehensive study of the charge generation and transfer mechanism in CIS NCs/polymer blends is presented. Therefore, systematic variations of the binary blends compositions were considered in both cases. A combination of PL and PIA spectroscopy was used to investigate long-lived excited species as well as photoinduced charge transfers in both P3HT/CIS NCs and PCPDTBT/CIS NCs blends. PL quenching is an indirect method to examine the charge transfer mechanism between donor and acceptor, but cannot generally distinguish between charge transfer and Förster [146, 147] or Dexter [148] type resonance energy transfers. In contrast, PIA is a useful method to directly investigate the photoinduced charge transfers in a blend. Besides quasi-steady state measurements, time-resolved photoluminescence (TRPL) spectroscopy was used to probe the kinetics of photoinduced charge transfers.

6.2 Charge carrier separation and transfer in P3HT/CIS NCs composites.

Figure 6.1 depicts the absorption and PL spectra as well as the energy levels of CIS NCs and pristine P3HT films. The absorption spectrum of the CIS NCs dissolved in chlorobenzene at RT (see Fig. 6.1(a), black line) is characterized by a broad band extending to ~ 800 nm (1.55 eV) with a shoulder at ~ 715 nm (1.74 eV).

The PL spectrum of the pristine P3HT film recorded at RT (see Fig.6.1(a) (red hollow)) shows a maximum at 724 nm (1.71 eV) as well as shoulders at 670 nm (1.85 eV) and 800-820 nm (1.5 - 1.51 eV), which correspond to the (0-1), (0-0) and (0-2) vibronic transitions, respectively. The Stokes shift between the (0-0) vibronic bands is 0.20 eV and the optical band gap is 1.95 eV. In the PL spectrum recorded at 80 K (Figs. 6.1(a), red line) the emission maxima undergo a red shift to 682 nm (1.82 eV), 747 nm (1.66 eV), 833 nm (1.49 eV) and 954 nm (1.3 eV), for the (0-0), (0-1), (0-2), and (0-3) vibronic transitions, respectively. At this temperature the intensity of the forbidden (0-0) transition is decreased significantly in good agreement to literature reports [149–151].

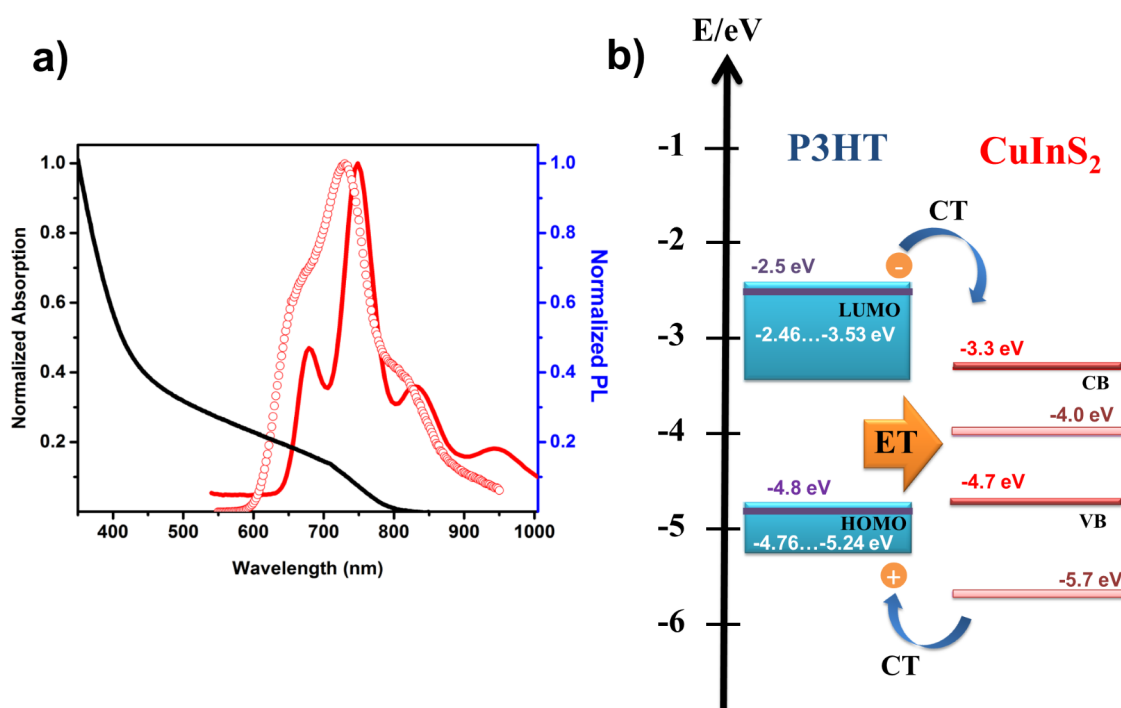


Figure 6.1: (a) The overlap of the donor PL spectrum with the acceptor absorption spectrum in the donor/acceptor systems consisting of P3HT/CIS NCs (PL of P3HT: at RT (hollow red circles) and at 80 K (red line); absorption of CIS NCs: black line) and (b) the scheme of the energy levels of P3HT and CIS NCs as well as possible energy and charge transfer processes; values for the energy levels are taken from the literature [8–14]

In the donor/acceptor system of P3HT/CIS composites, the values for the energy levels

as determined by cyclic voltammetry are compared to various literature reports in Fig. 6.1(b). This scheme concerns in particular the lowest unoccupied molecular orbital (LUMO) of P3HT as well as the valence and conduction band edges of CIS NCs. It is obvious that the values of the energy level of CIS NCs as well as the energy level values for P3HT determined by cyclic voltammetry vary strongly in the literature [8–14]. The energy levels, which were determined for CIS NCs with a wurtzite crystal structure in a previous work of our group [10] are substantially closer to the vacuum level than values measured by other groups for CIS NCs with a chalcopyrite crystal structure [14]. The large uncertainties in the values of the energy levels make it difficult to predict the nature of the heterojunctions. From the data available for the energy levels, it is not clear, whether the P3HT/CIS NCs system forms a type I or type II heterojunction. However, the observation of hole transfers from CIS NCs to P3HT in ESR measurements [152] rather suggests a type II heterojunction. The strong spectral overlap between the absorption of CIS NCs and the PL of P3HT (see Fig. 6.1(a)) indicates that an energy transfer from P3HT to CIS can be expected. Furthermore, the possibility of electron transfers from excited P3HT to the CIS NCs is suggested by the range of LUMO values of P3HT and the conduction band of CIS (Fig. 6.1(b)).

6.2.1 Steady state absorption and photoluminescence quenching

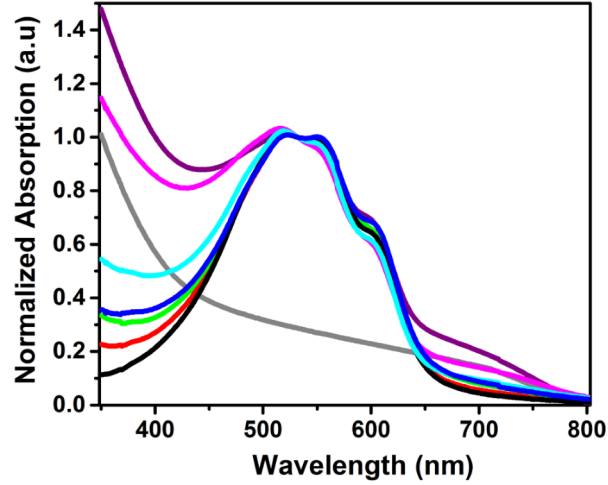


Figure 6.2: UV-Vis absorption spectra of CIS NCs in chlorobenzene solution (grey line) as well as P3HT/CIS NCs blends with different concentrations of CIS NCs in the blend: 0wt% (black line), 15wt% (red line), 30wt% (green line), 45wt% (blue line), 60wt% (cyan line), 75wt% (magenta line), and 90wt% (purple line); the spectra of thin films were normalized to the absorption at 532 nm (P3HT), which corresponds to the excitation wavelength used in PL and PIA experiments.

In order to investigate the energy and charge transfers from the polymers to the CIS NCs, the concentration of CIS NCs in the blends was systematically increased. Figure 6.2 shows the influence of the CIS NCs on the UV-Vis absorption spectra of P3HT/CIS NCs thin films as well as the UV-Vis absorption of CIS NCs dissolved in chlorobenzene. Increasing the concentration of CIS NCs in the P3HT/CIS NCs blends does not result in significant changes or band shifts for P3HT, but clearly yields an increased absorption in the spectral regions below 500 nm and above 650 nm, respectively (see Fig. 6.2). This indicates that the CIS NCs absorb light in a spectral region which is complementary to that of pristine P3HT (for absorption of pristine P3HT, see Fig.6.2, black line).

The changes in the PL spectra of the polymers with increasing concentrations of CIS NCs in the blends (recorded at 80 K) are presented in Fig. 6.3(a). The intensities of

the spectra are corrected by the absorption intensity of the polymer component in the composite films at the excitation wavelength as follows (see Chapter 3, section 3.3.1 for details):

$$A_{Polymer} \approx 1 - T_{Polymer} = 1 - 10^{-x \cdot OD_{10,blend}} \quad (6.1)$$

The PL spectra of the P3HT/CIS NCs films with different CIS NCs concentrations (see Fig. 6.3(a)) show features comparable to those of pristine P3HT (see discussion for Fig. 6.1(a)). A deconvolution of the spectra by a combination of four Gaussian peaks (Fig. 6.3(b)) did not result in significant changes of the wavelengths or relative intensities of the maxima for any of the different CIS NCs concentrations (see fitting results in Fig. 6.3(b) as well as FWHM and peak centers in Fig. 6.3(c)). The overall emission intensities of the PL signals, on the other hand, continuously decrease with increasing CIS NCs content (see Fig 6.3(c.ii)). Monitoring the PL intensity as a function of CIS NCs concentration reveals that the PL decreases with an increasing amount of CIS NCs, e.g., for the blend with 90wt% CIS NCs the PL intensity of pure P3HT is quenched by a factor of about 90%.

The observation of a PL reduction suggests a fast deactivation of the P3HT singlet exciton caused by a photoinduced electron or energy transfer from P3HT to the CIS NCs. The Stern-Volmer analysis depicted in Fig. 6.3(d) shows a linear regime for low CIS NCs concentrations, but a superlinear increase above 60wt% CIS NCs concentrations in the blend. A comparable superlinear behavior was also observed by Fan et al. in blends of conjugated polymers/Au NCs, who interpreted the superquenching as an indication for efficient energy or charge transfer between the polymers and the Au NCs [76]. Hence, the results presented in this work suggest that the energy or charge transfer in P3HT/CIS NCs blends becomes efficient for CIS NCs concentrations above 60wt%.

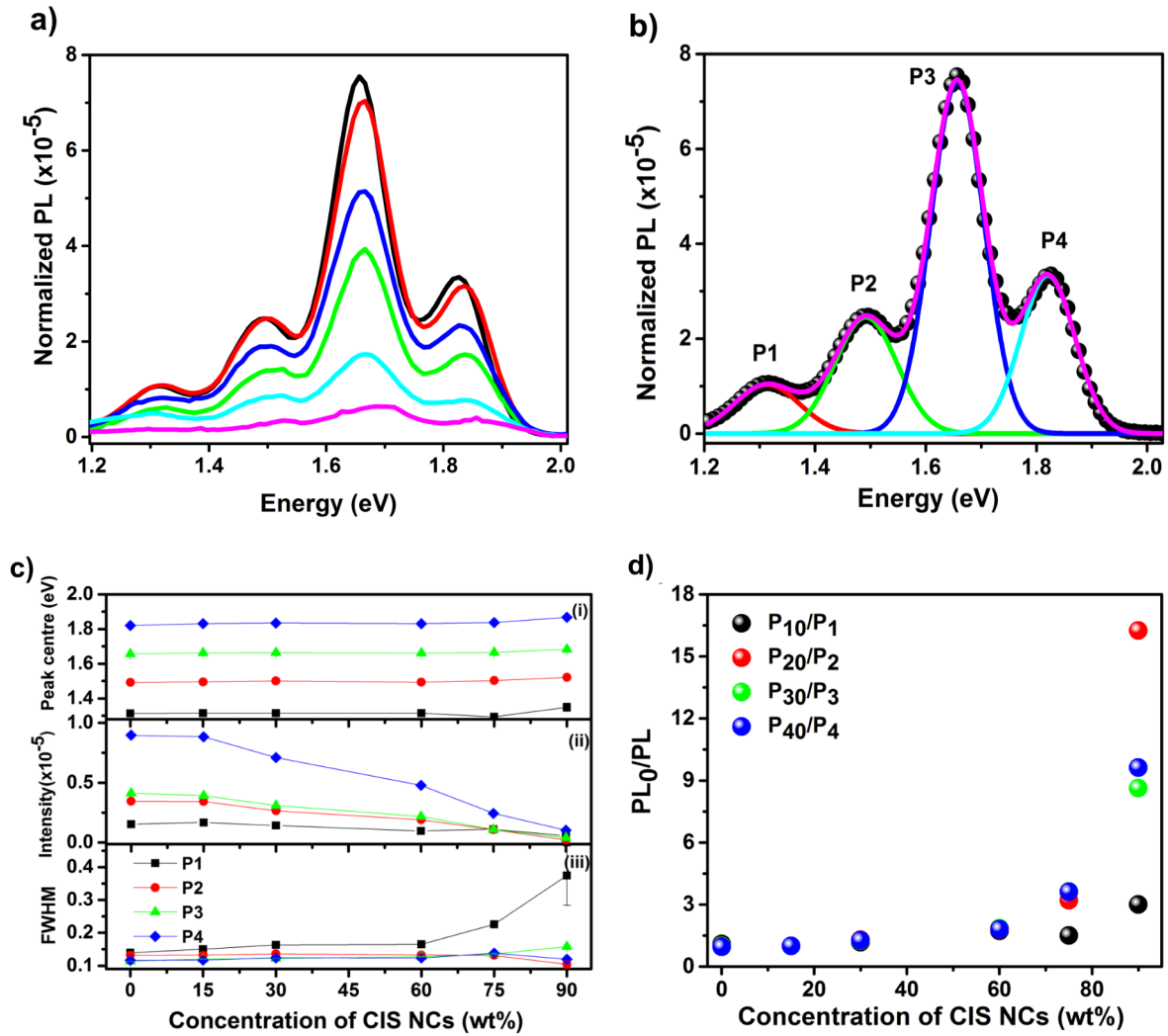


Figure 6.3: (a) PL quenching of P3HT/CIS NCs blends with different CIS NCs concentration: 0wt% (black line), 15wt% (red line), 30wt% (blue line), 60wt% (green line), 75wt% (cyan line), and 90wt% (magenta line); (b) deconvoluted peaks of the PL spectrum of P3HT into four Gaussian peaks located at 1.3 eV, 1.49 eV, 1.66 eV and 1.82 eV; (c) (i) peak centers, (ii) intensities and (iii) FWHM of the deconvoluted peaks; (d) Stern-Volmer plot of PL₀/PL vs. CIS NCs concentration for the Gaussian peaks P1, P2, P3 and P4 shown in (b).

6.2.2 Time-resolved photoluminescence decay study²

In this section, the detailed investigation of the charge generation in the blends of pristine P3HT films and P3HT/CIS NCs films by PL decay measurements at room temperature is presented. Figure 6.4 shows the PL decays obtained for pristine P3HT as well as blended P3HT/CIS NCs films. The CIS NCs concentrations in these films were again varied systematically. The films were excited at 500 nm and the corresponding decays recorded by monitoring the PL emission maxima at 675 nm (1.83 eV, see Fig. 6.4(a)), and 725 nm (1.71 eV, see Fig. 6.4(b)), as discussed before in section 6.2.1.

