Picosecond dynamics of charge and energy transfer in polymer/fullerene composites

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Abstract

Composites of conjugated polymer and fullerenes are promising functional materials for photonic devices such as solar cells. The prime property of these blends is the occurrence of a photoinduced electron transfer reaction. To gain insight in the electron transfer mechanism in polymer/C$_{60}$ blends, a set-up for 2-color time-resolved photoinduced absorption has been built, and the decay dynamics on the picosecond time has been studied. In a comparative study of the photoinduced absorption of P3HT and P3HT:PCBM an electron back transfer time of $2.5\pm0.5$ ns was found. A Non-Degenerate Four-Wave Mixing set-up has been developed for decay measurements on a transient photorefractive grating. It was found that the higher pulse energies than presently available are needed to successfully perform these kind of measurements. The lifetime of the photoluminescence of OPV$_n$ ($n=2$-$5$) and OPV$_n$-C$_{60}$ dyads ($n=3,4$) in toluene has been measured using Time-Correlated Single Photon Counting. The photoluminescence of the OPV$_n$-C$_{60}$ dyads is found to decay bi-exponentially: the short life time component was within the experimental resolution and attributed to the OPV-moiety; the long life time component was attributed to an impurity. The photoluminescence spectra of the dyads are found to be not just a superposition of the spectra of the compounds. A red shift of the photoluminescence band of the OPV$_n$ is observed.
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Chapter 1

Introduction

Semiconducting polymers are promising candidates for nonlinear optical applications. When photoexcited, bond relaxation in the excited state leads to the formation of electronic states within the energy gap of the semiconductor. These gap states change the optical properties of the polymer. In this sense, semiconducting polymers are inherently nonlinear in their optical response.

The optical properties of semiconducting polymers are significantly changed with the addition of C_{60}. After photoexcitation across the $\pi-\pi^*$ gap, the electron transfers from the polymer to the C_{60}. This electron transfer takes place on a femtosecond timescale (ultrafast), therefore, the quantum efficiency of the transfer is approaching unity. Due to this property, semiconducting/fullerene blends are promising functional materials for photonic devices, such as solar cells.

In these blends dynamic holography with good diffraction efficiency has been shown and attributed to the electron transfer. Holographic gratings are a principal component of dynamical optical systems based on nonlinear optical materials; holographic gratings are useful in a variety of optical applications, including interconnection networks, optical memories and optical computing. Inorganic photorefractive crystals have been the most widely studied materials for such applications. Recently, organic holographic materials such as photorefractive polymers, photochromic molecules, and semiconducting polymers, have received considerable attention. One of the major problems constraining the practical use of holographic materials has been the trade-off between speed and diffraction efficiency inherent in many classes of materials. Due to the ultrafast electron transfer and stability of the charge separated state, semiconducting/fullerene blends offer potential as high-performance holographic materials.

To gain insight in the physical mechanism responsible for the nonlinear processes, the decay dynamics of the photoinduced charge carriers is studied in this report.

In chapter 2, an introduction to semiconducting polymers and the nature of the charge carriers is given. In chapter 3, measurements of the life times of the photoluminescence of OPV_n (n=2-5) and OPV_n-C_{60} dyads (n=3,4), as well as of other oligomers, are presented. Since efficiency of the electron and energy transfer to the fullerene is nearly unity, the photoluminescence of the OPV_n-
C$_{60}$ dyads is quenched. The very weak luminescence that is left, has been investigated on a nanosecond time scale using Time-Correlated Single Photon Counting. In chapter 4, the decay dynamics of the photoinduced bleaching and the photoinduced absorption of a P3HT:PCBM blend is studied. For this a pump-probe instrumentation was build. In chapter 5, a set-up for a Four-Wave Mixing experiment is described. In a polymer/fullerene blend, two interfering laser beams will create a photorefractive grating due to the charge transfer to the fullerene. Measurement of the decay of the transient photorefractive grating will provide information of the lifetime of the charge transfer. In chapter 6, the conclusions made in this report are presented and recommendations are made.
Chapter 2

Theory

2.1 Conjugated polymers

In saturated polymers, such as polyethylene, \((CH_2)_n\) (see figure 1a), every carbon atom is bonded to the neighboring carbon and hydrogen atoms by a \(\sigma\)-bond. These polymers are insulators, since the excitation of the electron from a bonding \(\sigma\)-orbital to an anti-bonding \(\sigma^*\)-orbital requires an energy of 6 eV or more. Furthermore, when excited, the polymer chain will degrade, since the electrons in the bonding \(\sigma\)-orbital keep the chain together. In contrast, in conjugated polymers, three electrons reside in \(\sigma\)-bonding orbitals and the fourth electron in the delocalized \(p_z\)-orbital. The \(p_z\)-orbitals of the adjacent carbon atoms overlap to form \(\pi\)-bonds. Conjugated polymers are schematically depicted as a series of alternating single and double bonds, see figure 1b).

\[
\text{(a)} \quad \text{(b)} \quad \text{(c)}
\]

Figure 2.1: Chemical structure of: (a) trans-polyethylene (b) polyacetylene (c) PPV.

The number of \(\pi\)-bonds in a conjugated polymer is determined by the number of carbon atoms in the monomer. For an even number, \(2n\), of carbon atoms in the monomer, the \(\pi\)-band is divided in \(2n\) sub-bands. Since each sub-band can hold two electron per atom (spin up and spin down), the lowest \(n\) sub-bands are filled (the \(\pi\)-sub-bands) and the highest \(n\) sub-bands are empty (the \(\pi^*\)-sub-bands). The conjugated polymer is not metallic, since the bands are completely filled. For instance, poly(phenylene vinylene), PPV, is a semiconductor, since the energy difference between the highest occupied \(\pi\)-sub-band (HOMO) and the lowest unoccupied \(\pi\)-sub-band (LUMO), de \(\pi-\pi^*\) energy gap, is approximately 2.5 eV.
2.2 Electronic structure and bond relaxation in excited states

The optical properties of conjugated polymers have been explained by both band-based and exciton-based models. Still, there is some controversy over the description of the elementary excitations. The electronic structure of conjugated polymers is described by the SSH model, in terms of a quasi-one-dimensional tight binding model in which the $\pi$-electrons are coupled to distortions in the polymer backbone by the electron-phonon interaction. In the SSH-model, photoexcitation across the $\pi-\pi^*$ gap creates self-localized, nonlinear excitations: solitons, polarons and bipolarons (described below).

The SSH-model was successfully used to describe the origin of the band gap in trans-poly(acetylene). Trans-poly(acetylene), containing one carbon atom in the monomer, has one $\pi$-band that is half-filled with one $p_z$ electron. Thus polyacetylene would be a metal. However, polyacetylene is a semiconductor with an energy gap greater than 1.5 eV [1]. This is due to the relaxation of the carbon lattice with the position of the double bond. The double bond is shorter than the single bond. This breaks the symmetry of the $(CH)_n$ chain. This so-called Peierls-instability result in doubling of the unit cell (dimerization) and halving of the first Brillouin Zone. The $\pi$-band splits into two sub-band, one completely occupied valence band and an empty conduction band.

2.3 Charge carriers and charge transport

Doping of semiconducting (conjugated) polymers leads to different effects. Doping can take place in a number of ways and is based upon adding a positive or negative charge. In this report, the attention is focussed only to doping by photo-exciting the charge carriers in the material: photo-doping. Through absorption of light, locally, an electron-hole pair (exciton) is generated on the polymer, see figure 2.2. Upon dissociation of this pair, a free electron (oxidation) and a free hole (reduction) are created. Subsequent recombination of the electron and the hole may lead to luminescence.

