7 Charge Transfer between Polymers and CQDs

In this chapter, a conjugated D-A polymer is mixed with PbS CQDs and their excited states interaction is investigated. A charge transfer between the two components can be observed only when the CQDs are capped with short-chain BDT ligands. Their native oleic acid is too long to allow for an efficient interaction. With their complementary absorption, these materials seem to be good candidates for hybrid absorption layers in thin film solar cells. Manufactured devices, however, exhibit a poor performance, which is linked to conduction-hampering disorder and the poor quality of cast films.

7.1 Introduction

Research in organic solar cells aims at large scale manufacturing of devices on flexible substrates from solution via printing techniques. While the improvement in power conversion efficiency (PCE) has been considerable during the last decade, devices often still suffer from two important drawbacks. Firstly, the relatively low permittivity of organic semiconductors demands the intermixing of electron donor (D) and acceptor (A) materials to successfully dissociate the generated excitons and transport formed charge carriers. Secondly, despite recent promising results with non-fullerene acceptors, commonly employed fullerene-derivatives, such as PCBM, exhibit low extinction coefficients, leading only the donor component to significantly contribute to solar light harvesting in these blends. Although a plethora of conjugated materials has been synthesised, the band gap in most efficient cases is wider than 1.5 eV. Given the significant portion of sun energy below this value, this poor coverage of the solar spectrum seriously limits the PCE.

PbS colloidal quantum dot solar cells (QDSC), on the other hand, are based on a pure film of colloidally deposited quantum dots. The absorption onset of CQDs can be tuned due to the quantum size effect (section 2.4.2). Lead sulphide is of particular interest for solar cells, given its narrow band gap of 0.41 eV in bulk. Crucially, though, the absorption profile of these CQDs

7.2 Results and Discussion

The molecular structure of PCPDTBT and the energy levels of the materials are depicted in Figure 7.1(a). It is crucial to note that these levels are determined collectively, i.e. for the neat bulk polymer and an ensemble of dissolved CQDs capped with oleic acid (OA). The values may differ for a local level at an interface and the determination for the CQDs involves a particularly large uncertainty. Furthermore, while the band gap is generally not affected by the ligands, it has been shown that they may significantly shift the HOMO (or valence level) and LUMO (con-
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Nevertheless, assuming the depicted levels, one would expect a favourable type-II heterojunction to form between these two materials, albeit with a relatively small energy offset between the HOMO levels. As illustrated in (a), there are three processes of interest which might give rise to efficient photocurrent generation exploitable in solar cells. In the following, it will be convenient to distinguish between photons absorbed by the polymer and those absorbed by the CQDs. Both events offer the opportunity for a charge carrier transfer towards the other material, i.e. an electron transfer from the polymer towards the CQDs or a hole transfer vice versa. Moreover, photons absorbed by the polymer may lead to a Förster-like energy transfer, since the polymer PL and CQD absorption overlap.

The absorption spectra of thin films depicted in Figure 7.1 (b) exhibit two bands for the neat polymer around 3 eV and from 2.1 to approximately 1.5 eV. The CQDs display a first excitonic peak at 1.2 eV and a strongly increasing absorption towards higher energy. When blended together and exchanging the ligand to the bidentate linker, 1,4-benzenedithiol (BDT), the excitonic peak shifts slightly to lower energy. Cross-linking generally reduces the band gap and shifts the absorption of CQDs towards lower energy due to the increased inter-dot coupling (section 2.4.3). In this case, however, the blend with the polymer (9:1 in weight of CQD:PCPDTBT) simultaneously decreases the permittivity of the CQD environment, which would lead to a higher transition energy and thereby counters the effect of the increased inter-dot coupling.

In order to study the excited states’ interaction, steady-state PL spectra were taken of both neat and blended films. As depicted in Figure 7.2 (a), the polymer exhibits a broad emission with two distinct peaks (at 1.4 and 1.3 eV), analogous to the absorption in Figure 7.1 (b). The OA covered CQDs emit around 1.00 eV, thus giving rise to two distinct emission regions attributable to PCPDTBT and to PbS respectively. Upon blending the materials, the two emission regions are both still visible. Notably, though, the PbS peak shifts to higher energy (1.05 eV), which can be ascribed to the decreased permittivity of the blend, as stated above. Furthermore, the emission of PbS broadens significantly, as expected from the increased (inter-site) disorder in this film.

Similarly, the emission of PbS_BDT is initially found at 1.03 eV, but shifts towards 1.07 eV for the blended sample. For these ligand exchanged CQDs, the emission is even farther broadened, as the replacement of OA commonly increases the inter-site disorder.