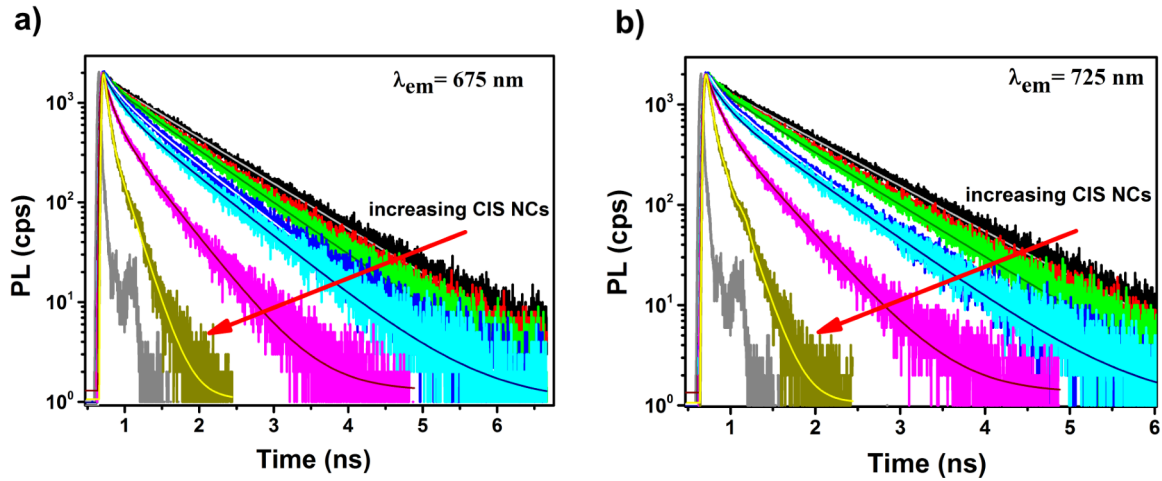


Figure 6.4: PL decays of P3HT films with (a) $\lambda_{em} = 675$ nm, (b) $\lambda_{em} = 725$ nm; the P3HT/CIS NCs blends have CIS NCs concentrations of: 0wt% (black), 15wt% (red), 30wt% (green), 45wt% (blue), 60wt% (cyan), 75wt% (magenta), 90wt% (dark yellow); the instrumental response function (grey line) is given in order to confirm that the time resolution of the setup is faster than the decays studied.

The PL decays recorded at 675 nm (1.83 eV, see Fig. 6.4(a)) shows non-exponential trends. Here, the pristine P3HT film displays the slowest PL decay, whereas in the presence of CIS NCs the PL decays faster with increasing CIS NCs concentration. A similar trend is observed for decays recorded at 725 nm (1.71 eV, see Fig. 6.4(b)). These

²The time-resolved PL measurements were done by cooperation partners, namely Y. Firdaus, E. Fron and M. Van der Auweraer, who also contributed to the discussion in the paper [153]. The results obtained from this measurements are given in Table 6.1

results indicate that the reduction of the PL decay time can be attributed to the presence of CIS NCs in the blend and supports the observation of PL quenching in the steady state measurements (see Fig.6.3(a)).

In order to obtain more detailed information about the PL quenching in the blends, the TRPL spectra were fitted to a sum of two exponentials as described in Chapter 3 (section 3.3.8):

$$I_{PL}(t) = A_1 \cdot \exp\left(-\frac{t}{\tau_1}\right) + A_2 \cdot \exp\left(-\frac{t}{\tau_2}\right) \quad (6.2)$$

The two decay times, however, allow the calculation of the amplitude-weighted average decay time $\langle\tau\rangle$ according to [2, 95]:

$$\langle\tau\rangle = \frac{A_1\tau_1 + A_2\tau_2}{A_1 + A_2} \quad (6.3)$$

with the amplitudes of the decay components at $t = 0$ s A_1 and A_2 . The relative contribution P_n of the n -th component to the stationary PL can be calculated by:

$$P_n = \frac{A_n\tau_n}{\sum_j A_j\tau_j} \quad (6.4)$$

So then the relative contributions of each component P_1 and P_2 are described as

$$P_1 = \frac{A_1\tau_1}{A_1\tau_1 + A_2\tau_2} \quad (6.5)$$

$$P_2 = \frac{A_2\tau_2}{A_1\tau_1 + A_2\tau_2} \quad (6.6)$$

The efficiency of the quenching in the different blends compared to the pristine polymer can be defined as:

$$\eta_Q = \left(1 - \frac{\langle\tau_{blend}\rangle}{\langle\tau_{polymer}\rangle}\right) \cdot 100\% \quad (6.7)$$

with the amplitude-weighted average PL decay time of the blend and pristine polymer film $\langle\tau_{blend}\rangle$ and $\langle\tau_{polymer}\rangle$, respectively.

The obtained biexponential decay parameters for all measurements of P3HT/CIS NCs blends are listed in Table 6.1. The error estimation for the lifetimes is about 10 ps, and the relative error of the amplitudes is below 10%. The TRPL analysis revealed in the framework of a biexponential fluorescence decay for the pure P3HT film a component with a short decay time τ_1 of about 70 ps and a long decay time τ_2 of about 950 ps, which are both within the experimental error independent of the emission wavelength (675 nm and 725 nm) (see Table 6.1). Mikhnenko *et al.* [154] reported, that a pronounced biexponential PL decay in thin films is usually observed in polymers with a large degree of energetic variation, such as P3HT. In the same report, they estimated the PL decay of P3HT films to occur on time-scales in the range of 600-900 ps [154], whereas Banerji *et al.* reported a shorter decay time of about 470 ps [155].

The long decay time τ_2 component in P3HT films can clearly be assigned to the monomolecular decay of the singlet exciton state, which is in agreement with various results from the literature [48, 155, 156]. Furthermore, the short decaying τ_1 component of the emission of pristine P3HT has been attributed to several processes [70, 157], namely molecular relaxations, energy transfer to more stable exciton states or nonfluorescent states [155, 158–162] and singlet-singlet, singlet-triplet and singlet-polaron annihilation [131, 163–165].

The average decay time $\langle\tau\rangle$ determined for the excited state in pristine P3HT is about 600-700 ps at both detection wavelengths, which is in agreement with values of the average decay time reported previously in the literature [155, 156]. By increasing the CIS NCs loading, the PL decay of P3HT increases progressively. Here, the contribution of the fast decaying component increases, whereas those of the long decay time and the average decay time decrease progressively. Both at 650 and 725 nm similar trends and decay parameters are observed.

As can be seen from Table 6.1, at both detection wavelengths the PL decay is quenched (with an efficiency η_Q) by approximately 30%, 70%, and 90% at CIS NCs loadings of 60wt%, 75wt%, and 90wt% CIS NCs, respectively. The broad range of decay times obtained for the quenching (which probably reflects a nonexponential decay) is due to the fact that the charge or energy transfer, which occurs on a time scale of a few tens of

picoseconds for P3HT chromophores adjacent to CIS NCs, has to be preceded by exciton hopping for P3HT chromophores located at larger distances from the QDs [166].

The observation that even at a loading of 90%, where in the case of homogeneous mixing all polymer chains should be in contact with CIS NCs, still a component with a decay time close to 200 ps is observed suggests the occurrence of a phase separation with a significant fraction of the P3HT chains being located too far from the CIS NCs to be quenched without preceding exciton hopping. The quenching can be attributed to either charge or energy transfer from the excited state of P3HT to the CIS NCs.

Table 6.1: PL decay parameters from biexponential fitting of P3HT films with increasing concentration of CIS NCs.

Compound	A_1	A_2	τ_1 (ps)	τ_2 (ps)	$\frac{A_1}{A_1+A_2}$	$\frac{A_1}{A_1+A_2}$	P_1 (%)	P_2 (%)	$\langle\tau\rangle$ (ps)	η_Q (%)
P3HT + CIS NCs (wt%)										
$\lambda_{em} = 675nm.$										
0	9	20	66	946	0.31	0.69	3.0	97.0	676	-
15	10	18	83	853	0.35	0.65	4.9	95.1	586	13
30	11	16	124	828	0.41	0.59	9.3	90.7	541.2	20
45	12	20	182	744	0.37	0.63	12.5	87.5	537	21
60	16	16	177	727	0.50	0.50	19.6	80.4	452	33
75	24	12	113	455	0.66	0.34	32.7	67.3	229	66
90	10	35	44	184	0.78	0.22	54	46	74.2	89
$\lambda_{em} = 725nm.$										
0	8	19	72	951	0.29	0.71	3.0	97.0	699	-
15	9	16	140	869	0.36	0.64	8.5	91.5	603	14
30	10	16	148	832	0.39	0.61	10.4	89.7	563	19
45	15	14	133	694	0.52	0.48	17	83.0	405	42
60	15	15	182	729	0.49	0.51	19.6	80.4	459	34
75	22	12	122	461	0.65	0.35	32.5	67.5	243	65
90	9	36	38	173	0.81	0.19	51.6	48.4	64.2	91

The plot of the ratio between the average decay time in pristine P3HT and the blends $\langle\tau_{P3HT}\rangle / \langle\tau_{blend}\rangle$ for both detection wavelengths is shown in Fig. 6.5(a). The ratio strongly increases at about 60wt% for both detection wavelengths, which means that

the decay time reduction becomes more pronounced above this concentration. This result is additionally supported by the PL quenching efficiency (η_Q) plotted in Fig. 6.5(b).

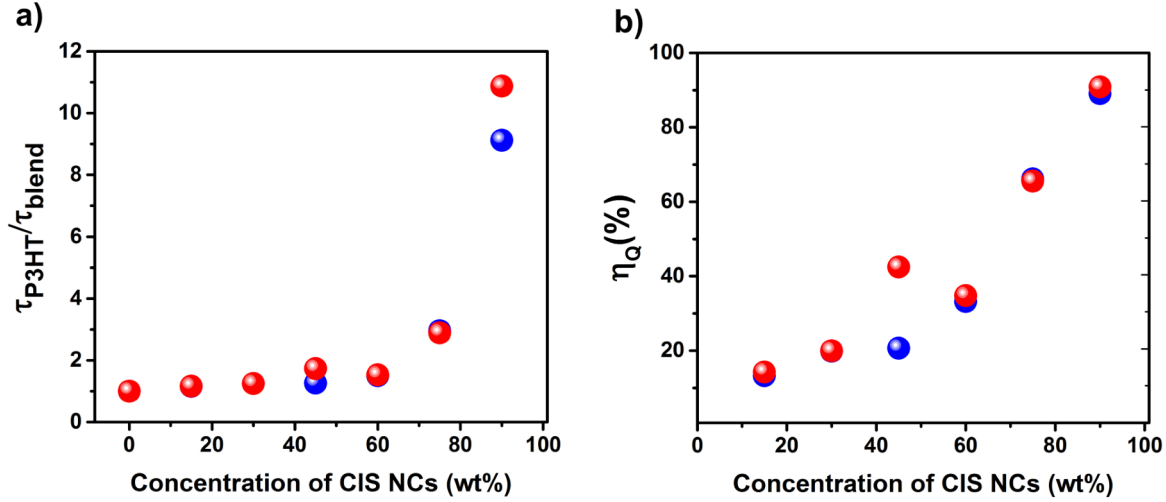


Figure 6.5: (a) The lifetime ratios of the average lifetime $\langle\tau_{P3HT}\rangle / \langle\tau_{blend}\rangle$ in pristine P3HT and P3HT/CIS NCs blends and (b) the PL quenching efficiency (η_Q) ; excitation wavelengths: 675 nm (blue dots) and 725 nm (red dots).

6.2.3 Photoinduced absorption in P3HT/CIS NCs blends

As mentioned before, PL quenching alone cannot distinguish between photo-induced charge transfer and other intermolecular interactions such as energy transfer. Quasi-steady state PIA monitors the change in the transmission spectrum caused by absorption by long-lived species such as polarons or triplets. Therefore, PIA spectroscopy is suitable to investigate the occurrence of charge transfer reactions at the donor-acceptor interface.

Figure 6.6 shows the PIA spectrum of pristine P3HT film (blue line) with contributions from photoinduced absorption (PIA, positive signals) as well as photobleaching (PB, negative signals). In the fingerprint region the PB bands of pristine P3HT are observed as negative signals around 2.0 eV, which is in agreement with literature reports [48, 138]. These signals are due to ground state depletion of the absorption of the conjugated polymer. Furthermore, pristine P3HT shows a broad PIA signal between 1.05 eV and 1.85 eV, which consists of three main absorption peaks in the near infrared and visible region at 1.05 eV, 1.23 eV, and 1.83 eV.

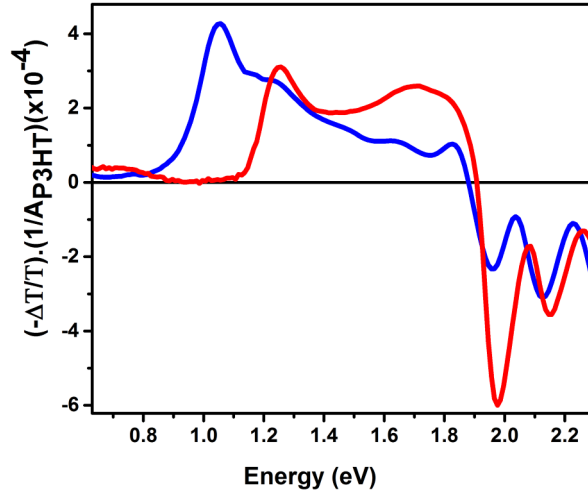


Figure 6.6: PIA spectra of pristine P3HT (blue line) and the donor/acceptor system P3HT/PCBM (red line) recorded at $T=80$ K with an excitation wavelength of 532 nm.

The peak at 1.05 eV was previously assigned to the triplet-triplet absorption of P3HT by Beek *et al.* [48]. However, no further indications of triplet exciton formation were detected [3, 134, 156, 167], neither in solution [156] nor by magnetic resonance measurement [134, 167]. Therefore, the transient absorption spectra rather suggest the efficient formation of polarons [3, 134, 156, 167], on the other hand, PIA spectra measured by magnetic resonance measurement assigned the peak to a spin-singlet interchain exciton [134, 167]. Therefore the peak at 1.05 eV is most probably indicating a long-lived singlet species of unclear nature.

The peaks at 1.24 eV and 1.83 eV are characteristic of polarons generated in P3HT [3, 4, 134, 138, 167]. The peak at 1.24 eV corresponds to the dipole-allowed transition from the semi-occupied molecular orbital (SOMO) to the LUMO of P3HT, whereas the peak at higher energy (1.83 eV) can be assigned to the corresponding transition in the case of delocalized polarons, as was previously suggested in the literatures [48, 134, 138, 168]. For comparison, the PIA spectrum of a P3HT/PCBM blend is also presented (see Fig. 6.6). The presence of PCBM in the blend results in the disappearance of the peak at 1.05 eV, whereas the peaks at 1.24 eV and 1.83 eV increase. Hwang *et al.* suggested that the transfer of mobile polarons in P3HT/PCBM films is initiated by the charge transfer (CT) into an intermediate CT bound state [138].