![Figure 2.2: Subsequent excitation of the polymer, forming of exciton and recombination leads to luminescence.](image)

Rapid bond relaxation of the excited state in polyacetylene leads to the formation of so called solitons (discussed in the next section), which counteracts the luminescence. Also, adding an acceptor to the polymer leads to quenching of the luminescence, as a result of charge transfer.
2.3.1 Solitons

Consider polyacetylene in figure 2.3. This molecule has a degenerate ground state. Adding a charge results in relaxation of the chain into two different configurations. The boundary between the two possible configurations is called a soliton. This soliton is stable, because it is delocalized on the chain, spanning an area of about seven carbon atoms, see figure 2.3(d) and 2.3(e).

Figure 2.3: Polyacetylene (a) undimerized structure of trans-polyacetylene (b) degenerate ground states of trans-polyacetylene (c) cis-polyacetylene (d) soliton in trans-polyacetylene (e) delocalized soliton in trans-polyacetylene.

The relaxation of the chain results in the formation of the soliton state with an energy level in the mid of the band gap. If an electron is removed (added), a positively (negatively) charged atom is left, but there are no unpaired spins. The soliton state is unoccupied (fully occupied). If the state is singly occupied, the carbon is uncharged, but a spin is introduced to the chain. Due to the symmetry of the molecule, the soliton is stable and mobile, and charge is transported on the chain. The different solitons and corresponding chemical designations are shown in figure 2.4.
2.3.2 Polarons and bipolarons

Now, consider polythiophene in figure 2.5a, this molecule has an aromatic structure in the ground state. Upon adding a positive charge (removing an electron from the π-band), a shift of the electrons along the chain occurs, see figure 2.5b. This changes the geometrical structure of the molecule into a so called quinoid structure. Since the quinoid structure corresponds to a higher energy state than the aromatic structure, the ground state is non-degenerate. Therefore, the soliton in polythiophene is unstable. However, a soliton-antisoliton pair is stable. Such a pair is called polaron or bipolaron. A polaron can be thought of as a bound state of a charged soliton and a neutral soliton, whose mid-gap energy states hybridize, see figure 2.6. A positive (negative) polaron is a hole (electron) dressed with the accompanying lattice distortion. A bipolaron is a bound state of two equally charged solitons, see figure 2.7. The attractive interaction between the solitons is made possible by a local structural distortion of the polymer chain [21]. A bipolaron can also be regarded as two equally charged polarons, whose neutral solitons annihilate each other. Polarons and bipolarons are localized charged states, that are mobile on the polymer chain. These are the charge carriers responsible for conduction.

In figures 2.6 and 2.7, the dipole-allowed transitions are given (labeled P₁, P₂, etc). These transitions give rise to the bands observed in photoinduced absorption spectra (discussed below). As an example, for the positive polaron these transitions are explained: the P₁ transition is from the double occupied level (a_u) to the singly occupied level (b_g); the P₂ transition is from the singly occupied b_g level to the lowest empty level (a_u); the transition from the singly occupied polaron level (b_g) to the conduction band (b_g) is symmetry-forbidden.
Figure 2.5: Polytiophene. (a) aromatic structure (b) quinoid structure

Figure 2.6: Polarons in polythiophene: energy levels, associated transitions and structure.

Figure 2.7: Bipolarons in polythiophene: energy levels, associated transitions and structure.
2.3.3 Polaron pairs

In a number of studies [18, 25, 10, 33] so called polaron pairs have been found. A polaron pair is composed of two oppositely charged polarons. The Coulomb interaction between the polarons pushes down the HOMO of the negative polaron and pulls up the LUMO of the positive polaron, so that only two singly-occupied levels remain in the gap. A schematic diagram of a polaron pair and associated optical transitions is shown in figure 2.8.

![Schematic diagram of polaron pair energy levels and optical transitions.](image)

**Figure 2.8:** Schematic diagram of polaron pair energy levels and optical transitions.

2.3.4 Excitons

Upon adding two oppositely charged carriers to the conjugated chain, for instance by photoexciting an electron from the HOMO to the LUMO and thereby introducing a hole in the HOMO, a localized, thus geminately bound, electron-hole pair is formed (exciton). Due to the resulting relaxation of the chain, in literature it is called a neutral bipolaron, neutral polaron exciton or self-trapped exciton. Concerning the energy states of an exciton, three effects are of importance, e.g. polaronic effects (lattice-relaxation), the Coulomb-interaction between hole and electron, and the de spin-orbit coupling, see figure 2.9.

![Diagram of excitons](image)

**Figure 2.9:** Exciton: (a) singlet exciton, (b) triplet exciton, (c) splitting of the energy levels and (d) structure.

2.4 Photoinduced charge and energy transfer

When a conjugated polymer is doped by an acceptor like buckminsterfullerene, C_{60}, charge and energy transfer can occur, after photoexcitation. Conjugated polymers in their undoped, semiconducting state are electron donors upon photoexcitation. C_{60} is an excellent electron acceptor capable of taking on as many
as six electrons. The donor and acceptor units are either covalently bound or spatially close but not covalently bound.

Upon photoexcitation of either the donor or the acceptor molecule, a number of processes can occur:

- the excited electron (hole) can be transferred to the acceptor (donor), resulting in a positive polaron on the donor molecule
- the energy of the excited donor (acceptor) can be transferred to the acceptor (donor).
- the excited electron and hole can recombine while emitting radiation (fluorescence);
- the excited electron and hole can recombine without emitting radiation;
- the excited electron can enter a triplet state (intersystem crossing) and decay to the ground state while emitting radiation (phosphorescence);
- the excited electron can enter a triplet state and decay to the ground state without emitting radiation

These processes are competing processes, but whether a process will occur depends on certain conditions.

### 2.4.1 Electron and hole transfer

Figure 2.10 shows a schematic energy level diagram of the photoinduced electron (or hole) transfer process, as acceptor C₆₀ is taken. The photoexcited electron in the conduction band of the polymer is transferred to lower lying LUMO of the C₆₀. When the C₆₀ is excited, an electron from the ground state in the polymer can be transferred to hole in the HOMO of the C₆₀, thus a hole is transferred from the C₆₀ to the polymer.

![Schematic diagram of electron and hole transfer](image)

**Figure 2.10**: Photoinduced charge transfer by (a) exciting the donor (b) exciting the acceptor.

The electron transfer can be described *schematically* in the following steps [27]:

1. \( D + A \rightarrow ^{1,3} D^* + A \) (excitation on D)
2. \(1^1,3D^* + A \rightarrow 1^1,3(D - A)^*\) (excitation delocalized on D-A complex)

3. \(1^1,3(D - A)^* \rightarrow 1^1,3(D^{5+} - A^{5-})^*\) (charge transfer initiated)

4. \(1^1,3(D^{5+} - A^{5-})^* \rightarrow 1^1,3(D^+ - A^-)\) (ion radical pair formed)

5. \(1^1,3(D^+ - A^-) \rightarrow D^+ + A^-\) (charge separation),

where the donor (D) and acceptor (A) units are either covalently bound (intramolecular), or spatially close but not covalently bonded (intermolecular); 1 and 3 denote singlet or triplet excited states, respectively. Step 3 is strongly dependent on the polarity of the surrounding medium (solvent). The stability of a positively or negatively charged state increases with the polarity of the medium. Step 4 describes the formation of an ion radical pair, which does not occur unless

\[
I(D^*) - A(A) - U_C < 0, \tag{2.1}
\]

where \(I(D^*)\) is the ionization potential of the excited donor, \(A(A)\) is the energy needed to reduce the acceptor (electron affinity), and \(U_C\) is the Coulomb energy of the separated radicals. Step 5, charge separation by whole electron transfer, can be enabled only when the resulting positive charge on the donor (positive polaron/bipolaron), is stable. The stability of this polaron on a conjugated polymer is known to be greater when it is delocalized on the chain. The longer the chains, the smaller \(I(D^*)\) becomes [16]. These conditions for electron transfer applied for a solution are given in the Weller-equation [2]:

\[
\Delta G_{CT} = E_{ox}(D) - E_{00} - E_{red}(A) - \frac{e^2}{4\pi\varepsilon_0\varepsilon_s R_C} - \frac{e^2}{8\pi\varepsilon_0} \left( \frac{1}{r^+} + \frac{1}{r^-} \right) \left( \frac{1}{\varepsilon_{ref}} - \frac{1}{\varepsilon_s} \right), \tag{2.2}
\]

where \(E_{ox}(D)\) denotes the energy needed to oxidize the donor, \(E_{00}\) denotes the energy level from which the electron transfer occurs, \(E_{red}(A)\) denotes the energy needed to reduce the acceptor, \(R_C\) denotes the Coulomb distance between the positive and the negative charges in the charge separated states, \(r^+\) and \(r^-\) denote the radii of the positive and the negative ions, \(\varepsilon_s\) is the relative permittivity of the solvent and \(\varepsilon_0\) the vacuum permittivity. The Weller-equation can be used to describe both intrachain electron transfer and interchain electron transfer, for interchain electron transfer the term containing \(R_C\) is neglected.