Time resolved photoluminescence (TRPL) was measured to determine the lifetimes and examine possible differences. The respective traces were taken either from the emission region of the polymer (I), as indicated in Figure 7.2 (a) and displayed in (b), or from the emission of the CQD region (II), as shown in (c) and (d).

Fitting the decay of the neat polymer’s emission (red) with a monoexponential function \( I = I_0 \cdot e^{-t/\tau_1} \) leads to a lifetime of approximately \( \tau_1 = 118 \) ps, which is in agreement with previous
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Figure 7.2: Steady state photoluminescence spectra of the investigated samples (a) and their respective transients, extracted from the polymer emission region (I) (b) and the region predominantly assigned to the CQD PL (II) (c), (d).

investigations of this material. The blended sample with OA capped PbS (dark blue) offers a similar lifetime for the polymer (128 ps; a summary of extracted values is given in Table 7.1). Upon blending the polymer with BDT capped PbS (light blue), however, the lifetime is significantly reduced and needs to be fitted with a biexponential function $I = I_0 \cdot e^{-\tau_1/t} + A_2 \cdot e^{-\tau_2/t}$. By doing so, one obtains two faster components of approximately $\tau_1 = 5$ and $\tau_2 = 75$ ps, of which the former approaches the resolution of the set-up (about 4 ps). Since exposing neat PCPDTBT to BDT did not affect the lifetime, the quenching is attributed to the presence of the CQDs.

For the CQD emission region in (c) and (d), extracted lifetimes are significantly longer. Here, the difference between the neat and the blended films is also less pronounced, in accordance with an investigation involving a wider band gap polymer carried out before. CQDs capped with oleic acid exhibit a biexponential decay with lifetimes of around 46 and 275 ns. Interestingly, the lifetime becomes prolonged when blending with PCPDTBT (Figure 7.2 (c)). Since the initial decay of the CQDs coincides with the polymer tail (consider steady-state spectra in (a)), the decay at early times is not considered here and the lifetime of the fitting process is omitted. While such behaviour could arise through an energy transfer from the polymer to the CQDs, such a process would also lead to a reduction of the polymer PL lifetime (consider Chapter 5). As this is
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Table 7.1: Summary of the PL data for the neat films and blends in the polymer (I) and CQD (II) spectral region. The emission in the PbS region marked with ":" is eclipsed by the PL of the polymer.

<table>
<thead>
<tr>
<th>Emission</th>
<th>Sample</th>
<th>$E_{\text{max}}$ / eV</th>
<th>$\tau_1$</th>
<th>$\tau_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCPDTBT (I) Neat</td>
<td>1.40</td>
<td>118 ps</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>blend_OA</td>
<td>1.39</td>
<td>128 ps</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>blend_BDT</td>
<td>1.40</td>
<td>5.0 ps</td>
<td>75.3 ps</td>
<td></td>
</tr>
<tr>
<td>CQDs (II) PbS_OA</td>
<td>1.00</td>
<td>45.7 ns</td>
<td>275 ns</td>
<td></td>
</tr>
<tr>
<td>blend_OA</td>
<td>1.05</td>
<td>-</td>
<td>474 ns</td>
<td></td>
</tr>
<tr>
<td>PbS_BDT</td>
<td>1.03</td>
<td>-</td>
<td>236 ps</td>
<td></td>
</tr>
<tr>
<td>blend_BDT</td>
<td>1.07</td>
<td>-</td>
<td>196 ps</td>
<td></td>
</tr>
</tbody>
</table>

not observed, the slower decay is instead attributed to changes in morphology and permittivity. Following the explanation of Wehrenberg et al., \[19\] for example, the radiative lifetime $\tau_r$ of a spherical particle is proportional to $[(\epsilon_p + 2\epsilon_h)/(3\epsilon_h)]^2$, where $\epsilon$ is the (optical) permittivity of the particle $p$ or the host $h$. Reducing the matrix's permittivity by adding the polymer thus increases the radiative lifetime. It should be noted, though, that this theory is strictly only valid for isolated particles in a homogeneous matrix.

The obtained lifetimes for the PL of PbS_BDT are significantly shorter when comparing with PbS_OA. This is a well-known phenomenon \[6\] that can be attributed to a more efficient exciton dissociation in the former, as discussed in section 2.4.3. Additionally, trap induced recombination due to a decreased surface passivation after ligand exchange (consider Chapter 8) will further reduce the lifetime of excited states. Fitting the decays of neat PbS_BDT and of the blend gives rise to lifetimes of 236 and 196 ps respectively. The lifetime-reduction for PbS_BDT in the blend points to an interaction between the two components, which can be attributed to a hole transfer towards the polymer.