Figure 6.7 shows the PIA spectra of pure CIS NCs films. The most prominent feature is a peak at ~ 1.6 eV, which roughly matches the energy of the first excitonic transition in CIS NCs and can therefore be assigned to photobleaching of the ground state.

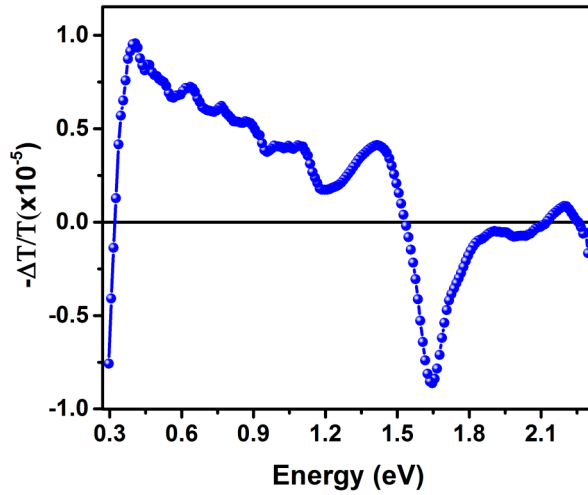


Figure 6.7: PIA spectrum of a CIS NCs film recorded at $T = 80$ K with a modulation frequency of 80 Hz and an laser excitation wavelength of 532 nm.

The in-phase PIA signal for P3HT and P3HT/CIS NCs blends recorded at (a) 80 K and (b) 295 K with an excitation wavelength of 532 nm and a modulation frequency of 80 Hz for the investigation of the P3HT/CIS NCs blend are shown in Fig. 6.8. At $T = 80$ K, all spectra show broad photoinduced absorption features below the bandgap of P3HT ($E_g \sim 1.8$ eV) indicating the generation of long-lived charge species by the laser light irradiation. All measured spectra consist of positive (PIA) and negative (photobleaching, PB) peaks. As discussed previously, the peak at 1.05 eV is assigned to a long-lived singlet exciton state in P3HT. In the films of P3HT/CIS NCs blends, this signal decreased upon addition of CIS NCs and disappears, when the loading with CIS NCs reaches 90wt%. The delocalized polaron signature at 1.83 eV, on the other hand, is slightly increased with a simultaneous appearance of, a new peak at 0.38 eV, which can be assigned to a transition from the HOMO of P3HT to the SOMO associated with localized polarons. This peak increases strongly for CIS NCs loadings of 75wt% and 90wt%.

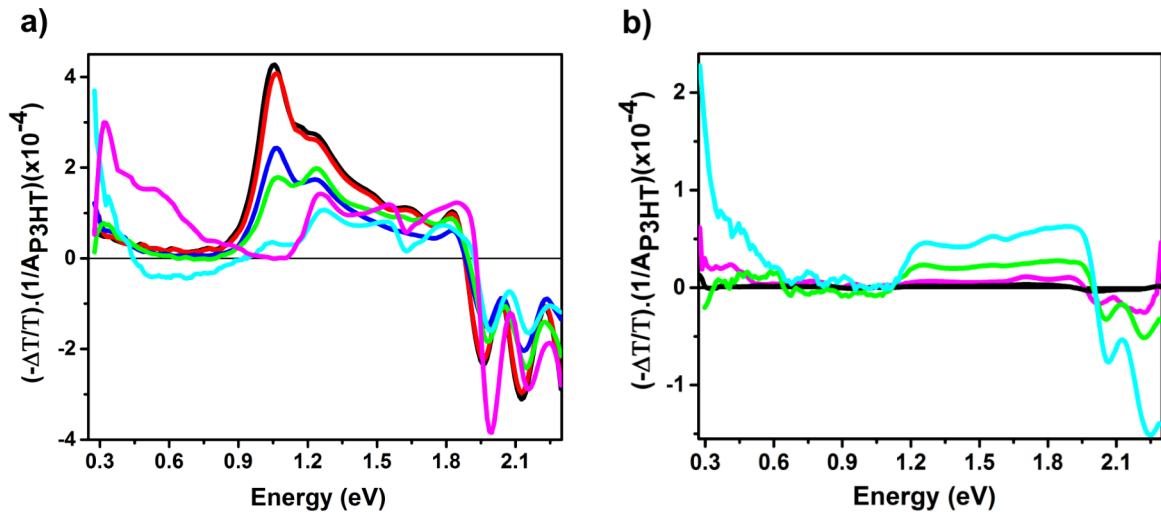


Figure 6.8: PIA spectra of P3HT/CIS NCs blends measured at (a) 80 K and (b) 295 K with an excitation wavelength of 532 nm; the loading of the polymer films with CIS NCs is 0wt% (black line), 15wt% (red line), 30wt% (blue line), 60wt% (green line), 75wt% (cyan line), and 90wt% (magenta line); the spectra are normalized to the absorption of P3HT at the excitation wavelength (see section 3.3.1).

In comparison with the P3HT/PCBM blend, the decreased of the singlet exciton band of P3HT (in Fig. 6.6) gives an indication of effective charge separation in the donor/acceptor interfaces, which was also observed in the P3HT/CIS NCs blends (compare Fig. 6.8 (a)). The charge separation in P3HT/CIS NCs composites, however, is more effective for higher loadings of CIS NCs. Furthermore, the efficiency of the electron transfer increases strongly for loadings of CIS NCs higher than 75 wt% in the P3HT blends, which is in good agreement with the results of the PL decay (see Table 6.1). A further increase of the CIS NCs loading to 90 wt% results in a broad PIA peak in the range of 0.3-0.7 eV. Since the pure CIS NCs films exhibit a weak PIA signal in this region (compare for Fig. 6.7), this feature, which is only observed for high CIS NCs loadings, most probably derives from species, such as polarons present in larger domains of CIS NCs.

Figure 6.8(b) depicts the PIA spectra at RT, which is closer to the real conditions for solar cell operation. At this temperature the peaks around 1.0-1.8 eV get broader. Upon addition of 75wt% CIS NCs to the blend the PIA signal of the polaron transition at ~ 0.3 eV as well as a pronounced feature indicative for delocalized polarons (around 1.8 eV)

appear in the spectrum, which provides evidence for charge transfer at room temperature. Contrary to what was observed at 80 K the amplitude of the PIA signal is smaller for a sample with 90wt% CIS NCs loading compared to a sample with 75wt% loading. This, however, might be attributed to larger carrier mobilities (electrons) leading to a faster recombination and hence smaller pseudo-stationary signal [154].

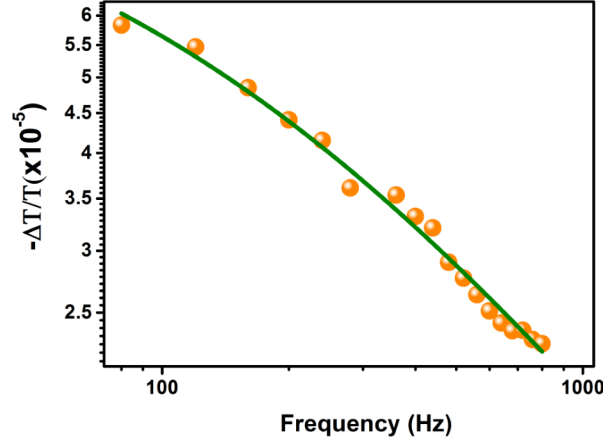


Figure 6.9: Double-log plot of the frequency dependence of the delocalized polaron peak observed at $E = 1.24$ eV during a measurement at $T = 80$ K (orange dots) fitted according to the dispersive recombination mechanism (green line).

Figure 6.9 shows the frequency dependence of the delocalized polaron peak (at 1.24 eV) of a P3HT/CIS NCs (75wt% CIS NCs) film in a double-log plot. The frequencies of the modulation were varied from 80 Hz to 1000 Hz at $T = 80$ K. The PIA signal intensity decreases with increasing frequency modulation (see Fig. 6.9, orange dots). As discussed in Chapter 2, the modulation frequency dependence of PIA signals give information about the recombination processes and life times characteristics in the blends [169]. In an amorphous blend, the relaxation process is usually described by the so-called dispersive recombination [82], which can be derived from:

$$\frac{\Delta T}{T} = \frac{(\Delta T/T)_0}{1 + (\omega\tau)^\gamma} \quad (6.8)$$

with the dispersive parameter $\gamma < 1$, is the mean lifetime τ and the steady state response at zero frequency $(\Delta T/T)_0$. The modulation frequency dependence for delocalized po-

larons at 1.25 eV in Fig. 6.9 is well-fitted with values of $\gamma = 0.72$ and $\tau = 7 \pm 0.18$ ms. The dispersive recombination process is observable in polymer/NCs films, as a consequence of trapping and de-trapping processes in NCs surface [80]. Epshtein *et al.* proposed that the γ value is related to trapping and de-trapping process in the blend, which is indicated by the multiple decay processes in the blend film due to the presence of the traps in bulk heterojunction solar cells [82]. The γ with smaller values point to a large charge carrier population in trap states, whereas the values close to unity indicate a small population of charge carriers in trap states. Heinemann *et al.* reported that the dispersive parameters for PCBM in a P3HT/PCBM blend and for CdSe NCs in a P3HT/CdSe film are about $\gamma_{PCBM} = 0.98$ and $\gamma_{CdSe} = 0.52$, respectively [79]. Their results show that the charge transfer process in P3HT/PCBM films is more effective than that in P3HT/CdSe NCs films, which is also indicated by the performances of solar cells with P3HT/CdSe NCs films [79].

6.2.4 P3HT/CIS NCs BHJ solar cell performances.

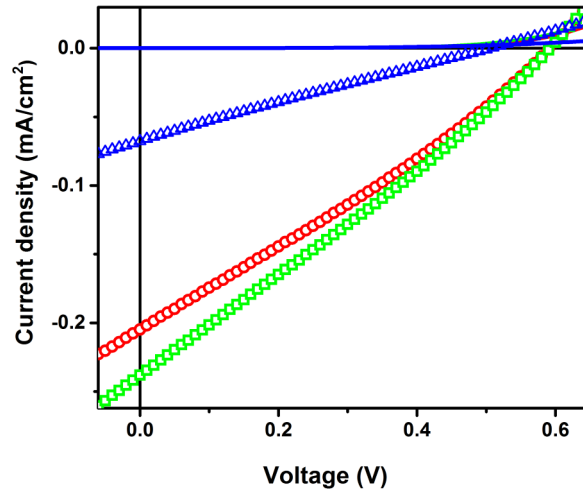


Figure 6.10: J-V curves of BHJ solar cells with CIS NCs loadings in the blends of 60wt% (red line), 75wt% (green line) and 90wt % (blue line).

Figure 6.10 shows the performance of P3HT/CIS NCs solar cells with higher concentrations ($> 60\text{wt}\%$) of CIS NCs in the P3HT/CIS NCs blends. The results show that the

most efficient solar cells devices with P3HT/CIS NCs blends are those with 75wt% CIS NCs, which exhibit values of PCE of 0.037%, $J_{SC} = 0.23 \text{ mA/cm}^2$, $V_{OC} = 0.59 \text{ V}$ and $FF = 27.6\%$) (see Fig. 6.10 and Table 6.2). The performance values of all solar cells are listed in Table 6.2.

Table 6.2: Average solar cell performances of P3HT/CIS NCs blends with different concentrations of CIS NCs (under 1 sun AM 1.5G illumination; devices structure: ITO/PEDOT:PSS/P3HT:CIS NCs/Al); values in brackets are the best values obtained.

Samples	J_{SC} (10^{-2} mA/cm^2)	V_{oc} (V)	FF (%)	PCE ($10^{-3}\%$)
P3HT/CIS NCs 60wt%	22 ± 2 (23)	0.57 ± 0.02 (0.59)	28.6 ± 0.2 (27.9)	36 ± 1 (38)
P3HT/CIS NCs 75wt%	23 ± 1 (24)	0.59 ± 0.01 (0.59)	27.6 ± 0.2 (27.9)	37 ± 3 (39)
P3HT/CIS NCs 90wt%	6 ± 1 (6)	0.49 ± 0.01 (0.52)	23.7 ± 0.2 (23.9)	7 ± 1 (8)

6.3 Charge carrier separation and transfer in PCPDTBT/CIS NCs composites

The film of pristine PCPDTBT has a broad absorption band (see grey line in Fig. 6.11(a)), with two main electronic transitions around $\sim 415 \text{ nm}$ and $\sim 730 \text{ nm}$. In the latter transition two shoulders at 701 nm (1.77 eV) and 740 nm (1.68 eV) are observed which can be attributed to the (0-1) and (0-0) vibronic transitions. At RT the emission of a pristine film of PCPDTBT (see hollow blue line in Fig. 6.11 (a)) has a maximum at 845 nm (1.49 eV) and a shoulder at 935 nm (1.33 eV), which can be attributed to the (0-0) and (0-1) vibronic transitions. The Stokes shift between the (0-0) vibronic bands amounts to 0.19 eV, which is comparable to the value of 0.20 eV obtained for P3HT (see discussion in section 6.2), whereas the optical band gap amounts to 1.60 eV. Compared to the results obtained at RT the emission maxima for the (0-0) and (0-1) vibronic transitions observed at 80 K are red-shifted to 880 nm (1.41 eV) and 992 nm (1.25 eV), respectively. In analogy to P3HT the intensity of the (0-1) transition is increased significantly relative to that of the (0-0) transition (compare Fig. 6.1(a)).

Moreover, for the CIS NCs thin films, which show no emission at RT, a narrow band is observed at 80 K with a maximum at 980 nm (1.27 eV) (see green line in Fig. 6.11(a)).

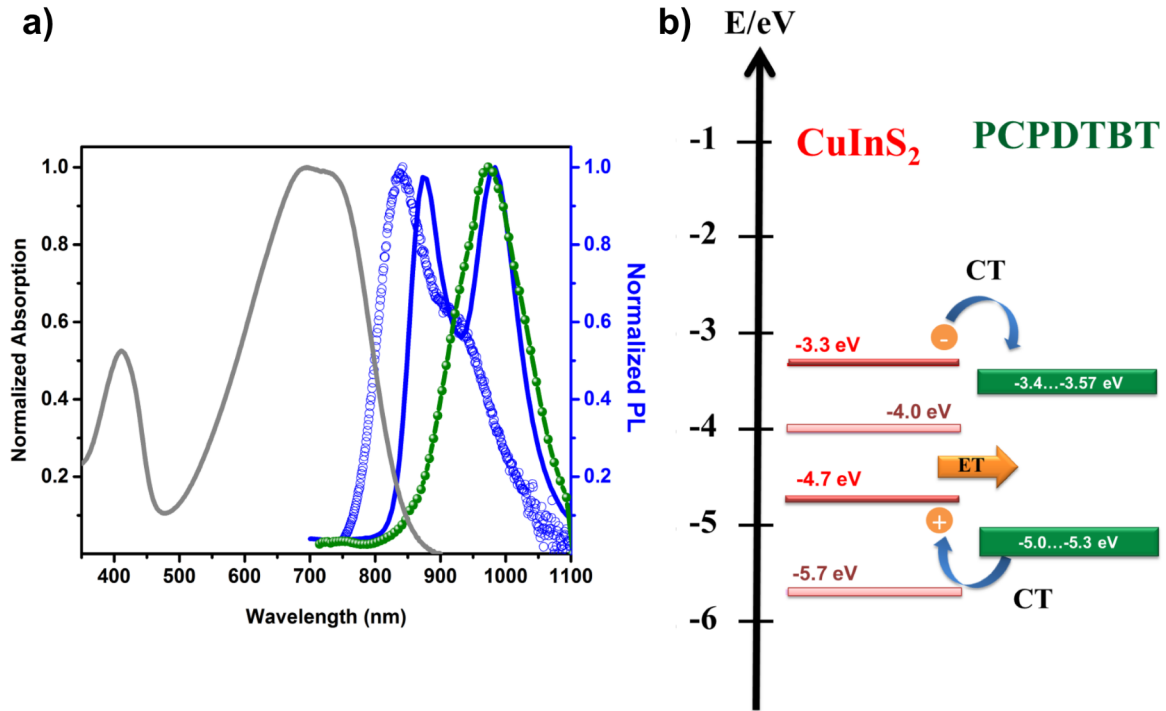


Figure 6.11: (a) The overlap of the donor PL spectrum with the acceptor absorption in the donor/acceptor systems consisting of CIS NCs/PCPDTBT (absorption of PCPDTBT (grey line), PL of CIS NCs (dotted green line), PL of PCPDTBT: at RT (hollow blue) and 80 K (blue line)); (b) scheme of the energy levels of CIS NCs and PCPDTBT and possible energy or charge transfer processes; values for the energy levels were taken from the literature [10, 14–16].