Photoinduced electron transfer from the excited state of conducting polymers onto C\(_{60}\) has been reported (see [22, 4, 23, 19, 20]). The quenching of the photoluminescence and the subpicosecond time-resolved photoinduced absorption demonstrate that electron transfer from the excited state of the conducting polymer to C\(_{60}\) occurs within 1 ps after photoexcitation with energy greater than \(\pi-\pi^*\) gap. Since charge transfer occur nearly \(10^3\) times faster than any competing process, the quantum efficiency for photoinduced electron transfer is of order unity. Early time recombination is inhibited by the spatial separation of the electron and the hole on acceptor and the donor, respectively. In [33], it is speculated that inefficient C\(_{60}\) doping in some conjugated polymers leads to exciton dissociation into geminate intrachain polaron pairs (see above), rather than a complete photoinduced charge transfer.
2.4.2 Energy transfer

Energy transfer is a process in which the excited molecule (molecule A) transfers its energy to a different type of molecule (molecule B). Then molecule B turns to an excited state and molecule A decays to its ground state. This is described in figure 2.11. The efficient energy transfer from molecule A to molecule B can only occur when the energy $E_B$ needed to excite molecule B is less than the energy $E_A$ released as molecule A decays to the ground state.

![Energy transfer](image)

Figure 2.11: Energy transfer from molecule A to molecule B.

2.5 Introduction to photoinduced absorption spectroscopy

Photoinduced absorption (PIA) spectroscopy is used to measure the spectral transitions that take place after excitation of the donor or acceptor molecule. The excitation wavelength is usually chosen near the wavelength at which the molecule absorbs most, which can be determined from an UV/Vis absorption measurement. After excitation a white light probe beam is focussed on the sample. The change in transmission of the probe beam is detected at the wavelengths of interest. Also the transmission of the probe beam without exciting the sample (T), and the emission by the sample by only exciting the sample (photoluminescence) is measured. The change in transmission corrected for the photoluminescence and divided by the transmission $T$ results in the PIA signal

$$-\frac{\Delta T(t)}{T} = \Delta \alpha(t) d = n(t) \sigma d,$$

(2.3)

where $\Delta \alpha$ is the change in the linear absorption coefficient $\alpha$, $d$ the sample thickness, $n(t)$ is the density of photoexcited states and $\sigma$ is the absorption cross-section for the excited states [10].

As an example, the PIA spectrum of a MEH-PPV:C$_{60}$ composite film is shown in figure 2.12. The spectrum is dominated by two bands with onsets at 0.25 eV (LE band) and 1.18 eV (HE band). Upon photoexcitation electron transfer to the C$_{60}$ takes place, leaving behind a radical cation (positive polaron) at the PPV [6]. The LE and is associated with the 'P1' transition and the HE band with the 'P2' transition, see figure 2.6. Near the absorption maximum of the PPV (~2.1 eV) the PIA signal changes of sign (labelled E), this band is the so called bleaching band. This band corresponds to the $S_1 \rightarrow S_0$ transition and arises due to the reduced number of molecules (depletion) being in the ground state after photoexcitation.
Figure 2.12: Photoinduced absorption spectrum of MEH-PPV:C₆₀ (1:1) at 4K, pumped by an Ar⁺ laser.
Chapter 3

Photoluminescence

In this chapter, time-resolved and time-integrated photoluminescence measurements on oligo(p-phenylene vinylene \( \text{OPV}_n \), \( n=2-5 \)) and \( \text{OPV}_n-\text{C}_{60} \) dyads \( (n=3,4) \) are presented. Since efficiency of the electron and energy transfer to the fullerene is nearly unity, the photoluminescence of the \( \text{OPV}_n-\text{C}_{60} \) dyads is quenched. To detect the very weak luminescence that is left, Time-Correlated Single Photon Counting has been employed. Also the life times of the photoluminescence of three low oxidation potential oligomers have been measured, these measurements are presented in the Appendix.

3.1 Introduction

To gain insight into intramolecular processes, such as energy and electron transfer, many \( \text{C}_{60} \)-based donor-acceptor molecules have been synthesized and investigated recently. In this study, \( \text{OPV}_n-\text{C}_{60} \) dyads are investigated by time-resolved photoluminescence measurements. In \( \text{OPV}_n-\text{C}_{60} \), the \( \text{OPV}_n \) is the donor moiety that is covalently attached to \( \text{MP-C}_{60} \), the acceptor moiety. \( \text{OPV}_n \) is a \( \pi \)-conjugated oligomer, \( n \) denotes the number of phenyl rings. In figure 3.1, the structures of the \( \text{OPV}_n \), \( \text{MP-C}_{60} \) and the dyads, are shown. The \( \text{OPV}_n-\text{C}_{60} \) were solved in toluene. The dielectric constant of toluene is small \( (\epsilon_s=2.38) \). By using the Weller-equation 2.2 it was derived in [15] that the change in free energy for charge separation is positive for all \( \text{OPV}_n-\text{C}_{60} \) dyads. Thus, electron transfer will not occur in toluene.
3.2 OPVn and OPVn-C60: a literature survey

In figure 3.2a the absorption spectra of the OPVn-C60 dyads in solvent are given. For all dyads the spectra exhibit strong absorptions from 200 to 250 nm and weak absorption at 704 nm. Further, for OPV2-C60, OPV3-C60 and OPV4-C60, absorption bands around 450 nm are observed. Upon comparison to the absorption spectra of the molecular OPVn and MP-C60 shown in figure 3.2b, it is concluded that the spectrum of the dyad is a superposition of the spectra of the individual components. Thus, the absorption bands around 450 nm are attributed to the π-π* transition of the OPV moieties. The absorption band at 704 nm is characteristic for the C60-derivative. Figure 3.2a shows that laser light of 395 nm will excite mostly the OPV3 and OPV4 moieties, and the C60 moiety only very little. The OPV2 moiety can not be excited selectively.

![Figure 3.1](image)  
Figure 3.1: The structures of (a) α,ω-dimethyl oligo(p-phenylene vinylene)(OPVn) (m=n-1) (b) N-methylfulleropyrroolidine (MP-C60) and (c) the OPVn-C60 dyads.

![Figure 3.2](image)  
Figure 3.2: (a) UV/Vis spectra of OPVn-C60 (in dilute chloroform solutions) and (b) UV/Vis spectra of reference compounds OPVn and MP-C60 (from [15]).

After photoexcitation, the $S_1$ state of the OPVn molecule has been found to decay via fluorescence, see figure 3.3b, or by intersystem crossing to the triplet $T_1$ state [14]. The triplet excited state lifetimes of OPV3 and OPV4 was measured to be 7.9 and 3.6 ms, respectively.