Transient absorption (TA) spectroscopy, finally, can offer valuable insight into carrier dynamics. This technique especially allows to determine which species of carrier is present in a system. It is known that positive polarons, singlet- and triplet-excitations can form and can be tracked on PCPDTBT, all of which give rise to photoinduced absorption bands in the region around 2 eV. \[20-23\] Tracking the dynamics of neat PCPDTBT, and the two blends with PbS CQDs, when pumping at 1.77 eV (700 nm), i.e. the region of pronounced polymer absorption, and probing at 1.03 eV (1200 nm) is thus a feasible way to examine whether differences occur for excited states of the polymer. Since samples of neat PbS, capped with either OA or BDT, did not exhibit features in this region, all signals discussed below can therefore be attributed to the polymer.

The transient for neat PCPDTBT, depicted in Figure 7.3 (red), can be fitted with a monoexponential function and a lifetime of roughly 90 ps. This value is of the magnitude of the lifetime observed for the PL and suggests the measured signal to be the photoinduced absorption from the polymer singlet exciton ($S_1 \rightarrow S_2$). This assumption is in agreement with results from litera-
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Figure 7.3: Transient absorption of neat PCPDTBT and when blended with PbS_OA or PbS_BDT (a), displaying a long-lasting photoinduced absorption for the latter. EQE spectra of Schottky-type solar cells (architecture illustrated in the inset) comprising an absorption layer of either neat PbS_BDT or the hybrid blend.

ture. The same behaviour is obtained for the blend comprising OA capped CQDs. Given the striking resemblance between these two samples and their PL (as discussed above), it can thus be concluded that the probed signal here is also the polymer singlet exciton. Hence, no considerable charge transfer occurs between PCPDTBT and PbS_OA.

For BDT capped PbS, blended with PCPDTBT, a strikingly different behaviour manifests. After a steep increase, the PIA signal stays virtually constant within the measurement window of approximately 800 ps. Such a long lifetime could either be evoked by a triplet exciton or by a hole polaron on PCPDTBT. Though the former cannot fully be excluded, there is sufficient evidence both in literature and from the external quantum efficiency (EQE) measurements discussed in the following, to clearly assign this signal to positive polarons on the polymer. These form due to the transfer of the electron from the polymer LUMO to the CQD conduction level (depicted in Figure 7.1 (a)) analogous to what occurs in the prototypical donor:acceptor blend with PCBM.

Based on the observations above, it seems promising to use a blend of PCPDTBT with PbS_BDT as active layer (AL) in a thin film solar cell. Such cells were fabricated using the simple Schottky-like architecture (vide inset of Figure 7.3 (b)). The measured external quantum efficiency of both types of cells (with and without PCPDTBT) are depicted in Figure 7.3 (b), where the black curve, referring to the CQD-only device, exhibits a pronounced contribution of the excitonic peak centred around 1.2 eV and a steep increase towards higher energy, ultimately exceeding 60% at 3 eV. Crucially, also a dip in the intermediate spectral region is observable. The device comprising the blended AL exhibits an increased EQE in this intermediate spectral range, which coincides with the absorption spectrum of the neat polymer (Figure 7.1 (b)). As expected from the transient absorption, both materials thus take part in the photocurrent generation of the hybrid device.
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Figure 7.4: J-V curves of the fabricated solar cells, displaying the corruption of the PCE for the blended active layer (a). AFM images of the neat and the hybrid active layer (b). The latter exhibits a significantly higher surface roughness.

A significant drawback, however, appears when considering the spectral regions of pronounced CQD contribution. Adding the polymer reduces the EQE from 15.6 to 11.2% around the excitonic peak and from 63.1 to 41.8% at 2.95 eV. The extent of this reduction cannot be justified by a mere difference in CQD content (90% of CQDs in the blend). A possible explanation might be the increased disorder in the CQD phase which hampers the carrier transport.

Their J-V curves in the fourth quadrant are shown in Figure 7.4 (a). The device with a hybrid AL exhibits inferior values for all relevant solar cell parameters, i.e. short circuit current ($J_{SC}$), open circuit voltage ($V_{OC}$) and fill factor (FF). Besides a lower current delivered by the device, that should nominally exhibit a better coverage of the sun spectrum, its poor transport properties and probably increased recombination losses reduce both $V_{OC}$ and $FF$.