The PCPDTBT/CIS NCs composite shows a small overlap between the absorption of the CIS NCs and the PL of PCPDTBT as well as between the absorption of PCPDTBT and the PL of CIS NCs. Hence, there is an only small probability for energy transfer for this system, which is due to the large Stokes shift of both PCPDTBT and the CIS NCs. Figure 6.11 (b) shows the energy levels of PCPDTBT and CIS NCs determined by cyclic voltammetry taken from the references [10, 14–16]. The energy level alignment of PCPDTBT/CIS NCs corresponds more clearly to a type II heterojunction suitable for charge separation at the interface. With the levels measured for the wurtzite-type

CIS NCs used in this work, the nanoparticles most probably play the role of the electron donor and the polymer the role of the acceptor, which was recently also reported for blends of PCPDTBT with alloyed (ZnS)_x(CuInS₂)_{1-x} nanocrystals [170].

6.3.1 Steady state absorption and photoluminescence quenching

Figure 6.12 depicts the absorption spectra of PCPDTBT blend films with different concentrations of CIS NCs. Upon increasing the loading of CIS NCs in the PCPDTBT/CIS NCs blend, the feature at ~ 730 nm remains unaffected, whereas a pronounced increase of absorption is observed in the range below 600 nm due to absorption of the CIS NCs.

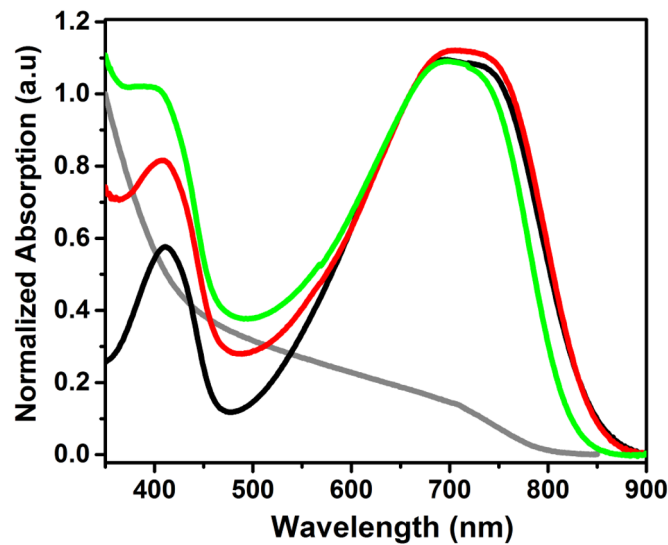


Figure 6.12: UV-Vis absorption spectra of CIS NCs in chlorobenzene solution (grey line) as well as PCPDTBT/CIS NCs blends with different concentrations of CIS NCs: 0wt% (black line), 60wt% (red line), and 75wt% (green line); the spectra of the thin films were normalized to the absorption at 660 nm, which corresponds to the excitation wavelength for PL and PIA experiments (see sections 6.3.1 and 6.3.3).

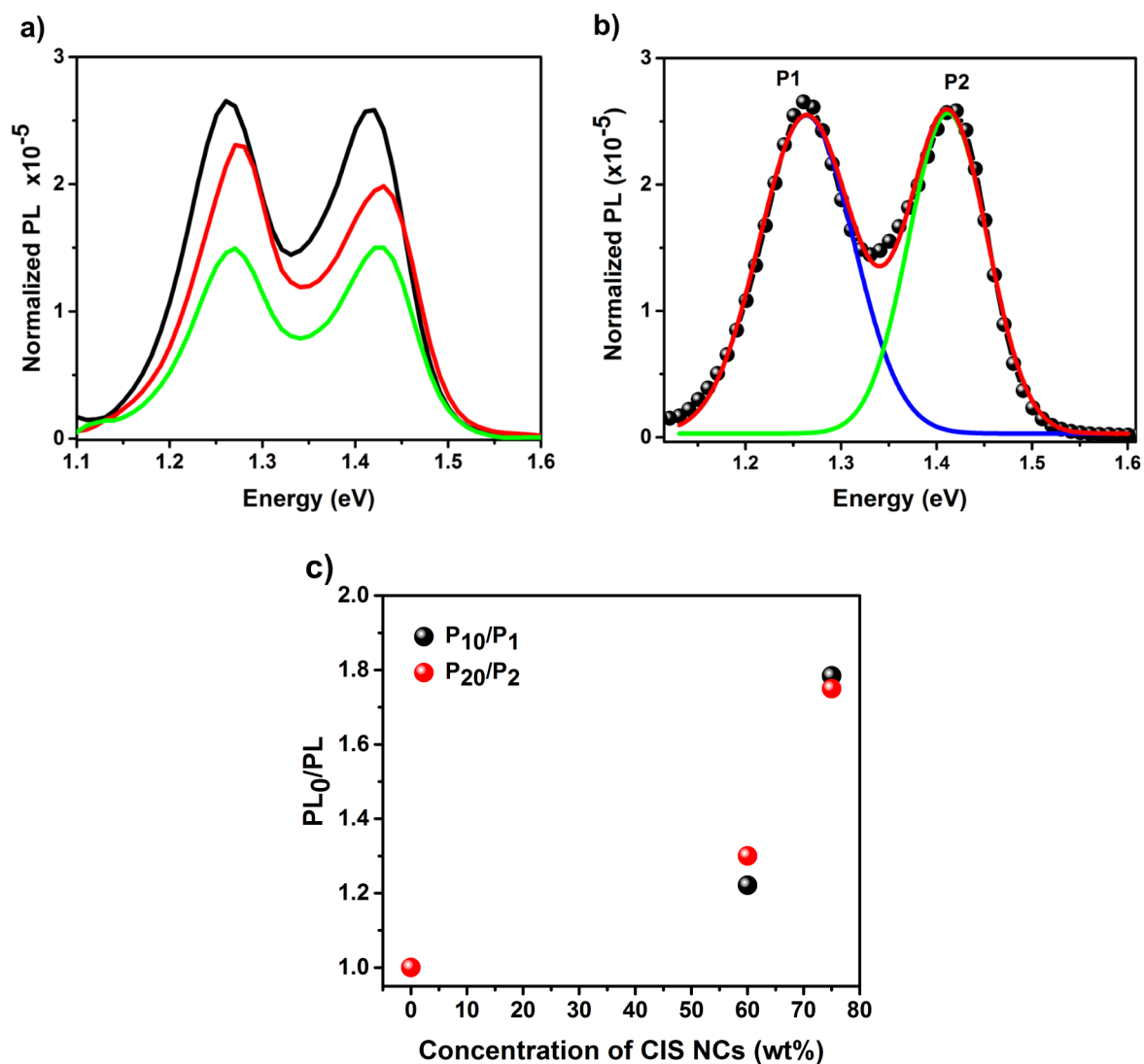


Figure 6.13: (a) PL quenching of PCPDTBT/CIS NCs blends with different CIS NCs concentrations: 0wt% (black line), 60wt% (red line), and 75wt% (green line) (spectra are normalized to the absorption of the PCPDTBT component at 660 nm), (b) deconvolution of the PL spectrum of pristine PCPDTBT into two Gaussian peaks located at 1.28 eV and 1.44 eV and (c) Stern-Volmer plot of PL_0/PL vs. CIS NCs concentration for the Gaussian peaks P1 and P2 shown in (b).

Figure 6.13(a) shows the changes in the PL spectra of PCPDTBT films with increasing concentrations of CIS NCs in the blends at 80 K. The intensity of the spectra is corrected in intensity by the absorption of the polymer component in the composite films at

the excitation wavelength (see Chapter 3, section 3.3.7 for details). The PL spectrum of a pristine PCPDTBT thin film can be deconvoluted into two Gaussian peaks (see Fig. 6.13(b)). Upon addition of CIS NCs the PL intensity of the blends decreases compared to that of the pristine PCPDTBT film (see Fig. 6.13(a)). Here, a CIS NCs concentration as high as 75wt% leads to a PL quenching by 40% of both emission peaks. Hence, PCPDTBT/CIS NCs blends show less quenching than the P3HT/CIS NCs system (compare for Fig. 6.3(a)), which indicates less photoinduced transfer in the PCPDTBT/CIS NCs blends and/or substantial back electron transfer to the π - π^* excited state of the polymer.

Furthermore, the Stern-Volmer plot of PCPDTBT/CIS NCs composites shows only a slight increase of the quenching for the highest concentration of CIS NCs in the blends (75wt%, see Fig. 6.3 (c)) indicating a less pronounced charge transfer. It should be noted that due to the small overlap of the PL spectrum of PCPDTBT and the absorption spectrum of the CIS NCs (Fig. 6.12) the possibility of energy transfer is reduced strongly compared to the system P3HT/CIS NCs.

6.3.2 Time-resolved photoluminescence decay³

Figure 6.14 depicts the PL decays of pristine PCPDTBT and blends of PCPDTBT and CIS NCs excited at 660 nm and recorded at $\lambda_{\text{em}} = 850$ nm (1.45 eV), which corresponds to the (0-0) transition of PCPDTBT. Qualitative inspection of the decays shows stronger decays with increasing loadings of CIS NCs in the blends. However, the increase of the decay rate is less pronounced than for the combination of P3HT and CIS NCs. For all samples the fluorescence decay could be analyzed as a sum of two exponentials according to Eq. (6.2).

³The time-resolved PL measurements were done by cooperation partners, namely Y. Firdaus, E. Fron and M. Van der Auweraer, who also contributed to the discussion in the paper [153]. The results obtained from this measurements are given in Table 6.3

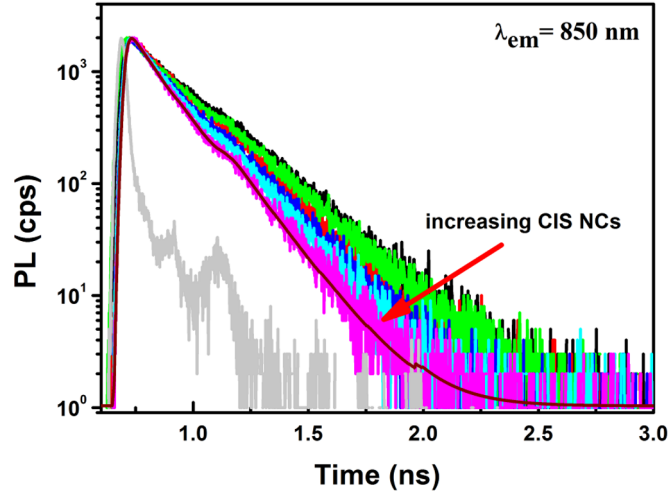


Figure 6.14: PL decays of PCPDTBT films with $\lambda_{em} = 850$ nm; the CIS NCs/PCPDTBT blends have CIS NCs concentrations of: 0wt% (black), 15wt% (red), 30wt% (green), 45wt% (blue), 60wt% (cyan), 75wt% (magenta); the instrumental response function (grey line) is given in order to confirm that the time resolution of the setup is faster than the decays studied.

Similar to P3HT, the PL decay of pristine PCPDTBT also can be analyzed as a sum of two exponentials with a fast decaying component with a decay time τ_1 of 31 ps, which is at the limit of the time resolution of the set-up, and a slower decaying component with a decay time τ_2 of 226 ps, which results in an average decay time $\langle\tau\rangle$ of 150 ps (see Table 6.3). The decay time of the slowly decaying component, τ_2 , of pristine PCPDTBT is consistent with the decay rate obtained in previous reports of the excitonic decay in PCPDTBT, where it was attributed to the decay of the population of singlet excited species of PCPDTBT [139, 171].

Furthermore, picosecond pump-probe experiments by Hwang *et al.* on pristine PCPDTBT showed a bi-exponential decay with decay times of 20 ps and 120 ps for the singlet excited state [171]. The shorter decay time obtained for the slow decaying component in their report could be due to the occurrence of singlet-singlet, singlet-triplet and singlet-polaron annihilation due to the high intensities of the pump laser pulse used in pump-probe experiments [163–165, 172]. Jarzab *et al.* [139] obtained a broad range of PL decay times for PCPDTBT, which is probably related to the exposure of the samples the

sample to oxygen. In their study, samples exposed to oxygen were reported to have population decay times of ~ 78 ps [139] was reported, freshly prepared samples showed longer population decay times (~ 220 ps) comparable to the one observed here. Despite the smaller energetic disorder compared to P3HT, which was expected to result in a mono-exponential decay [154], it is observed that the addition of a second fast decaying component to the analysis of the decays results in a significant quality improvement of the fits to the decay curves.

In analogy to the results obtained for the P3HT/CIS NCs blends, the addition of CIS NCs in the PCPDTBT blends leads to a slight decrease of the average decay time as well as that of the long decay time component (and thus its relative weight), whereas the decay time of the fast decaying component shows a slight increase with increasing CIS NCs concentration in the blends (see Table 6.1). Contrary to the results obtained for P3HT/CIS NCs blend, the changes in the decay of the PL became pronounced in PCPDTBT/CIS NCs blends only for CIS NCs loadings of at least 30wt% to 45wt%. Here, for PCPDTBT/CIS NCs blend with a high CIS NCs loading of, e.g., 75wt% the efficiency of the quenching amounts only about 21%.

Table 6.3: Photoluminescence decay parameters from biexponential fitting of PCPDTBT samples with increasing concentration of CIS NCs.

Compound	A_1	A_2	τ_1 (ps)	τ_2 (ps)	$\frac{A_1}{A_1+A_2}$	$\frac{A_1}{A_1+A_2}$	P_1 (%)	P_2 (%)	$\langle\tau\rangle$ (ps)	η_Q (%)
PCPDTBT + CIS NCs (wt%)										
$\lambda_{em} = 850\text{nm.}$										
0	12	19	31	226	0.39	0.61	8	92	150	-
15	8	25	67	199	0.24	0.76	9	91	167	0
30	11	18	42	224	0.38	0.62	10	90	155	0
45	11	23	57	186	0.32	0.68	12	88	144	4
60	13	22	68	176	0.37	0.63	19	81	136	10
75	16	19	75	161	0.46	0.54	28	72	122	20

Plots of the average decay time ratio ($\tau_{PCPDTBT}/\tau_{blend}$) and the PL quenching efficiency (η_Q) are shown in Fig. 6.15. It is observed that the increase of the ratio with increasing CIS NCs loading in the PCPDTBT/CIS NCs blends is considerably less pronounced compared to the P3HT/CIS system. In addition, the limiting value of the short decay

time at high loadings is much larger than that obtained for the P3HT/CIS NCs system, which indicates that the charge and/or energy transfer between the excited PCPDTBT and the adjacent CIS NCs is significantly slower.