Photoexcitation of MP-C60 in solution results in photoluminescence at 712
**Figure 3.3:** (a) UV/Vis absorption and (b) photoluminescence spectra of OPV$_n$ molecules recorded in 2MeTHF at 290 K, normalized (from [15]).

**Figure 3.4:** Schematic diagram representing the energy levels of the OPV$_n$ and C$_{60}$. In the molecular OPV, intersystem crossing to the triplet state occurs after excitation, in the dyad energy transfer to the C$_{60}$ occurs.

nm. Different singlet state lifetime have been reported (1.45 and 1.28 ns [16]) and a long lived triplet state (200 μs [16]).

Steady state photoluminescence measurements in [15] (excited at maximum absorption of the OPV$_n$) of the dyads in toluene showed the fluorescence of C$_{60}$ at 715 nm and a strong quenching of the fluorescence of the OPV moiety. PIA spectra of the solution showed the characteristic absorption at 1.78 eV with a shoulder at 1.52 eV of the C$_{60}$($T_1$) triplet state. Therefore, it was concluded that in a solution of the dyad in toluene, intramolecular singlet energy transfer occurs, upon which the singlet excited state of the MP-C$_{60}$ decays via fluorescence (very weak) and by intersystem crossing to the triplet state. The steady-state fluorescence has been measured again, and is shown in the Appendix, figure A.8.

In figure 3.4, a schematic overview of the energy transfer from the OPV$_n$ to the C$_{60}$ is shown.
An estimation for the rate constant \( k_{ET} \) of the intramolecular singlet energy transfer from the OPV moiety to the C\(_{60}\) can be made from the extent of quenching of the fluorescence of the OPV and the photoluminescence lifetime of the separate OPV\(n\)s via [15, 16]:

\[
k_{ET} = \left[ \frac{\phi(\text{OPV}n)}{\phi} - 1 \right] / \tau(\text{OPV}n),
\]

where \( \tau(\text{OPV}n) \) is the lifetime of the singlet excited state of the separate OPV\(n\) molecules, and \( \frac{\phi(\text{OPV}n)}{\phi} \) is the quenching ratio. Based on steady-state fluorescence measurements, an estimate of \(~500\) fs for OPV\(3\)-C\(_{60}\) and \(~900\) fs for OPV\(4\)-C\(_{60}\) was obtained.

### 3.3 Experiment

The set-up used for the photoluminescence measurements is schematically depicted in figure 3.5. The output of a cavity dumped dye (Rhodamine 6G) laser pumped by the second harmonic of an actively stabilized mode-locked Nd:YAG (Neodymium Yttrium Aluminium Garnet) laser is frequency doubled by a LiIO\(_3\) crystal to obtain \(~5\) ps pulses at 305 nm (Setup III). To obtain 395 nm pulses the output of a mode-locked Ti:Sapphire laser (Setup IV) is frequency doubled by the crystal. The frequency doubled beam is aligned close to the edge of a cuvette containing the oligomer solution to prevent reabsorption of the photoluminescence. To prevent light other than 305 or 395 nm to reach the sample, color filters were placed in the beam. The photoluminescence of the solution perpendicular to the pump beam is focussed by two lenses on the slit of a double monochromator. By using a double monochromator a spectral resolution of 1 nm was obtained. The monochromator was calibrated using the known emission of a xenon spectral source. To prevent light other than the laser beam to enter the monochromator, the slit was shielded by black paper. Also even the desk light, which light contains no specific time dependence, had to be switched off since it produced a nonuniform spectral output, which was measured as substantial peaks in the PL-spectra.

After passing the monochromator the photoluminescence is detected by a multi-channel plate photomultiplier. The output of the photomultiplier is converted in TTL pulses which was measured by a rate meter and a multi channel analyzer (MCA) to obtain the photoluminescence spectra (Setup I). To prevent distortion of the spectra due to pulse pile-up effects, the count rate was kept below \(10^5\) counts s\(^{-1}\) by the use of a neutral density filter. To read out the MCA and to control the monochromator, homebuild software was used. In this way PL-spectra for wavelengths between 400 and 720 nm were measured.

To measure the life time of the photoluminescence the output of the photomultiplier was amplified and converted to fast-negative NIM output logic pulses (NIM-pulses) by an amplifier and timing discriminator. The converted signal was connected to the start-input of a time-to-pulse height converter (TPHC) and the start-output of a time calibrator. The stop-output of the time calibrator and the stop-input of the TPHC was connected to the delayed NIM-pulses.
produced by a photodiode placed in a part of the pump beam. Thus the TPHC is triggered by the first PL-pulse and stopped by the corresponding pump pulse. This reverse mode of operation is necessary, since the repetition frequency of the pump pulses is too high (78 MHz) to trigger the TPHC.

The output of the TPHC was connected to the MCA. MAESTRO software was used to read out the MCA. In this way the time-integrated PL in a time window of maximum 13 ns was measured.

Time-resolved photoluminescence measurements were obtained by connecting the single channel analyzer (SCA) on the TPHC to the MCA. By using the SCA the time-window was changed (Setup II). The smallest possible time-window was 6.768 ±0.002 ps (corresponding to one channel). However, the obtained time resolution was 70 ps. The resolution of the photomultiplier was 40 ps, on top of that comes the error in the triggering of the NIM-pulses by the the electronic equipment.

All measurements have been done at room temperature.

3.3.1 Observations regarding the experimental apparatus

When the Ti-Sapphire laser was used to excite the samples, it was observed that the TPHC could not properly detect the 78 MHz trigger pulses. Only after changing the threshold of the amplitude and timing discriminators, the pulses could be detected. Due to the high repetition rate, four pulses were detected in the time spectrum. Erroneous behavior of the TPHC was visible for the pulse that was detected as last (fourth) in the time-window.

Also, in the PL spectra it was observed that extra peaks are detected around and above 730 nm, when the Ti-Sapphire laser was instable.
1 Coherent Antares 76-YAG Mode-locked by Coherent 7600 Mode-Locker
2 Second harmonic 532 nm
3 Coherent 7670 AAS Active Stabiliser
4 Coherent 700 Dye Laser containing Dye Rhodamine 6G 2 and Saturable Absorber DODCI
5 Coherent 7220 Cavity Dumper
6 Ti-Sapphire laser
7 Femtochrome Research autocorrelator model FR-103
8 Antel Optronics AR-S silicon photodetector
9 LiF crystal
10 Quartz cuvette containing polymer solution
11 Bentham M300 Double monochromator
12 Hamamatsu R3809u-51 multi-channel Plate Photomultiplier and Hamamatsu MCP-photomultiplier cooler C4878-02
13 Color filter
14/15 EG&G Ortec 1-GHz Amplifier & Timing Discriminator 9327
16 Ortec EG&G 449-2 Log/Lin Ratemeter range=10^5 time constant=0.3 s
17 Ortec EG&G 492 Time Calibrator period=0.01 µs range=0.08 µs
18 Ortec 467 Time to Pulse Height Converter/Single Channel Analyzer range=0.05 µs multiplier=1
19 Ortec 425A Delay 63 ns
20 LRS 688 AL Level Adapter
21 PC, Multi Channel Analyzer and MAESTRO software
22 Homebuild I/O Connector

Figure 3.5: Schematic diagram of the set-up used for the time-resolved photoluminescence measurements.
3.4 Results

3.4.1 Life time measurements of the photoluminescence of OPV2, 3, 4 and 5

In figure 3.6, the life time measurements of the photoluminescence of OPV2, 3, 4 and 5 are shown. The samples were excited at 305 nm. The excitation density was 0.4 mW/mm². The emission was measured near the top of the steady state fluorescence, see figure 3.3. The slow rise time of the photoluminescence is due to the experimental resolution (70 ps). The measurements are fitted using an single exponential decay between 1 and 20 ns. The error in the fit is 0.01 ns. The single exponential decay did not fit in the first nanosecond after excitation. Initially, the molecules are randomly oriented and the PL is depolarized. Due to the monochromator used, the detection of the PL is more sensitive in one direction than in the other. This may explain the deviation from the fit. Also, the PL of the OPV5 did not fit completely to the single exponential decay for times greater than 5 ns. This could be attributed to aggregate formation due to the longer chain length of the OPV5, see [14]. The life time of the PL of

![Graph showing normalized photoluminescence spectra of OPV2, 3, 4 and 5](image)

**Figure 3.6:** Normalized photoluminescence spectra of OPV2, 3, 4 and 5

OPV3 is also measured at 500 nm, see figure A.1 in the Appendix, and found to be 1.54±0.01 ns.