Figure 7.4 (b) and (c) furthermore depict atomic force microscopy (AFM) images of the two active layers. While the film containing only CQDs (b) exhibits a relatively smooth surface with a peak-to-valley distance of 7 nm, the blend displays a strikingly different picture. The entire surface is marked by broad and connected, fibre-like, areas with a width of around 200 µm, separated by equally broad valleys. The peak-to-valley distance amounts to approximately 70 nm and is therefore tenfold larger than for the neat film. Independent of the composition of the respective regions, such an inhomogeneous and rough surface is highly detrimental for proper contacting towards the extracting LiF/Al electrode. A poor interface between the active layer and the cathode, however, will reduce the efficiency for charge carrier extraction and thereby increase their recombination. Since the CQDs should be cross-linked and immobile after the treatment with BDT, it is furthermore likely that the broad fibres are due to the polymer chains. In this case the hole-transporting PCPDTTBT would be accumulated at the electron-extracting electrode, which would furthermore hamper the efficient extraction of charge carriers in these devices.
7.3 Conclusion

Optical properties and charge carrier dynamics of a hybrid organic-inorganic system, comprising a narrow band gap polymer and lead sulphide colloidal quantum dots were investigated in this chapter. Their interaction upon photoexcitation depends on both the absorbing component and the ligand capping the CQDs.

For light absorbed by PbS_OA, no interaction with the polymer is observed, which is attributed to the long ligands acting as a barrier for charge carrier transfer. When exchanging them for the shorter BDT, a reduced PL lifetime emerges and is ascribed to a hole transfer from PbS towards PCPDTBT.

For photons absorbed by the polymer, the analogous behaviour is observed. In blend with PbS_BDT the PL lifetime is significantly reduced and a long-lasting photoinduced absorption on the polymer is observed. Both aspects are assigned to an efficient dissociation of excitons at the heterointerface, leading to the formation of a positive polaron on PCPDTBT and an electron on the CQDs. Accordingly, both materials contribute to the EQE spectrum of solar cells.

Despite this promising interaction, fabricated solar cells did not outperform their neat inorganic counterparts, which is attributed to a significantly deteriorated transport of charge carriers in the hybrid blend. Besides the increased disorder in the CQD phase, evoked by the presence of the polymer chains, a strongly inhomogeneous morphology with a rough surface is observed. This drastically reduces the quality of the contact towards the extracting electrode and is expected to increase recombination at the interface.
7.4 Methods

**Sample preparation:** PbS CQDs were synthesised analogously to previous reports.\(^{[27]}\) PCPDTBTT was purchased from Konarka Technologies GmbH and used as received. All samples were cast under nitrogen atmosphere from solutions of 10 mg mL\(^{-1}\) concentration. Films comprising OA capped CQDs were drop cast and both neat PbS_BDT and polymer comprising films were fabricated \(via\) spin-coating in a layer-by-layer fashion. For the ligand exchange, the cast layer was immersed in a solution of BDT in acetonitrile (2.85 mg mL\(^{-1}\)) for 30 s. The film was spun dry at 4000 rpm for 60 s before the following layer was deposited. A complete removal of OA ligands for this method has previously been confirmed.\(^{[26,28]}\) QD-comprising films were annealed at 140°C, analogously to QDSCs.

**UV/vis:** Absorption spectra were recorded with a Shimadzu 3600 UV-vis-NIR spectrometer. Films were cast on glass substrates.

**Photoluminescence:** Films were deposited on quartz substrates, sealed, using epoxy glue, and excited at 3.1 eV (400 nm) using the second harmonic of a mode-locked Ti:sapphire laser at a repetition rate of 76 MHz. Steady-state spectra were recorded with an InGaAs detector from Andor. Time-resolved traces were taken with a Hamamatsu streak camera working either in the synchroscan or single sweep mode. An optical pulse selector was used to vary the repetition rate of the exciting pulses where necessary.

**Transient absorption:** Transient absorption spectra were recorded using a super continuum laser source (SuperK Extreme, NKT Photonics) that provided both the pump and probe at a MHz repetition rate. The pulse duration amounted to approximately 1 ps and the pump power was kept below 4 \(\mu J\) cm\(^{-2}\) to avoid thermal effects, sample degradation as well as non-linear higher order processes. The signals were measured with an auto-balanced photoreceiver (Nirvana 2017, New Focus) and amplified with a Lock-In amplifier (SR 830 DSP, Stanford Research Systems). All measurements were carried out at room temperature.

**Solar cell fabrication:** Active layers were deposited as explained above, with a thickness of approximately 150 nm on pre-patterned indium tin oxide (ITO) substrates. The devices were annealed at 140°C for 10 min, before thermal evaporation of 1 nm LiF and 100 nm Al as top contact. Device areas were defined by the overlap of the Al and ITO electrodes to be 16 mm\(^2\). External quantum efficiencies were measured near short circuit conditions using a 250 W quartz tungsten halogen lamp (6334NS, Newport) with lamp housing (67009, Newport). Monochromatic light was generated using narrow band pass filter (Thorlabs) with a full width at half maximum (FWHM) of 10±2 nm from 400 to 1300 nm and a FWHM of 12±2.4 nm from 1300 to 1400 nm. The light intensity was determined by calibrated photodiodes (PD300 and PD300IR, Ophir Optics).
Bibliography


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