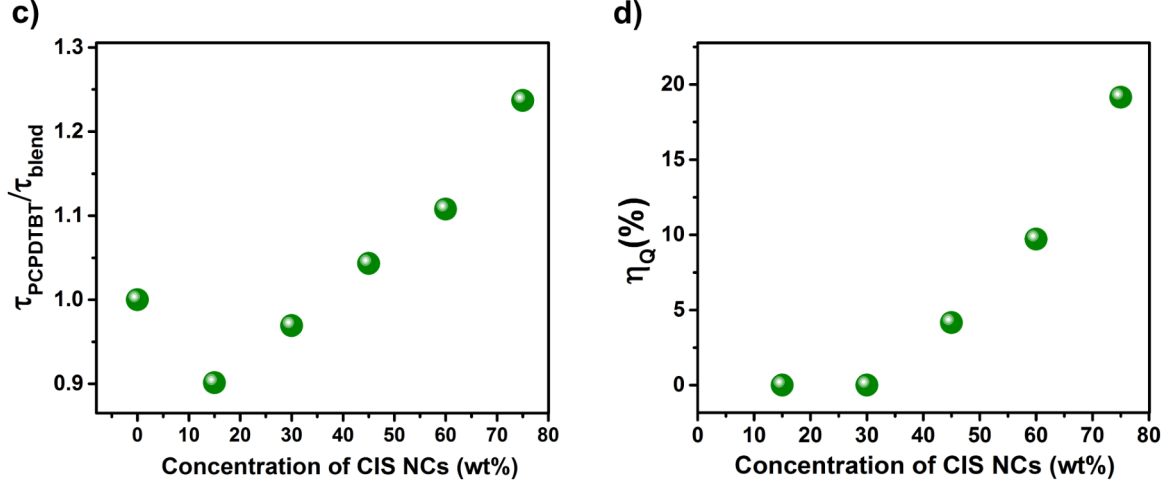


Figure 6.15: (a) The average lifetime ratios ($\tau_{\text{PCPDTBT}}/\tau_{\text{blend}}$) and (b) the PL quenching efficiencies (η_Q) (detected at 850 nm) of pristine PCPDTBT and PCPDTBT/CIS NCs blends with different CIS NCs loadings.

6.3.3 Photoinduced absorption in PCPDTBT/CIS NCs blends

Figure 6.16 shows the PIA spectrum of a pristine PCPDTBT and PCPDTBT/PCBM blends films recorded at $T = 80$ K. The spectrum of pristine PCPDTBT (see green line in Fig. 6.16) exhibits a negative band centered at 1.55 eV, which is in good agreement with previous reports [171, 173] and can be assigned to ground state depletion. The PIA signals further exhibit a strong peak at 1.0 eV and a broad peak between 0.3-0.7 eV. Transient absorption measurements by other groups indicated the presence of singlet excitons generated after photo-excitations with decay times of about 60-78 ps in the range of 0.62-1.03 eV [171, 173]. Moreover, the TRPL measurement of a pristine PCPDTBT film depicted in Fig. 6.14 shows that the decay time of the excited single state is about 200 ps, which points to the possibility that the formation of singlet excitons occurring immediately after photo-exciton generation. This means that this species might be converted at least partially by an intersystem crossing to the lowest triplet energy

state. It is quite unlikely that signals in the PIA spectra can be attributed to these singlet excited species as their very small decay time will lead to an extremely low concentration of those singlet excited state.

The peak observed at 1.0 eV in Fig. 6.16 (green line) is comparable to that assigned to a triplet-triplet absorption in pristine PCPDTBT films in a previous report by Di Nuzzo *et al.* [137]. The broad peak observed in Fig. 6.16 between 0.3 eV and 0.7 eV is assigned to the dipole-allowed transition of the free polarons of PCPDTBT, as was proposed for a similar feature observed in a study of PCBM/PCPDTBT blends [137].

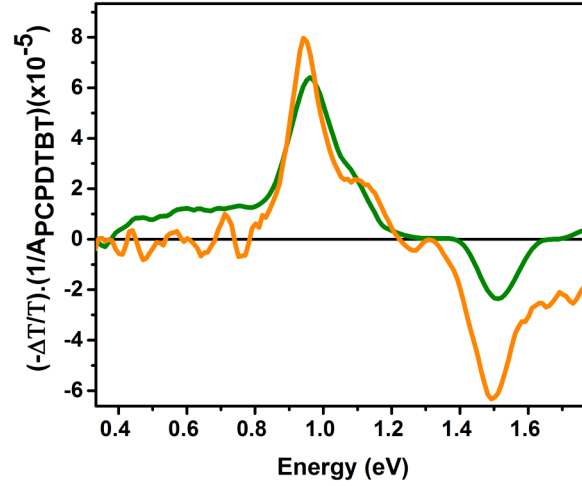


Figure 6.16: (a) The average lifetime ratios ($\tau_{\text{PCPDTBT}}/\tau_{\text{blend}}$) and (b) the PL quenching efficiencies (η_Q) (detected at 850 nm) of pristine PCPDTBT and PCPDTBT/CIS NCs blends with different CIS NCs loadings.

In the presence of PCBM, the PIA signal of triplet-triplet state at about 1.0 eV is increasing, on the other hand, the free polaron peak (at 0.3-0.7 eV) is decreasing. Furthermore, the PB peaks became more negative in the presence of PCBM, which indicates a bleaching of exciton absorption. This result points to a preferable charge rather than energy transfer processes.

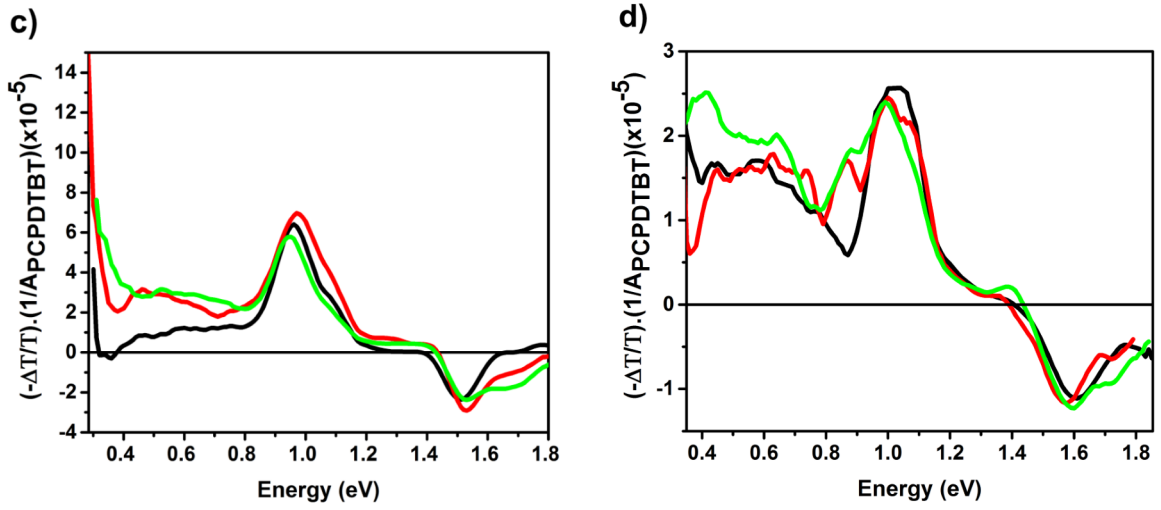


Figure 6.17: PIA spectra of PCPDTBT/CIS NCs blends measured at (a) 80 K and (b) 295 K with an excitation at 660 nm; CIS NCs loadings of the PCPDTBT/CIS NCs blends: 0wt% (black line), 60wt% (red line) and 75wt% (green line); the spectra are normalized to the absorption by polymer component at the excitation wavelength as described in the experimental section (see section 3.3.1).

Figure 6.17(a) depicts the PIA spectra of a pristine PCPDTBT film (see black line) compared to those of PCPDTBT/CIS NCs blends with different CIS NCs concentrations recorded at $T = 80$ K. In the case of PCPDTBT/CIS NCs, the features at 0.3-0.7 eV are more pronounced compared to those observed for pristine PCPDTBT as a consequence of the population of a triplet excited state by back-electron transfer from the conduction band (CB) of the CIS NCs to the LUMO of PCPDTBT. Furthermore, an addition of 60wt% CIS NCs to the PCPDTBT blend leads to a slight increase of the peak intensity at 1.0 eV. However, the peaks remain similar with further addition of CIS NCs in the blend. On the other hand, the intensity of the broad peak in the IR region (from 0.3 eV to 0.7 eV, see Fig. 6.17) increases with increasing CIS NCs concentration, which indicates that the presence of CIS NCs in the blend has no effect on the triplet state population in PCPDTBT but rather on the population of polarons. The broad peak observed in the PIA spectra of the PCPDTBT/CIS NCs film in the NIR region from 0.3 eV to 0.7 eV might at least partially originate from the CIS NCs phase compared to the PIA spectra of the pure CIS NCs film in NIR region (see Fig. 6.7).

The PIA spectrum obtained at RT for the PCPDTBT/CIS NCs blend with a loading

of 60wt% CIS NCs shows persistent signals compared to pristine PCPDTBT (see Fig. 6.17(b)). With a 75wt% CIS NCs loading in the blend the PIA signal in the NIR region is slightly increased in comparison to the other CIS NCs concentrations. In summary, these results indicated that the charge transfer process is less effective in PCPDTBT/blends compared to the P3HT/CIS blends.

6.3.4 PCPDTBT/CIS NCs BHJ solar cell performances.

Figure 6.18 shows the performance of PCPDTBT/CIS NCs solar cells. Compared to the results in Fig. 6.10 for P3HT/CIS NCs solar cells, PCPDTBT/CIS NCs solar cells show relatively poor current density leading to reduction of the solar cells efficiency. The PCPDTBT/CIS NCs solar cells with 75wt% CIS NCs show the best performance for PCPDTBT/CIS NCs solar cells with different concentrations, with PCE of about 0.002 % and $J_{SC} = 0.028 \text{ mA/cm}^2$ (see Fig. 6.18 and Table 6.4). The performance values of all solar cells are listed in Table 6.2.

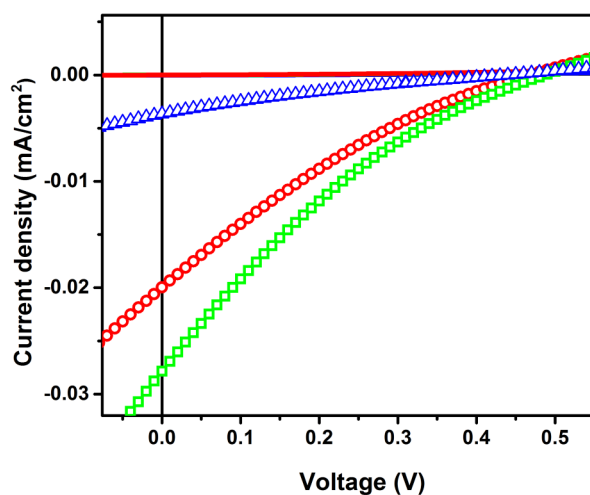


Figure 6.18: J-V curves of BHJ solar cells with CIS NCs loadings in the blends of 60wt% (red line), 75wt% (green line) and 90wt % (blue line).

Table 6.4: Average solar cell performances of P3HT/CIS NCs blends with different concentrations of CIS NCs (under 1 sun AM 1.5G illumination; devices structure: ITO/PEDOT:PSS/P3HT:CIS NCs/Al); values in brackets are the best values obtained.

Samples	J_{sc} (10^{-2} mA/cm ²)	V_{oc} (V)	FF (%)	PCE ($10^{-3}\%$)
P3HT/CIS NCs 60wt%	1.7 ± 0.2 (2)	0.45 ± 0.02 (0.49)	19.2 ± 0.2 (20.1)	1 ± 0.1 (1.4)
P3HT/CIS NCs 75wt%	2.3 ± 0.3 (2.8)	0.50 ± 0.01 (0.51)	17.9 ± 0.4 (18.3)	2 ± 0.3 (2.3)
P3HT/CIS NCs 90wt%	0.28 ± 0.06 (0.4)	0.41 ± 0.03 (0.45)	20.3 ± 0.57 (22)	0.2 ± 0.04 (0.3)

6.4 Conclusion

The fate of photo-generated electron-hole pairs in composite films of CIS NCs and the conductive polymers, P3HT and PCPDTBT was studied by combined PL quenching and PIA measurements. In both composites, CIS NCs quench the photoluminescence and the photoluminescence life time of the conjugated polymers. The extent of PL quenching increases with the amount of CIS NCs in the films. Since PL quenching alone cannot distinguish between charge transfer at the donor-acceptor interface and concurring processes like energy transfer, PIA spectroscopy was applied additionally. These measurements provided a strong indication for successful charge transfer via the detection of long-lived polarons generated in P3HT/CIS NCs blends. Systematic variations of the CIS NCs/polymer ratio revealed the charge transfer to be most efficient at a CIS NCs loading of 75% by weight.

The PIA spectra of PCPDTBT/CIS NCs blends, on the other hand, showed only weak polaron signals. Furthermore, PL quenching and the reduction of the decay time of singlet excitons were less pronounced in the films with PCPDTBT. All this indicates that photoinduced charge transfer between CIS NCs and PCPDTBT is less effective than in the P3HT/CIS NCs system. The increased triplet signal in the PCPDTBT/CIS NCs blends suggests a decay of the initially formed geminate electron-hole pair by back electron transfer leading to a triplet excited state of PCPDTBT. Additionally, an only

small overlap of absorption and PL spectra of the materials implies a limited probability of energy transfer in the PCPDTBT/CIS NCs films.

Chapter 7

Ligand effect on charge separation and transfer in hybrid P3HT/NCs films

The ligands surrounding CIS NCs after the synthesis affect the performances of the solar cells considerably. Here, two different ligand exchange methods, namely solution-phase and post-deposition ligand exchanges, are investigated. The solution-phase ligand exchange was conducted with either hexanethiol or pyridine ligands, whereas, benzenedithiol was used for post-deposition ligand exchange. Furthermore, a combination of the two ligand methods, (pyridine solution-phase and subsequent BDT post-deposition ligand exchange) is introduced. The obtained results for the ligand effect on charge separation and transfer in P3HT/CIS NCs blends are compared to those of P3HT/PbS QDs blends as a comparison system.¹

¹a) A manuscript is in preparation: **R. Miranti**, Y. Baeten, Y. Firdaus, E. Fron, M. Van der Auweraer J. Parisi, H. Borchert.

b) Parts of the study of P3HT/PbD QDs in this chapter has been published in: Y. Firdaus, **R. Miranti**, E. Vandenplas, E. Fron, A. Khetubol, R. Gehlhaar, D. Cheyns, H. Borchert, J. Parisi, M. Van der Auweraer, J. Appl. Phys. 2015, 118, 055502.

7.1 Motivation

As discussed in Chapter 4, the as-synthesized CIS NCs are shielded by long alkyl chain ligands, namely 1-DDT, OLAM and TOPO. These ligands control the growth conditions and ensure the post-synthesis solubility of the CIS NCs. In Chapter 6, the charge transfer processes of blends from as-synthesized CIS NCs in combination with two different polymers, namely P3HT and PCPDTBT have been discussed. It was found that the P3HT/CIS NCs composite shows more efficient charge transfers than the PCPDTBT/CIS NCs film.