Thus, it is observed that with increasing conjugation length, the life times of the PL of the OPVns decrease. This is also found in [15] and attributed to the increase in radiative and non-radiative decay with increasing conjugation.
3.4.2 Time-resolved photoluminescence spectra of OPV3 and OPV4

In figure 3.7, the time-resolved measurements of the photoluminescence of OPV3 in toluene are shown. The spectra shown in this chapter are corrected for response of the monochromator used, unless mentioned otherwise. The samples were excited at 395 nm. The excitation density was 0.4 mW/mm². It is observed that the spectra do not change after the first 100 ps. Two peaks are present, one at 465 nm and the other at 495 nm. These are the vibronic transitions 0-0 and 0-1, respectively. In figure 3.8, the same spectra are shown after correction for the response of the monochromator. In figure 3.9 PL spectra of OPV4 in toluene are shown. In contrast to the OPV3, the spectrum does still change after 90 ps, the 0-0 vibronic transition is not yet present.

![Figure 3.7: Photoluminescence spectrum of OPV3, recorded in different time-windows after excitation at 395 nm (not corrected for response of the used monochromator).](image-url)
Figure 3.8: Photoluminescence spectrum of OPV3, recorded in different time-windows after excitation at 395 nm.

Figure 3.9: Photoluminescence spectrum of OPV4, recorded in different time-windows after excitation at 395 nm.
3.4.3 OPV3-C\textsubscript{60} and OPV4-C\textsubscript{60}

In this section, time-resolved PL spectra of OPV3-C\textsubscript{60} and OPV4-C\textsubscript{60} solved in toluene are presented. The samples were excited at 395 nm, the excitation density was 0.4 mW/mm\textsuperscript{2}. At characteristic points in the spectra, also the life time is measured. Expected is that the life time of the luminescence is very short, due to the quenching of the PL by the energy transfer to the C\textsubscript{60}. Thus, a life time smaller than 70 ps is expected (the experimental resolution) at 500 nm. At 720 nm, the life time should be 1.45 ns, that of C\textsubscript{60}.

**Life time measurements of the luminescence of OPV3-C\textsubscript{60} and OPV3-C\textsubscript{60}**

Life times of OPV3-C\textsubscript{60} and OPV4-C\textsubscript{60} have been measured at different wavelengths and are presented in figure A.6 and A.7 in the Appendix. Typically, the decay of the photoluminescence is bi-exponential at wavelengths between 420 and 600 nm. For wavelengths greater than 700 nm, the decay of the PL is mono-exponential.

In figure 3.10, the decay of the photoluminescence of OPV3-C\textsubscript{60} at 452, 460, 500 and 715 nm is shown.

![Figure 3.10: Life time the luminescence of OPV3-C\textsubscript{60} excited at 395 nm, measured at different wavelengths.](image)

In the figure very fast components of the decay are observed at 440, 452, 460 and 500 nm. The fast decay at 440, 452 and 460 nm is attributed to the Raman scattering of the toluene (see the next section). The decay time of these
components are within the experimental resolution. The long life time component (shown in the inset) of the PL at 500 nm is measured to be 1.2-1.3 ns, which is shorter than life time of the PL of the OPV3 (1.54 ns). It is not clear what this life time should be attributed to. The life time at 720 nm is measured to be 1.47±0.07 ns, which is the known life time of the PL of the C60 (1.45 ns).

In figure 3.11, the decay of the photoluminescence of OPV4-C60 at 442, 460, 500 and 715 nm is shown.

![Figure 3.11: Life time the luminescence of OPV4-C60 excited at 395 nm, measured at different wavelengths.](image)

In the figure fast components of the decay are observed at 440, 460 and 500 nm. Again, decay at 440 and 460 nm is attributed to the Raman scattering of the toluene. The long life time component (shown in the inset) of the PL at 500 nm is measured to be ~1.5 ns, which is larger than the life time of the PL of the OPV4 (1.21 ns). The life time of the 720 nm PL is measured to be 1.55±0.07 ns, which is similar to the known life time of the PL of the C60 (1.45 ns).

The short life time at 500 nm that is measured agrees with the theory of the fast energy transfer. However, the long life time components measured are not expected. To gain insight in the processes that takes place after photoexcitation, the time-resolved photoluminescence spectra of OPV3-C60 and OPV4-C60 have been measured. These are presented in the next sections.
**Time-resolved photoluminescence spectra of OPV3-\(C_{60}\)**

In figure 3.12 the time-resolved measurements of the very weak photoluminescence of OPV3-\(C_{60}\) are shown. Initially, the spectrum show a broad band from 420 nm until 700 nm, and a sharper band around 720 nm, which is due to the \(C_{60}\). By exciting at 395 nm, mostly the OPV3 is excited, see figure 3.2. Also seen during the first 100 ps is a sharp peak around 450 nm and, somewhat smaller, around 420 nm. These peaks are instantaneous, and attributed to Raman scattering of the toluene. In the first 150 ps after excitation, the maximum of the band around 500 nm shifts from 475 nm to 495 nm. This is due to the energy transfer that takes place within 1 ps, since the OPV3 is luminescent around 475 nm. However, this does not explain that the maximum of the PL is measured at 500 nm between 0.4 and 1.4 ns after excitation. Also, during the first nanosecond, the band at 720 nm, increases relative to the 500 nm band. After a few nanoseconds, this band is again less in magnitude relative to that of the 500 nm band. The longer life time at 720 nm explains the increase of the 720 nm band relative to the 500 nm band in the PL spectra during the first few nanoseconds. The time-integrated measurements shows a band at 500 nm and at 720 nm and resembles that of steady state fluorescence measurements.

To explain the PL at 495 nm, in figure 3.13, the PL spectra of OPV3, OPV3-\(C_{60}\) and toluene, are compared to the steady state PL spectrum of OPV3-Aldehyde, since the presence of impurities such as OPV3-Aldehyde may account for the PL around 495 nm. To allow comparison, the spectra are rescaled. From the figure, it can be concluded that the observed PL in the first 90 ps is due to the OPV3, although the vibronic transitions are not present. The PL at later times is not due to the OPV3, neither is it due to the OPV3-Aldehyde, nor is it due to the toluene. This suggests that the energy transfer is even faster than was estimated based on steady-state fluorescence measurements, see equation 3.1.

To verify that this PL is not due a change of the sample, due to degradation, UV/Vis and steady-state fluorescence spectra (see figure A.8) were measured before and after the time-resolved PL measurement. These measurements showed no significant change. However, a small change may account for the observed red shift of the PL.
Figure 3.12: Photoluminescence spectrum of OPV3-C₆₀, recorded in different time-windows after excitation at 395 nm.

Figure 3.13: Comparison of the measured PL spectra to that of OPV3-Aldehyde.
Time-resolved photoluminescence spectra of OPV4-C$_{60}$

In figure 3.14 the time-resolved measurements of the photoluminescence of OPV4-C$_{60}$ are shown. The spectra are similar to that of the OPV3-C$_{60}$, again mostly the OPV moiety is excited. The high energy PL band is shifted to the low energy side (to 510 nm), with respect to the PL of the OPV3-C$_{60}$. Again the Raman scattering of the toluene is observed. In the first few nanoseconds after excitation, the maximum of the band around 500 shifts from 500 nm to 510 nm. In contrast to the OPV3-C$_{60}$, this maximum does not shift further. The red shift is less pronounced than that of the OPV3-C$_{60}$. During the first nanosecond, the band at 720 nm, increases relative to the 500 nm band. After a few nanoseconds, this band is again less in magnitude relative to that of the 500 nm band.