The ligand exchange can be carried out in solution-phase or post deposition processes. The capping ligands on the CIS NCs after solution-phase ligand exchanges with hexanethiol and pyridine ligands have been investigated in Chapter 4. Whereas the solution-phase ligand exchanges with both ligands could not remove all long-chain ligands, pyridine successfully replaces 1-DDT and TOPO as ligands. Pyridine is widely used in ligand exchange processes due to its ability to remove the long-chain ligands owing to a weak interaction with NCs [29, 174]. A complete removal and replacement of the long-chain ligands can be achieved by a post-deposition ligand exchange following the solution-phase ligand exchange. Recent literature describes post-deposition ligand exchanges with short replacement ligands, such as amines [175] as well as thiols [41, 143, 176] – and here especially benzenedithiol (BDT) [177–179]. BDT is known as an effective replacement ligand, which leads to cross-linking of the NCs and thus increases the electronic coupling of NCs [176].

In this chapter, the photogeneration and charge transfer processes in P3HT/CIS NCs after solution-phase ligand exchange procedures are discussed. Subsequently, the impact of a post-deposition ligand exchange with 1,4-benzenedithiol (BDT) is investigated (BDT treatment).

As a comparison, the study of charge separation and transfer processes in P3HT/PbS QDs after post-deposition ligand exchanges will be discussed. PbS QDs have an advantage over CIS NCs regarding their energy gap, which is tuneable to the NIR region. In combination with conjugated polymers, the power conversion efficiency (PCE) of BHJ solar cells based on PbS was recently reported to be 4.23% [40, 41, 180–182]. Firdaus et al. recently showed that the post-deposition ligand exchange with BDT in case of a BHJ solar cell based on a P3HT/PbS QDs blend result in the PCE of about 1% [37].

7.2 Ligand effect on the solar cell performances and charge transfer processes in P3HT/CIS NCs

The different approaches of ligand exchanges discussed in this chapter are, solution-phase procedures (with hexanethiol or pyridine), post-deposition processes (with BDT) as well as a combination of both ligand exchanges (with pyridine and BDT).

7.2.1 Solution-phase ligand exchange by hexanethiol ligand

In this section, CIS NCs after ligand exchange (CIS-Hex NCs) were used as an active layer for BHJ solar cells in combination with P3HT. The concentrations of CIS-Hex NCs in the blends varied between 60wt%, 75wt% and 90wt%.

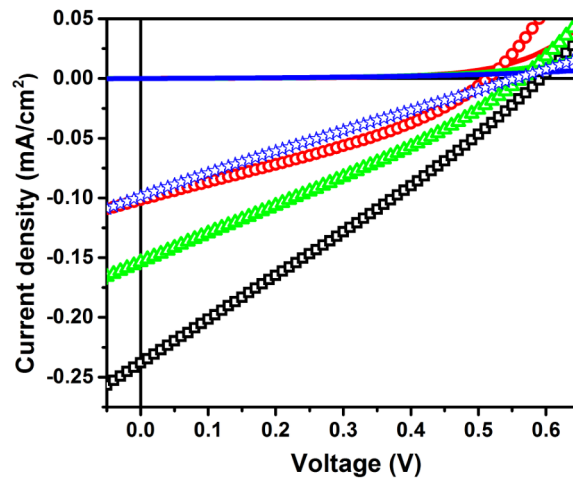


Figure 7.1: J-V curves of BHJ solar cells with as-synthesized CIS NCs (75wt% loading, black square line) and CIS NCs after hexanethiol ligand exchange (CIS-Hex NCs loadings: 60wt% (red circle line), 75wt% (green triangle line) and 90wt % (blue star line)).

Figure 7.1 show the current-voltage performances of CIS-Hex NCsin combination with P3HT with different particle concentrations in the blends. The highest short circuit current (J_{sc}) of 0.18 mA/cm² and open circuit voltage (V_{oc}) of 0.56 V were obtained for the blend with a CIS-Hex NCs concentration of 75wt%. An increased concentration of

CIS-Hex NCs to 90wt% leads to a decreased value of J_{sc} ($= 0.1 \text{ mA/cm}^2$). Nevertheless, the Fill Factor (FF) for the samples with 60wt% and 75wt% CIS-Hex NCs is slightly increased. The best power conversion efficiency (PCE) in the devices using CIS NCs after hexanethiol ligand exchange treatment are fairly low with about 0.03%. As discussed in section 4.3, the CIS NCs after hexanethiol ligand exchange only partly remove the initial ligands, which is most probably the reason for the results comparable to those obtained with the devices using as-synthesized CIS NCs and P3HT. The performances of all solar cells are listed in Table 7.1.

Table 7.1: Average solar cell performances of CIS NCs before and after hexanethiol ligand exchange (CIS-Hex NCs) blended with P3HT (under 1 sun AM 1.5G illumination; device structure: ITO/PEDOT:PSS/P3HT:CIS-Hex NCs/Al); the values in brackets represent the best values obtained.

Samples	J_{sc} (10^{-2} mA/cm^2)	V_{oc} (V)	FF (%)	PCE ($10^{-3}\%$)
P3HT/CIS NCs 75wt%	23 ± 1 (24)	0.59 ± 0.01 (0.59)	27.6 ± 0.2 (27.9)	37 ± 3 (39)
P3HT/CIS-Hex NCs 60wt%	10 ± 0.3 (10)	0.50 ± 0.01 (0.51)	32.8 ± 0.3 (33.2)	16 ± 0.7 (17)
P3HT/CIS-Hex NCs 75wt%	16 ± 2 (18)	0.54 ± 0.02 (0.56)	29.8 ± 0.8 (30.2)	28 ± 3 (30)
P3HT/CIS-Hex NCs 90wt%	10 ± 0.3 (10)	0.55 ± 0.04 (0.59)	27.6 ± 0.2 (24.9)	13 ± 0.6 (14)

The normalized PL spectra recorded of P3HT/CIS NCs-Hex blends with different CIS NCs concentrations at $T = 80 \text{ K}$ upon excitation at 532 nm are shown Fig. 7.2(a). The PL is quenched by 60% at CIS-Hex NCs concentrations of 60wt% and 75wt% in the blends. A CIS-Hex NCs concentration of 90wt% in the blends results in a PL quenching of about 90%. It is difficult to determine if the poor solar cells performances of the P3HT/CIS-Hex NCs blends are due to the lack of long-lived charge carrier or to other reasons by using PL only. Therefore, a quasi-steady state photoinduced absorption (PIA) spectroscopy was applied as a direct probe of charge transfer states.

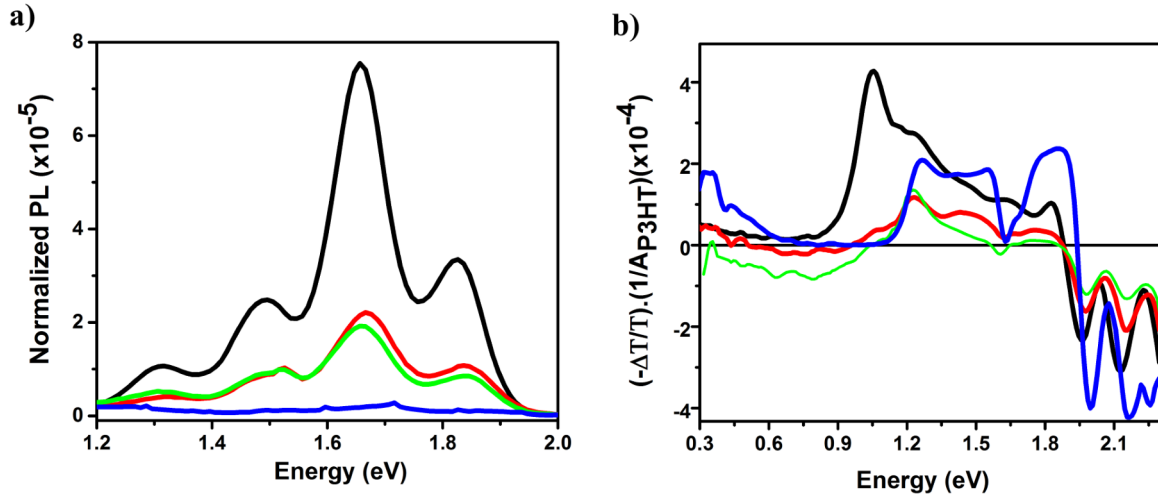


Figure 7.2: (a) PL and (b) PIA spectra of P3HT/CIS-Hex NCs blends with different CIS NCs concentrations: 0wt% (black line), 60wt% (red line), 75wt% (green line) and 90wt% (blue line); the spectra are normalized to the absorption by P3HT at the excitation wavelength (532 nm) as described in section 3.3.1.

Figure 7.2(b) show the PIA spectra of P3HT/CIS-Hex NCs with different CIS-Hex NCs concentrations. The PIA spectra of P3HT/CIS-Hex NCs film with CIS-Hex NCs concentrations of 60 wt% shows a comparably result to that with CIS-Hex NCs concentrations of 75 wt%. Both spectra show absence of polaronic absorption signals in the NIR regions. On the contrary, a broad peak in the NIR region appears by increasing the CIS-Hex NCs concentrations, which accompanied by the increasing of the polaron state (at 1.24 eV), delocalized polaron state (at 1.83 eV) and a broad band from 1.3 to 1.6 eV.

7.2.2 Benzenedithiol post-deposition ligand exchange

For the BDT treatment as-synthesized CIS NCs in chlorobenzene were blended with P3HT with a CIS NCs concentration of 75wt%. After deposition of a hybrid active layer, the samples were immersed in a 0.1 M BDT/acetonitrile solution for 60 s. Subsequently, the films were washed in acetonitrile for 60 s (see detail of post-deposition ligand exchange in section 3.2.3.2).

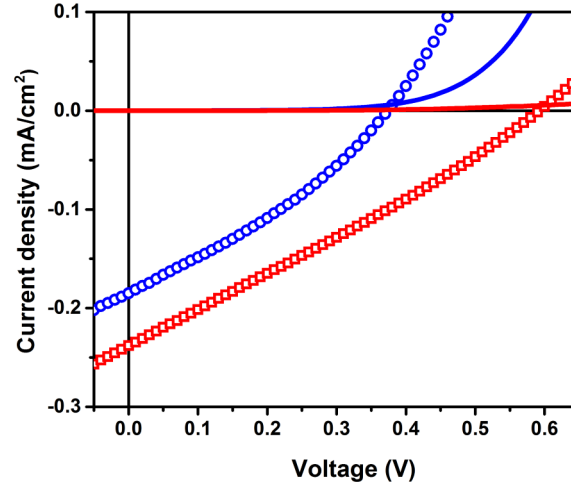


Figure 7.3: The current density-voltage curve of P3HT/CIS NCs before (red) and after post-deposition by BDT (blue).

The BDT post-deposition has been previously demonstrated in hybrid solar cells based on PbS QDs in order to replace the initial ligands and cross-linking agents [40, 70, 183]. As apparent from Fig. 7.3, the P3HT/CIS NCs after BDT post-deposition (P3HT/CIS-BDT NCs) on the exhibit both lower values of J_{sc} as well as V_{oc} . Whereas the ligand exchange results in a decrease of J_{sc} from 0.23 mA/cm^2 to 0.17 mA/cm^2 , V_{oc} decreases from 0.59 V to 0.38 V , which results in a significantly lower PCE of $(0.021 \pm 0.001)\%$. However, the BDT treatment leads to a slight increase of the FF to about 31.5%. The photovoltaic parameters of these corresponding devices are summarized in Table 7.2.

Table 7.2: Average solar cell performances of CIS NCs before and after post-deposition with BDT (CIS-BDT NCs) blended with P3HT (under 1 sun AM 1.5G illumination; device structure: ITO/PEDOT:PSS/P3HT:CIS-BDT NCs/Al); the values in brackets represent the best values obtained.

Samples	J_{sc} (10^{-2} mA/cm^2)	V_{oc} (V)	FF (%)	PCE ($10^{-3}\%$)
P3HT/CIS NCs 75wt%	23 ± 1 (24)	0.59 ± 0.01 (0.59)	27.6 ± 0.2 (27.9)	37 ± 3 (39)
P3HT/CIS-BDT NCs	17 ± 1 (19)	0.38 ± 0.01 (0.38)	31.5 ± 0.3 (31.7)	21 ± 0.1 (21)

After BDT treatment, the PL show an enhancement in the intensity and red shift by 0.3 eV compared to emission peaks of both, pristine P3HT and P3HT/CIS NCs films (see Fig. 7.4(a)). Wei *et al* [184] suggested the enhancement and red shift of PL peaks related to the appearances of the surface defects on the NCs.

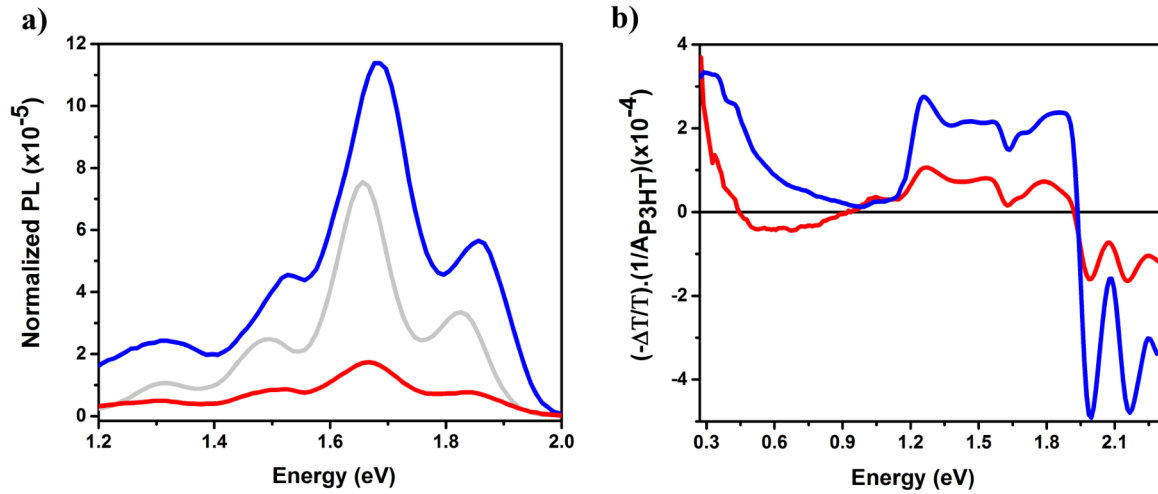


Figure 7.4: (a) PL and (b) PIA spectra of P3HT/CIS NCs before (red line) and after post-deposition with BDT (blue line); the PL spectrum of pristine P3HT is additionally shown as a reference; the spectra are normalized to the absorption by P3HT at the excitation wavelength as described in section 3.3.1.

Figure 7.4(b) shows the PIA signals before and after BDT treatment. As discussed in Chapter 6, all measured spectra consist of positive (PIA) and negative (photobleaching, PB) peaks. The PIA spectra of P3HT/CIS NCs blends (see discussion in section 6.2.3) indicate a long-lived singlet exciton state at 1.05 eV accompanied by the appearance of a localized polaron absorption peak at 0.3 eV and a delocalized polaron signature at 1.83 eV. Hence, P3HT/CIS NCs blends show an effective charge separation and electron transfer in P3HT/CIS NCs composites. After BDT treatment, however, a new broad peak in the NIR region of 0.35 eV – 0.9 eV increases significantly, which is followed by a pronounced increase of the PIA signals in the region of 1.24 eV – 1.83 eV (see Fig. 7.4(b)).

7.2.3 Combined solution-phase and post-deposition ligand exchange with pyridine and benzenedithiol.

The as-synthesized CIS NCs were submitted to a solution-phase ligand exchange with pyridine before the blending process with P3HT in chlorobenzene (for details see section 3.2.3.1). The solution was subsequently spin-coated on top of an ITO/PEDOT:PSS. The spin-coated films of the active layer were dipped in a 0.1 M BDT/acetonitrile solution for 60 s (for details see section 3.2.3.2).

The concentration of CIS NCs after pyridine ligand exchange (CIS-Py NCs) in the blend was 75 wt%. Figure 7.5 shows that the solution-phase ligand exchange with pyridine results in a decrease of V_{oc} from 0.59 V (for the P3HT/CIS NCs blend) to 0.34 V, whereas no influence on J_{sc} and the PCE is detected. Nevertheless, the pyridine solution-phase ligand exchange leads to an increase of the FF.

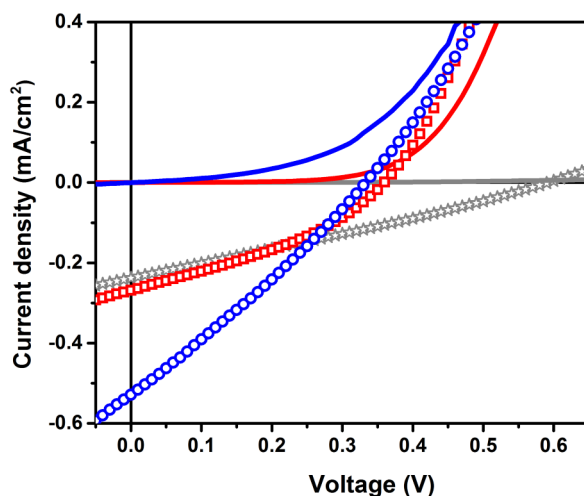


Figure 7.5: The current density-voltage (J-V) curves of P3HT/CIS NCs blends with as-synthesized CIS NCs (grey), CIS NCs after pyridine ligand exchange (CIS-PyNCs, red) and P3HT/CIS-Py NCs blends after BDT treatment (CIS-PyBDT NCs, blue).

The additional BDT post-deposition treatment of P3HT/CIS-Py NCs blends, on the other hand, results in an increase of J_{sc} by more 200% from 0.23 mA/cm² to 0.52 mA/cm², which is, however, not accompanied by any changes of V_{oc} (= 0.34 V). Although the combination of solution-phase and post-deposition ligand exchange with

pyridine and BDT results in a lower FF ($= 27.5\%$), the overall PCE is significantly increased to $(0.050 \pm 0.001)\%$. Here, the treatment with BDT shows a pronounced effect in the performance of the solar cells – contrary to the results obtained with either pyridine- or BDT-treated as-synthesized blends. This leads to the conclusion, that a combination of both treatments is required for these good results, which therefore are most probably due to the replacement of capping ligands. Based on the results obtained with the blends after BDT treatment (see section 7.1.2), which exhibit lower PCE values than those obtained with CIS-Py NCs (see Fig. 7.5, red line and Table 7.3), it is concluded that the BDT treatment most probably replaces not the remaining long-chain but rather the pyridine ligands and thus improves the electron coupling in the polymer/CIS NCs blends. The results for all devices are given in Table 7.3.

Table 7.3: Average solar cell performances of as-synthesized CIS NCs, pyridine-treated CIS NCs as well as pyridine- and BDT-treated CIS NCs (CIS-PyBDT NCs) blended with P3HT (under 1 sun AM 1.5G illumination; device structure: ITO/PEDOT:PSS/P3HT:CIS-BDT NCs/Al); the values in brackets represent the best values obtained.

Samples	J_{sc} (10^{-2} mA/cm ^{2})	V_{oc} (V)	FF (%)	PCE ($10^{-3}\%$)
P3HT/CIS NCs 75wt%	23 ± 1 (24)	0.59 ± 0.01 (0.59)	27.6 ± 0.2 (27.9)	37 ± 3 (39)
P3HT/CIS-Py NCs	27 ± 1 (28)	0.34 ± 0.01 (0.36)	35.7 ± 0.9 (36.8)	33 ± 1 (35)
P3HT/CIS-PyBDT NCs	52 ± 0.1 (53)	0.34 ± 0.003 (0.34)	27.5 ± 0.36 (27.8)	50 ± 0.1 (50)

Figure 7.6(a) show the PL spectrum after pyridine solution-phase ligand exchange followed by BDT treatment. Pyridine solution-phase ligand exchange (see Fig 7.6(a), red line)) result in comparably result as BDT treatment on P3HT/CIS NCs film exchange (see Fig 7.4(a), blue line). Here, the PL enhanced and red shifted by 0.3 eV compare to the PL of pristine P3HT. As discussed also for Fig. 7.4, this result gave an indication of the surface defects on CIS NCs due to the pyridine ligands. The BDT treatment on P3HT/CIS-Py NCs, on the other hand, leads to the pronounced PL quenching by 95%.

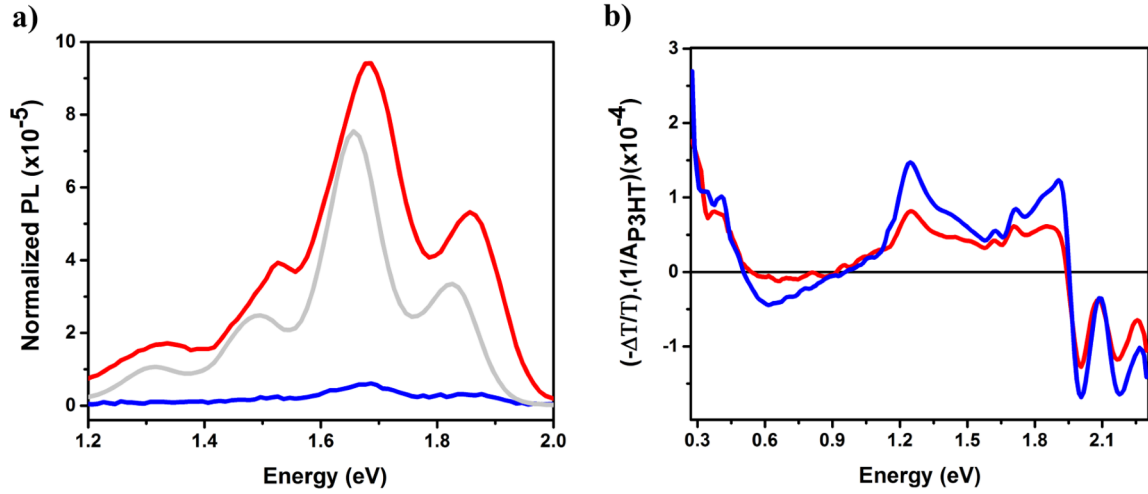


Figure 7.6: (a) PL and (b) PIA spectra of P3HT/CIS-Py NCs (red line) and P3HT/CIS-PyBDT NCs (blue line); the PL spectrum of pristine P3HT (grey) is shown as a reference; the spectra are normalized to the absorption by P3HT at the excitation wavelength (532 nm) as described in section 3.3.1.

Both PIA spectrum, before and after BDT treatment on P3HT/CIS-Py NCs, show a vanishing of singlet absorption peak at 1.05 eV (see Fig. 7.6(b) in comparison with PIA spectra of pristine P3HT, see Fig. 7.2(b) black line). After BDT treatment, the polaron state (at 1.24 eV) and delocalized polaron state (at 1.83 eV) increase significantly accompanied by increasing the polaron signal at 0.3 eV.

7.3 Ligand effect on charge separation and transfer in P3HT/PbS QDs²

In this section, the ligand effect on charge separation and transfer in P3HT/PbS QDs blends is investigated. P3HT was obtained from Rieke Metals (Mn = 13.9 kg/mol, regioregularity >96%). Figure 7.7 shows PL and PIA spectra of pristine P3HT (blue)

²Parts of the results have been published in [Y. Firdaus, **R. Miranti**, E. Vandenplas, E. Fron, A. Khetubol, R. Gehlhaar, D. Cheyns, H. Borchert, J. Parisi, M. Van der Auweraer, J. Appl. Phys. 2015, 118, 055502]. In this paper, RM contributed the contributed the experimental conduction, analysis and discussion of the PIA and TEM measurements. The results presented in the paper have also been published in Y. Firdaus' thesis (KU Leuven, Belgium). The PL measurements conducted at T = 80 K are presented in this chapter for the first time.

and P3HT/PbS blends before and after BDT post-deposition measured at $T = 80$ K upon excitation at 532 nm. The PL and PIA spectra were normalized by the P3HT absorption at the excitation wavelength. The PbS QDs concentrations in the P3HT/PbS QDs blends after BDT treatment with a 0.02 M BDT/ acetonitrile solution were 60wt%, 75wt% and 90wt%. The presence of PbS QDs before ligand exchange results in insignificant changes of the emission spectrum of pristine P3HT (see Fig. 7.7(a), dark yellow and black lines), whereas the PL is quenched significantly after BDT treatment of the blend.

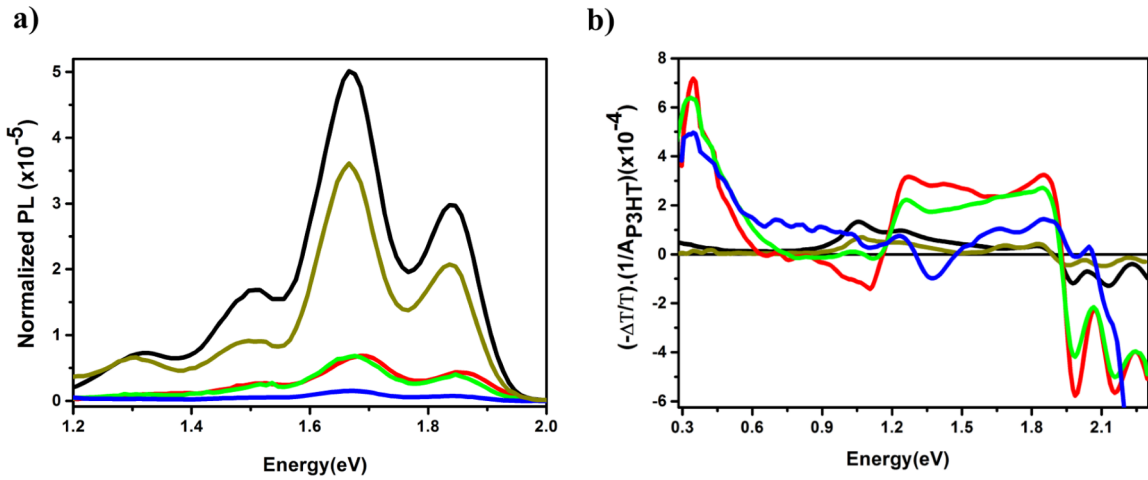


Figure 7.7: (a) PL and (b) PIA spectra of pristine P3HT (black) and P3HT/PbS before ligand exchange (60wt% loading of PbS QDs, dark yellow) and after BDT treatment (PbS-BDT QDs concentrations: 60wt% (red), 75wt% (green) and 90wt% (blue)); the spectra are normalized to the absorption by P3HT at the excitation wavelength (532 nm) as described in section 3.3.1.

Figure 7.7(b) shows the PIA spectra of P3HT/PbS QDs films before and after BDT ligand exchange as well as the PIA spectra of pristine P3HT. Prior to the ligand exchange, the singlet absorption peak at 1.05 eV observed for P3HT/PbS QDs is slightly changed compared to that of pristine P3HT, and no increase of the polaron state in the range of 0.3 - 0.7 eV is detected. These results are in agreement with the PL spectra (see Fig 7.7(a), dark yellow line), which show that the presence of PbS QDs before ligand exchange in the blend does not result in PL quenching by charge or energy transfer in comparison to P3HT. However, a new peak detected at 1.68 eV can be assigned to a new transition of delocalized polarons [79]. As the energy of 1.68 eV corresponds to the

PL maximum of P3HT, this region is sensitive to PL corrections.

Subsequent to the BDT ligand exchange, the PIA signal of the singlet species observed at 1.05 eV in Fig. 7.7(b) is not observed anymore, whereas the PIA signals attributed to the localized (at 1.24 eV) and the delocalized polarons (at 1.83 eV) as well as to the ground state depletion (at 2.0 eV) become more pronounced (see Fig. 7.7(b)). In analogy to the P3HT/PCBM and P3HT/CIS NCs blends (compare for Figs. 6.6 and 6.8, respectively) these similar features suggest an efficient charge transfer from the donor to the acceptor in the P3HT/PbS-BDT QDs blends. The PIA signals attributed to the polaron state (at 1.24 eV), the delocalized polaron state (at 1.83 eV) and a broad band from 1.3 to 1.6 eV show comparable trends for the blends with concentrations of 60wt % and 75wt% PbS-BDT QDs. These peaks are reduced when the PbS-BDT QDs concentration in the blend reached 90 wt %. On the other hand, for all P3HT/PbS-BDT QDs blends, pronounced polaron signals in the NIR regions at about 0.35 eV to 0.6 eV are observed. These peaks are most probably due to the HOMO to SOMO transition of the positive polarons. Zhang *et al.* [185] assigned this broad peak to a transition from below-gap state to the second excitonic level of the QDs.

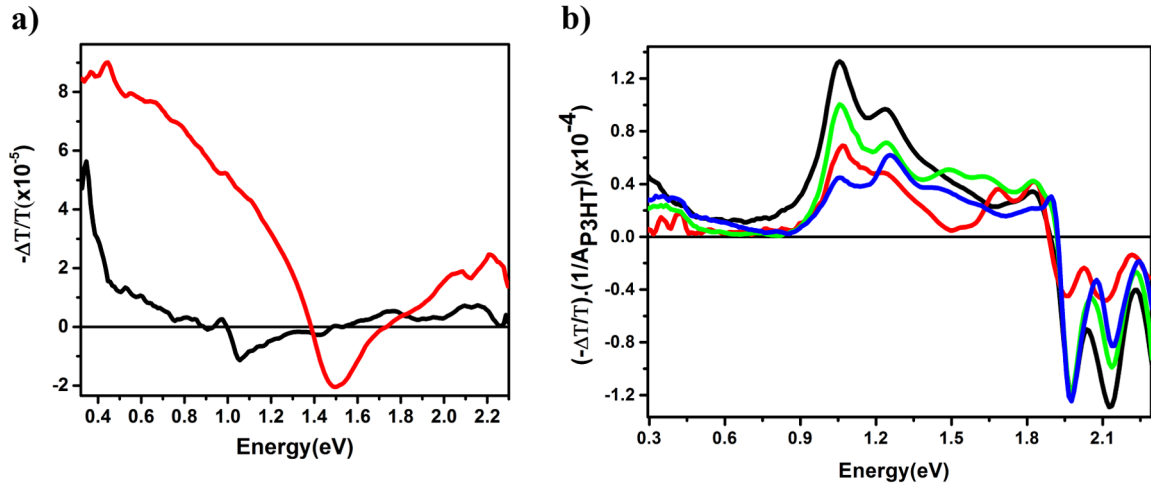


Figure 7.8: PIA spectra of (a) pure PbS QDs films before (black) and after BDT post-deposition (red) as well as (b) pristine P3HT (black) and P3HT/PbS QDs blends (with a PbS QDs concentration of 60wt%) before (red) and after ligand exchanges with octylamine (green) and octanethiol (blue).