In figure 3.15, the PL spectra of OPV4, OPV4-C$_{60}$ toluene, are compared to the steady state PL spectrum of OPV4-Aldehyde, since the presence of impurities such as OPV4-Aldehdye may account for the PL around 500 nm. To allow comparison, the spectra are rescaled. From the figure, it can be concluded that the observed PL in the first 100 ps at 500 nm is due to the OPV4, although the 0-1 vibronic transition is not present. At longer times it cannot be attributed the OPV4, and neither to the OPV4-Aldehyde. As was the case for OPV3-C$_{60}$, this suggests that the energy transfer is even faster than was estimated based on steady-state fluorescence measurements, see equation 3.1.

To verify that this PL is not due a change of the sample, due to degradation, UV/Vis and steady-state fluorescence spectra (see figure A.8) were measured before and after the time-resolved PL measurement. These measurements showed no significant change. Therefore, it is concluded that the degradation that occurs during a day of measuring has little effect on the measurements.

Also, strong yellow emission where the laser beam hits the surface of the cuvette was seen. This emission was much stronger for the OPV4-C$_{60}$ than for the OPV3-C$_{60}$. The detection of this emission was suppressed by shielding the emission from the entrance of the monochromator. After a day the emission was no longer present.
Figure 3.14: Photoluminescence spectrum of OPV4-C\textsubscript{60}, recorded in different time-windows after excitation at 395 nm.

Figure 3.15: Comparison of the measured PL spectra to that of OPV4-Aldehyde.
3.5 Conclusions

The life times of the photoluminescence of OPV\textsubscript{n} have been measured, and found to be 1.77, 1.54, 1.21 and 0.71 ± 0.01 ns for \textit{n}=2, 3, 4 and 5, respectively. Thus, it is observed that with increasing conjugation length, the life times of the PL of the OPV\textsubscript{n}s decrease. This is also found in [15] and attributed to the increase in radiative and non-radiative decay with increasing conjugation length.

The life times of the photoluminescence of TPT, Ph-An2-Al and Ph-TPT-Ph is measured to be 0.49, 2.15 and 0.79 ± 0.01 ns, respectively. Comparing the intensity of the PL of these three samples, it is concluded that the smallest amount of PL is generated by the Ph-AN2-Al.

Time-resolved photoluminescence spectra of OPV3-C\textsubscript{60} and OPV4-C\textsubscript{60} have been measured. Compared to the PL of the OPV\textsubscript{n} molecules, the PL is very weak. The PL is quenched due to the energy transfer from the OPV moiety to the C\textsubscript{60}.

The PL spectra show a band around 500 nm and smaller band around 720 nm. The initial PL shows a similarity to that of the pristine OPV\textsubscript{n}. A red shift of the PL is observed, that takes place within 150 ps. The shift is 20 nm for the OPV3-C\textsubscript{60} and 10 nm for the OPV4-C\textsubscript{60}. The maximum of the PL of the OPV3-C\textsubscript{60} shifts even further after 150 ps.

The decay of the PL at 500 nm is bi-exponential. The short time component is within 70 ps.

For the OPV3-C\textsubscript{60}, the long life time component is measured to be 1.2-1.3 ns, which is shorter than life time of the PL of the OPV3 (1.54 ns). For the OPV4-C\textsubscript{60}, the long life time component is measured to be ~1.5 ns, which is larger than the life time of the PL of the OPV4 (1.21 ns).

It is concluded that after excitation, the initial (0-90 ps) PL is that of the OPV\textsubscript{n} moiety. For longer times the PL at 720 nm is attributed to the C\textsubscript{60}. The PL around 500 nm is probably due to an impurity in the solution other than OPV\textsubscript{n} Aldehyde, although a relaxation of the energy levels is not ruled out. The fact that this PL is not due to the OPV\textsubscript{n} moiety, suggests that the energy transfer is even faster than previously estimated.
Chapter 4

Photoinduced absorption

In this chapter the known microsecond PIA-spectra of P3HT and P3HT:PCBM are discussed. Next the experimental set-up for the picosecond time-resolved photoinduced absorption measurements is described. Finally, the results are presented and discussed.

4.1 Introduction

The primary photoexcitations in $\pi$-conjugated polymers are intrachain singlet excitons. Since the excitation is strongly coupled with phonons (see section 2.3.4), a geometrical relaxation from free exciton to self-trapped excitons takes place. The self-trapped exciton thermalizes within one to several picoseconds by relaxation to chain segments with the lowest energy (longest conjugation). Excitons can decay by light emission, intersystem crossing to form triplet excitons, and possibly interchain charge transfer leading to the formation of polarons and polaron pairs. Interchain charge transfer is enhanced in doped polymers, in which the polymer acts as the donor molecule and the dopant as acceptor molecule. An example for such an acceptor molecule is C$_{60}$.

The conjugated polymers used in this experiment were films of P3HT, P3HT:PCBM and PTPTB:PCBM, see figure 4.1. P3HT was used in studies using four-wave mixing [1]. Therefore, in preparation of the four-wave mixing experiment described in the next chapter, P3HT:PCBM was the first blend that was measured. Pristine P3HT was also measured as a comparison with the results of the blend. In the blend, PCBM (which is a modification of C$_{60}$) was used instead of C$_{60}$ to allow larger amounts of C$_{60}$ to be mixed with the conjugated polymer without extensive phase segregation to occur [7].
4.2 Literature survey

4.2.1 P3HT and P3HT:PCBM

Photoinduced absorption

The photoinduced absorption spectrum of a P3HT-film at 80 K, pumped at 488 nm, see figure 4.2, shows a bleaching band around 2.0 eV and absorption bands around 1.1, 1.2 and 1.85 eV.

In [10], for regioregular P3HT, absorption bands were observed at 0.35 eV and 1.27 eV. The bands were assigned to 1D localized polarons, see figure 4.3. In [5] bands are found at 0.35 and 1.25 eV and attributed to bipolarons. Recent calculations of oligomer electronic states have predicted that polarons have two subgap transitions, whereas bipolarons have one [26] (see section 2.3.2). However, these absorption bands do not show in the P3HT sample that we measured. The absorption bands at 1.1 and 1.2 eV band is assigned to the T\textsubscript{n}+ T\textsubscript{1} transition. We conclude that the used samples in the mentioned studies must be doped somehow to account for the existence of polarons.

Upon doping the P3HT by PCBM, the PIA-spectrum changes dramatically (see figure 4.2): the photoinduced absorption is enhanced by a factor of 10, due to the electron transfer from the P3HT to the PCBM. Three strong absorption bands are observed located at 0.35, 1.25 and 1.85 eV. In addition, a strong bleaching band is observed around 2 eV.

In analogy to the PIA spectrum of P3OT:C\textsubscript{60} measured in [25, 26], the bands at 0.35 eV and 1.25 eV are assigned to the P\textsubscript{1} and P\textsubscript{2} transitions of the P3HT polaron, respectively. In spectrum no signature of the PCBM polaron
Figure 4.2: Photoinduced absorption spectrum of P3HT (dashed, x10) and P3HT:PCBM (solid) at 80 K, pumped at 488 nm (from [32]).

(expected at 1.24 eV [9, 29]) is observed, but it may well overlap with the 1.25 eV band of the P3HT polaron. The triplet absorption bands, observed in the PIA spectrum of the pristine P3HT, are completely quenched by the electron transfer.