Furthermore, the PIA spectrum of a pristine PbS QDs film after BDT post-deposition

(see Fig. 7.8, red line) shows a clear contribution of PbS QDs absorption. As observed in Fig. 7.8 the polaron signals in the region of 0.35 eV to 1.2 eV are significantly increased after BDT post-deposition. However, in comparison with the PIA spectra of P3HT/PbS QDs before ligand exchange (see dark yellow line in Fig. 7.7(b) as well as red line in Fig. 7.8(b)), the small amplitude of the PIA signal in the region of 0.35-0.6 eV more likely corresponds to polaronic transitions as a consequence of electron transfer from P3HT to PbS-BDT QDs. Increasing the concentration of PbS QDs in the blends leads to an intensity increase of the PIA peaks at 1.24 eV and 1.83 eV, but does not influence the signal at 0.35 eV and the broad peak between 1.36 eV and 1.8 eV. For a concentration of 90wt% PbS QDs in the blend the intensity of the peak at 1.36 eV is decreased to a negative value. This band could be related to the excitonic peak of PbS QDs. From the PIA and PL quenching results it can be concluded, that by an increase of the PbS QDs concentration an efficient charge transfer from P3HT to PbS-BDT QDs is achieved.

Figure 7.8(b) shows PIA spectra of a pristine P3HT blend and P3HT/PbS QDs blends with a PbS QDs concentration of 60wt% before and after post-deposition ligand exchanges with octylamine (Oam) and octanethiol (OT), respectively. In comparison to the results obtained after BDT treatment (compare for red line in Fig. 7.7(b)) the ligand exchanges with the other two ligands show less significant effects in the respective PIA spectra. After the Oam and OT ligand exchanges, the polaron peaks observed at 0.35 eV show similar signal as in pristine P3HT and no significant decrease of the singlet absorption peak at 1.05 eV (see Fig. 7.8(b)). The most prominent signal in the PIA spectra after both ligand exchanges is a broad peak in the region of 1.4 eV to 1.8 eV.

Figure 7.9 shows TEM images of P3HT/PbS QDs before and after BDT post-deposition with different concentrations of PbS QDs in the blends. The measurements were conducted in bright field mode without energy filter, so that the thickness could be identified by the image brightness. The TEM results at low magnification show no prevalent brightness, which can be correlated to the aggregation of the film. For the films before ligand exchange, the amount of film aggregation decreased with an increasing PbS QDs concentration (see Fig. 7.9 (a-f)). After BDT post-deposition, the brightness of the TEM images is observed to be increased significantly in general (see Fig. 7.9 (g-j)). Furthermore, the higher magnified TEM images show vacant and dense concentration regions, which indicate a cross-linking of the PbS QDs by the subsequent BDT treatment of P3HT/PbS QDs blends.

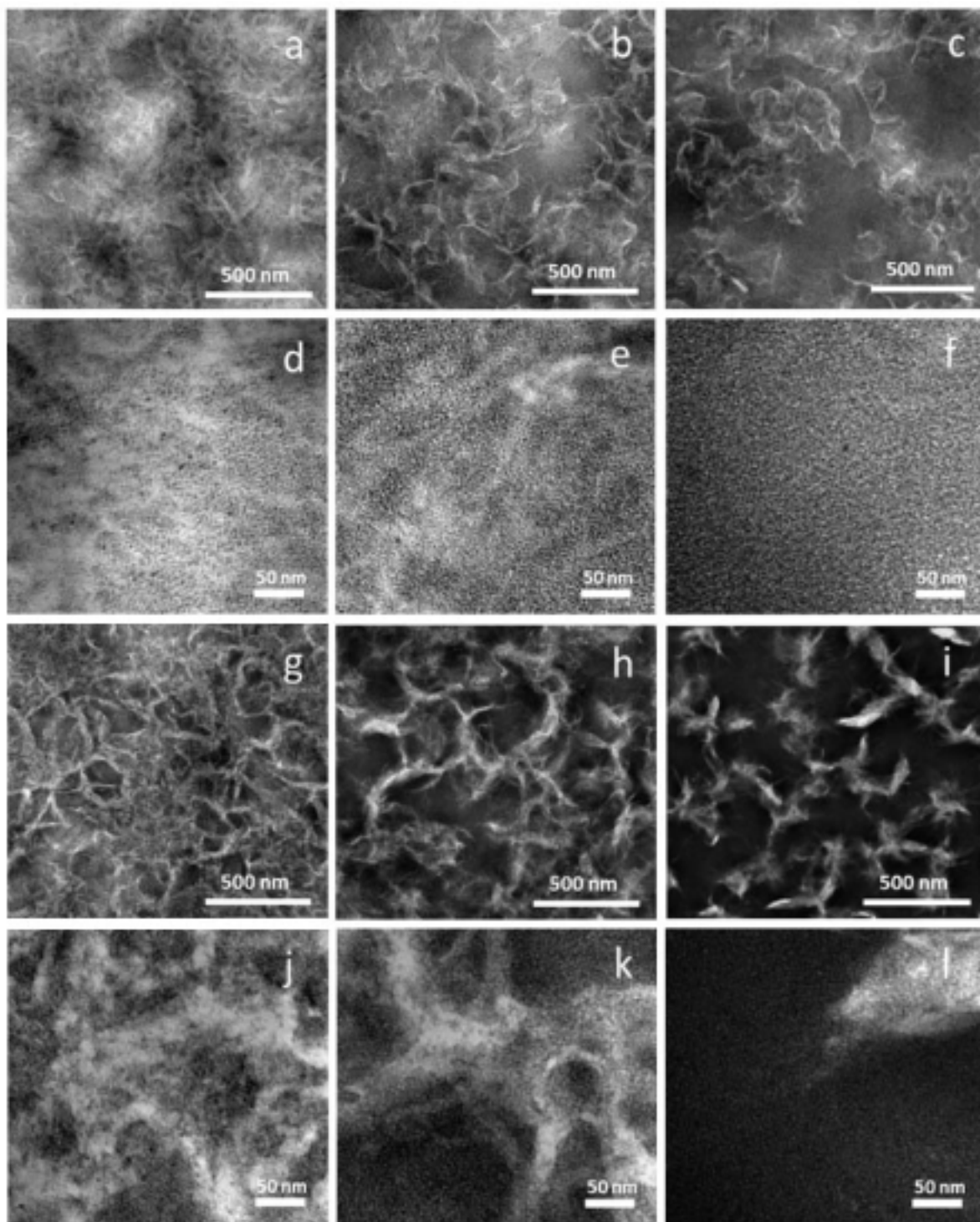


Figure 7.9: TEM images of different magnifications of P3HT/PbS QDs films (a-f) before ligand exchange with PbS QDs concentrations of (a,d) 60wt%, (b,e) 75wt% and (c,f) 90wt% as well as (g-l) after BDT post-deposition ligand exchange with PbS QDs concentrations of (g,j) 60wt%, (h,k) 75wt% and (i,l) 90wt%.

7.4 Conclusion

Solution-phase and post-deposition ligand exchanges were introduced as strategies for improving the performances of the solar cells. The solution-phase ligand exchange was carried out with either hexanethiol or pyridine as replacement ligands. On the other hand, benzenedithiol ligands were used for the post-deposition ligand exchange.

The hexanethiol solution-phase ligand exchange resulted in pronounced PL quenching but less photogeneration of polarons. Furthermore, measurements with solar cell devices after hexanethiol ligand exchange exhibited comparably low solar cell efficiencies compared to devices constructed with as-synthesized CIS NCs as well as with BDT-treated CIS NCs.

As also the pyridine solution-phase ligand exchange (by which the long-chain ligands 1-DDT and TOPO could successfully be replaced) did not result in any improvement of the solar cell performances, a subsequent post-deposition ligand exchange with BDT was performed. Subsequently, a significant increase of the short circuit current as well as the PCE was detected. Therefore, successive pyridine solution-phase and BDT post-deposition ligand exchanges are identified as a successful route in improving the photovoltaic performance of CIS NCs-based BHJ solar cells, which was also found for the reference system of P3HT/PbS blends, where a post-deposition ligand exchange of oleic acid ligands with BDT resulted in the most efficient charge generation and electron transfer. Solution-phase and post-deposition ligand exchanges were introduced as strategies for improving the performances of solar cells. The solution-phase ligand exchange was carried out with either hexanethiol or pyridine as replacement ligands. For the post-deposition ligand exchange benzenedithiol replacement ligands were used.

The hexanethiol solution-phase ligand exchange resulted in pronounced PL quenching but less photogeneration of polarons. Furthermore, measurements with solar cell devices after hexanethiol ligand exchange exhibited comparably low solar cell efficiencies compared to devices constructed with as-synthesized CIS NCs as well as with BDT-treated CIS NCs.

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as the PCE was detected. Therefore, successive pyridine solution-phase and BDT post-deposition ligand exchanges could be identified as a possible way to improve the photovoltaic performance of CIS NCs-based BHJ solar cells. This result could be confirmed by the finding for the comparable system of P3HT/PbS blends, where a post-deposition ligand exchange of oleic acid ligands with BDT resulted in the most efficient charge generation and electron transfer.

Chapter 8

Conclusion and Outlook

8.1 Conclusion

The CIS NCs investigated in this work were synthesized by a colloidal method in solution. This solution contained three different compounds namely 1-dodecanethiol (1-DDT), oleylamine (OLAM) and trioctyl phosphine oxide (TOPO), which served as particle-stabilizing ligands. As these ligands can have a disadvantageous influence on the charge transfer and transport, one method to enhance the performance of solar cells is an exchange of these long-chain ligands surrounding the CIS NCs with more conductive ones. This was carried out by a solution-phase ligand exchange with hexanethiol and pyridine as replacement ligands. Although both ligands were not able to remove all the long-chain ligands on the CIS NCs' surfaces, the 1-DDT ligand could partially be replaced by hexanethiol, whereas the process with pyridine was successful in removing and replacing all ligands except for OLAM.

The charge transport properties of the as-synthesized CIS NCs were investigated in comparison to those of P3HT. The charge transport characteristics of P3HT could be well described by trap free and field-independent models, by which a hole mobility of about

$10^{-3}\text{cm}^2/\text{Vs}$. During the investigation of CIS NCs films in hole- and electron-only devices a hole-dominated charge carrier transport was found. Whereas estimations from measurements with electron-only devices gave an electron mobility of about $10^{-9}\text{cm}^2/\text{Vs}$, by using field-dependent models, CIS NCs-based hole-only devices showed a hole mobility of CIS NCs of about $10^{-6}\text{cm}^2/\text{Vs}$, by applying field-independent as well as field-dependent models.

The bulk heterojunction (BHJ) solar cell measurements based on as-synthesized CIS NCs were performed with two different polymers in the respective active layer. P3HT/CIS NCs composites showed pronounced PL quenching and the reduction of the decay times at increasing CIS NCs concentrations in the blends. Furthermore, the generation of long-lived polarons indicates successful charge transfer processes in P3HT/CIS NCs blends. The P3HT/CIS NCs blends with a loading of 75wt.% CIS NCs showed the most effective charge transfer and solar cells performance. In the PCPDTBT/CIS NCs blends, PL quenching and the reduction of the decay time of singlet excitons were less pronounced compared to those obtained for the P3HT/CIS NCs blends. On the other hand, PCPDTBT/CIS NCs films show a limited probability of energy transfers in the PCPDTBT/CIS NCs films and the occurrence of a geminate electron-hole pair by back electron transfer leading to a triplet excited state of PCPDTBT. However, the less effective charge transfer in PCPDTBT/CIS NCs blends results in the significantly less efficient solar cells performance in comparison to the P3HT/CIS NCs films.

Two consecutive ligand exchange processes were carried out after the CIS NCs synthesis in order to enhance the performance of the solar cells: (i) the solution-phase and (ii) the post-deposition ligand exchange. The experiments after solution-phase ligand exchange with hexanethiol showed pronounced PL quenching but less photogeneration of polarons. Solar cells with CIS NCs after a hexanethiol ligand exchange exhibit less efficient performances than those with as-synthesized CIS NCs. Similar results were achieved by a subsequent post-deposition ligand exchange treatment of the CIS NCs with 1,4-benzenedithiol (BDT), which were used for solar cell construction and showed a significant decrease of the overall power conversion efficiency (PCE). The PCE of the devices constructed with CIS NCs after BDT post-deposition results in comparable values to those obtained with the device constructed with CIS NCs before ligand exchange.

Although long-chain ligands were successfully removed and replaced by the pyridine solution-phase ligand exchange in as-synthesized CIS NCs, there is no improvement in the performances of the solar cells. Hence, an additional post-deposition ligand exchange

with benzenedithiol (BDT) was carried out, by which – contrary to the remaining long-chain ligands - the pyridine ligands could be removed. As a result, a significant increase of the short circuit current as well as the PCE was detected. Therefore, successive pyridine solution-phase and BDT post-deposition ligand exchanges are identified as a successful route in improving the photovoltaic performance of CIS NCs-based BHJ solar cells. This result is supported by results obtained for the comparable system of P3HT/PbS blends, where a post-deposition ligand exchange of oleic acid ligands with BDT resulted in the most efficient charge generation and electron transfer.

8.2 Outlook

The results obtained in this work show that CIS NCs are generally applicable in BHJ solar cells. The combination of good charge transport as well as charge transfer properties, which can be enhanced by an alteration of the CIS NCs' surfaces subsequent to the synthesis, might makes this material a more environmentally friendly alternative to, e.g., PbS QDs and CdSe. In order to achieve this goal, however, further investigations should be made regarding possible improvements of the preparation technique and in-depth understanding by additional analysis methods.

The performances of solar cells constructed after pyridine and BDT ligand exchanges should be investigated based on the impact of different synthesis and preparation parameters, e.g., the type of sample cleaning procedures before and after ligand exchanges and post-annealing times. Furthermore, surface analysis methods like X-ray photoelectron spectroscopy (XPS) are needed to understand the impact of the ligands present on the NCs' surfaces. PIA measurements of working solar cells by applying a voltage bias might be of interest for deeper insight into the charge transfer processes in CIS NCs-based solar cells. Furthermore, investigations on the impact of the combined ligand exchanges on the charge transport in CIS NCs and CIS NCs/P3HT systems will lead to deeper understanding in the research of hybrid solar cell based on CIS NCs.

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List of Publications

Articles related to this thesis (in preparation and published in scientific journals):

1. **R. Miranti**, Y. Beaten, Y.Firdaus, E. Fron, M. Van der Auweraer, J. Parisi, H. Borchert. Ligand effects on charge transfer of CuInS₂ /P3HT blend. In preparation.
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2. **R. Miranti**, C. Krause, D. Scheunemann, J. Neumann, D. Fenske, Holger Borchert, Jürgen Parisi, Tuning the electronic properties of the CuInS_2 nanoparticles for application in hybrid solar cells, presented in the DPG spring meeting, Regensburg, 10-15 March 2013
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Talks related to this thesis :

1. **R. Miranti**, Y.Firdaus, C. Krause, M. van der Auweraer, H. Borchert, J. Parisi, Photoinduced charge transfer in CuInS₂ Nanocrystal/Polymer composites, presented in the DPG spring meeting, Dresden, 30 March – 4 April 2014

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Erklärung

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