Furthermore, the spectra show a band peaked around 1.85 eV. About this band there is some controversy in the literature. In [5] it is suggested that a similar PIA band at 1.9 eV, and also at 0.15 eV, of P3HT is due to deep traps for charge carriers introduced during preparation of the sample. And this band would vanish upon heat treatment during 20 hours at 170 °C, see figure 4.4. These charge carriers could be either bipolarons with an enhanced confinement parameter or singly charged trapped polaronlike states. ESR measurements in [21] found that upon heat treatment the number of photogenerated spins decrease. The lifetime of these photogenerated spins was measured to be ~1 second consistent with deep trapping on a defect.

In contrast, in [18] for highly ordered P3HT, this high energy band has been assigned to carriers that still have a polaronic nature, but that have a pronounced interchain character, with wavefunctions spreading over neighboring chains. It is suggested that the P3 transition in polarons, which is symmetry-forbidden in isolated molecules, may become very intense in the presence of interchain interactions, see figure 4.5. In [10] the absorption band at 1.8 eV was attributed to 2D delocalized polarons (see figure 4.3). In [25] these 2D
delocalized polarons are identified as polaron Coulomb-correlated pairs by use of PIA-detected magnetic resonance, see 2.3.3. They attribute the band at 1.85 eV to the PP$_2$ transition of the polaron pair.

For other samples similar features have been reported. In [11] in polydiacetylene at 1.8 eV a peak was measured in the absorption spectrum. In an electro-absorption measurement, at 1.8 eV they measured a feature which follows the first derivative of the absorption. In [19] the fast decaying ($\tau=300$ fs) component of the PIA band at 1.9 eV of P3OT has been attributed to a self-trapped singlet exciton, or a singlet polaron exciton.
Figure 4.4: Change in the PIA spectrum of P3HT upon heat treatment: dotted curve (before heat treatment) and solid curve (after heat treatment) (from [5]).

Figure 4.5: PIA spectrum of a highly ordered P3HT film. Inset: schematic one-electron energy levels of neutral molecules and isolated radical anions. The dotted C3 (in the text: $P_3$) transition is symmetry-forbidden in isolated molecules. (from [18]).
Decay dynamics

In previous studies the nanosecond-millisecond decay of the photoinduced excitations in P3HT and P3HT:PCBM was measured.

In [10] the modulation-frequency dependence and transient decay of the photoinduced absorption in regioregular P3HT has been measured. The result was fitted to two bimolecular decays of the polaron at 1.27 eV with lifetimes 65 µs and 2.2 ms. Photomodulation measurements of the triplet band show a decay time of the triplet state of \( \sim 100 \mu s \) [32].

In [22] the decay of the photoinduced charge carriers was measured in the subnanosecond to millisecond time scale. In the subnanosecond to microsecond timescale the decay was fitted with the power-law function \( A t^{-\alpha} \), where \( \alpha \) was found to be 0.21, see figure 4.6. Hence, most of the polaronic charge carriers would recombine within the first 30 ns after excitation, the remaining long-lived ones recombined on a millisecond time scale. The longevity of the polaronic charge carriers in comparison with the free charge carriers in inorganic materials can be explained by the low mobility of the charge carriers in organic materials (\( \sim 10^{-2} \text{cm}^2/\text{Vs} \) in P3HT:PCBM at 300 K). After diffusion along the polymer chains among randomly distributed recombination centers, the polaronic charge carriers recombine. Such dynamic behavior can be described by a stretched exponential

\[
A e^{-(\frac{t}{\tau})^{\beta}},
\]

with \( \beta = \frac{1}{3} \), or more complex or multi-exponential functions [19, 20, 22, 28].

![Figure 4.6](image-url)  
**Figure 4.6:** Time dependence of the photoinduced absorption of the P3HT:PCBM composite film monitored at 1275 cm\(^{-1}\) at 80 K. Excitation wavelength 532 nm, \( \sim 0.5 \text{mJ/pulse} \), pump fluence \( \sim 2 \text{mJ/cm}^2 \). The solid line represents the fit of \( A t^{-\alpha} \) with \( \alpha = 0.21 \) to the data (from [22]).

In comparative studies of P3OT and P3OT:C\(_{60}\) [19, 20], the fast decay at 1.45 eV was assigned to the self-trapped singlet exciton or singlet polaron exciton. This exciton is a short-lived intrachain excitation. The decay time was
measured to be 300 fs, see figure 4.7. An additional slow decay was attributed to charge separated excitations. Upon increasing the concentration of C$_{60}$ the decay of the charge separated excitations extended into the nanosecond time scale, and the fast component was quenched.

![Figure 4.7: Decay of the photoinduced absorption at 1.45 eV in pristine P3OT (open triangles), P3OT/C$_{60}$ (1%) (open squares), and P3OT/C$_{60}$ (10%) (open circles) at 300 K. The fits are to $Ae^{-t/\tau_1} + Be^{-t/\tau_2}$, $\tau_2$ is 20, 25, and 700 ps in pristine P3OT, P3OT/C$_{60}$, and P3OT/C$_{60}$ (10%), respectively. (from [19]).](image)

4.2.2 PTPTB:PCBM

PTPTB is a novel low optical band gap conjugated polymer, which exhibits a low optical band gap as a result of the alternation of electron rich and electron deficient units along the chain [29]. Photoinduced absorption (PIA) and fluorescence spectroscopy on blends of PTPTB with PCBM as acceptor gave direct spectral evidence of the photo-generation of a charge-separated state [30]. In figure 4.8 the PIA spectra of the pristine PTPTB and the blend are compared. The PIA spectrum of the pristine PTPTB shows a single peak at 0.87 eV, attributed to the $T_n \leftarrow T_1$ transition. The life time of the $T_1$ state was determined to be less than $\sim 50 \mu$s [29]. The PIA spectrum of the blend is significantly different and shows two new bands at 0.46 and 1.18 eV of the PTPTB radical cation. The $T_n \leftarrow T_1$ transition is not completely quenched. Compared to the PIA spectrum of the P3HT:PCBM blend, it is noticed that no band is observed at 1.5 eV, where we expect a band in analogy to the band at 1.7 eV in P3HT:PCBM. However, because of the enhanced absorption at the available pump wavelength (585 nm), see figure 4.9, this blend is studied.
Figure 4.8: Photoinduced spectra of PTPTB (solid line) and PTPTB:PCBM, 1:1 wt% (dashed line) recorded with excitation at 604 nm (50 mW) at 80 K and using a modulation frequency of 275 (from [29]).

Figure 4.9: UV/Vis absorption spectrum of PTPTB:PCBM 1:1 (from [29]).
4.3 Experiment

Synthesis of the P3HT:PCBM (1:1 wt%) blend is described in [32, 29]. The P3HT:PCBM blends were prepared by dissolving equal weight fractions of P3HT and PCBM in toluene and then spincoating on sapphire or glass substrate. This way a blend containing 50% PCBM was obtained. The samples on sapphire were optically not uniform. Due to the small size of the sapphire substrate (1 cm), spincoating did not produce a uniform film. To produce a optically uniform film, a glass substrate of dimensions (4 cm x 4 cm) was used, and after spincoating, the substrate was cut in parts. A sample thickness of 50-55 nm was obtained. The optical density (OD) at 585 nm was 0.1.

The PTPTB:PCBM (1:1 wt%) blend was synthesized as described in [29], and spincoated on a glass substrate. The optical density at 585 nm obtained, was 0.44.

The samples were mounted in a cryostat and were kept at a vacuum of $10^{-3}$ mbar. The samples were fixed on the sample-holder by heat conducting paste. Measurements have been done at 300 K and at 77 K by filling the cryostat with liquid nitrogen.

The pump-probe instrumentation that was built for the time-resolved photoinduced absorption (PIA) measurements is depicted schematically in figure 4.10. The second harmonic (532 nm) of an actively stabilized mode-locked Nd-YAG laser is used to pump two cavity dumped dye lasers. For the pump beam the output of first dye laser, containing Rhodamine 6G as gain dye and DODCI as a saturable absorber, was used. The first dye laser generated pulses, with a wavelength variable between 560 and 620 nm. The second dye laser contained Pyridine 2 as gain dye and DDI as a saturable absorber. The pulses generated by this dye laser were pulses of wavelength variable between 700 and 780 nm.

By using a saturable absorber the minimum pulse width that could be obtained was 1 picosecond. The repetition rate of the pulses could be varied between 4 MHz and 0.15 MHz. To measure the pulse width of the beams, part was split off to the autocorrelator. The cross-correlator was also used to measure the cross-correlation of the pump and the infrared beam. Depending of the amount of saturable absorber, a minimum cross-correlation of 7 ps was measured. The stability of the laser output was not very high: the measured jitter of the pulses measured on the cross-correlator was more than 1 picosecond. Also the variation in the output power was high, as much as 10% of the average power of the output, which was 50 mW for the pump and 25 mW for the infrared beam. During a time of several weeks, the absorber dye would bleach, therefore, absorber dye had to be added, to keep the dye lasers operating stable and to keep the pulses at a constant width. To ensure a relatively stable operation, the dyes and absorbers were cooled.

Picosecond time-resolved pump probe measurements have been carried out. For the pump beam the 585 nm wavelength was chosen since P3HT has the highest absorption around this wavelength and at 585 nm the highest output power could be achieved. Part of the pump beam was split off and used to probe with at 585 nm, and the infrared beam was used to probe at 720 nm.

To achieve picosecond time resolution the delay of the probe pulse relative
Figure 4.10: Schematic diagram of the set-up used for the time-resolved photoinduced absorption measurements.
to the pump pulse beam was varied by means of an optical delay line. The pump and the probe beam were focused at the sample by either a microscopic objective (set-up I) or a lens (set-up II), to achieve focus at an area of 0.03 mm and 0.3 mm in diameter, respectively. In this way, either a high, $\sim 2.8 \mu J \, mm^{-1}$, or a low excitation density $\sim 2.8 \times 10^{-8} \, J \, mm^{-1}$, was achieved at a pump power of 10 mW. The spatial overlap of the pump and the probe spots on the sample was achieved by imaging the spots on a CCD camera, after magnification ($\sim 5x$). The CCD camera magnified the image again by a factor of 100, whence the spots could be overlapped visually by translating the lens or microscopic objective in front of the sample. For a smaller focus, the beam diameter would have to be increased, however, this was not possible in the present set-up due to space restrictions when working with three separate beams. A special collimating set-up has been developed, as shown in figure 4.11, which enables us to illuminate the aperture of the microscopic objective with three perfectly parallel beams, allowing us to overlap the focus of each of the individual beams with the crossing point of the three beams. The overlap of the spots on the sample was complicated by scattering of the beams, due to irregularities of the sample.

![Figure 4.11: More detailed drawing of part of the set-up.](image)

Because of the small focal length of the microscopic objective (14 mm), a new sample-holder had to be made, see figure 4.12. The back side of the new sample-holder was painted black to avoid reflections.

To ensure that the spatial overlap of the pump and the probe spots on the sample did not change due to translation of the optical delay line, the path of the beam was aligned with the optical delay lines. This was done by reflecting the delayed beam on the wall, and monitoring the change of the position of
the spot on the wall after translation of the optical delay line. The path of the beam was adjusted until the position of the spot would not change anymore. However, due to the change in direction of the laser output, the pointing and the divergence of the laser beam, exact spatial overlap of the pump and probe spots during a measurement was not possible.

The amplitude of the transmitted probe beam was measured using a fast photodetector connected to a digital oscilloscope. The amplification of the photodetector was increased to $6.5 \times 10^6$ by replacing the internal resistance and capacitor.

The change in photoinduced absorption was detected by connecting the output of the photodetector to a lock-in amplifier model EG&G 5209 locked at the frequency of the chopper, which were placed in the pump beam. To avoid detection of the pump beam, the 585 nm probe was polarized perpendicular to the pump beam and a polarizer was placed in front of the photodetector to filter out the pump beam.

To measure the change in photoinduced absorption while keeping the polarizations parallel, a second lock-in amplifier was used. The pump beam was chopped at 1340 Hz and the probe beam at 30 Hz. The output of the photodiode was connected to the first lock-in amplifier locked at 1340 Hz and the output of the first lock-in amplifier was connected to the second lock-in amplifier locked at 30 Hz.

When the infrared beam was used as probe, a monochromator and a color filter was placed in front of the detector, effectively passing through only the 720 nm light.

The output of the lock-in amplifier was connected via a GPIB cable to a PC. Homebuild software, written in LabView, was available and only had to be modified for the used lock-in amplifier and optical delay lines. The program was used to read the lock-in output and to vary the optical delay lines by controlling the stepper motors.

### 4.3.1 Alignment and optimization of the signal

In this section the steps that were taken to acquire the pump-probe signal as measured are given:

1. the Nd-YAG laser is warmed up and stabilized
2. the pump mirrors of the dye lasers are tuned to minimize noise in the output of the dye lasers

3. the output of the dye lasers is optimized by monitoring the output on the autocorrelator: no satellites should be visible, while the pulse width is as narrow as possible

4. if necessary all mirrors and lenses are cleaned (for stability of the laser output, it is very important that the birefringent filter is clean)

5. if necessary, saturable dye is added

6. the path of the laser beams is made parallel with the delay lines, by reflecting the beam on the wall and ensuring that the spot on the wall stays in position during translation of the delay line

7. before entering the lens/objective, the beams are made parallel

8. the beams are focussed on the sample

9. the spots on the sample are imaged on the CCD camera

10. the spots as viewed on the camera are overlapped

11. the transmitted probe beam is aligned and focussed on the monochromator/detector

12. the optical delay is moved to the position at which the maximum output of the lock-in amplifier is achieved

13. at the maximum, the overlap of the beams on the sample is again adjusted until the output of the lock-in amplifier is optimal

14. during the course of the day, the output of the laser system will change, therefore, these steps are repeated before each measurement
4.4 Results

In this section the time-resolved photoinduced absorption measurements of P3HT and P3HT:PCBM are presented and discussed. Unless mentioned otherwise, the pump and probe wavelength was 585 nm, the repetition frequency of the pump pulses was 4 MHz, and the chopper frequency was 330Hz. For the results on the PTPTB:PCBM the reader is referred to the Appendix.

4.4.1 P3HT

All measurements performed on P3HT, were done at the high excitation density.

Decay dynamics

In figure 4.13 the decay of the photoinduced absorption of P3HT is shown at 585 nm. The probe beam was polarized perpendicular to the pump beam. The figure shows a photoinduced bleaching ($\Delta T/T>0$). The excitations giving rise to this bleaching are identified as self-trapped excitons or polaron excitons [19, 20, 28, 31].

On an expanded scale, an additional sharp peak at $t=0$ ps with FWHM of 2 ps is observed, as shown in figure 4.14. This peak is created instantaneously and its width corresponds to width of the laser pulse. This peak might be due to spectral hole burning. Spectral hole burning gives rise to a small peak in the inhomogeneous broadened bleaching band due to diffusion of the excitations to other chain segments. This spectral hole burning takes place during the overlap of the pump and the probe beams [28], in our case that is $\sim 2$ ps. The peak could also be due to the self-trapping of the exciton and the subsequent decay, since the lifetime of the self-trapped exciton is measured to be $\sim 2$ ps in [28].

Within 2.1 ps, the auto-correlation of the laser pulse, a second maximum is observed. The subsequent decay is multi-exponential. Within 20 ps, 25% of the excitations decay. This fast decay might be due to the diffusion of the excitations to other chain segments. Measurements in [19] of the dichroic ratio show that the polaron excitons (self-trapped excitons) decay and/or diffuse within ten picoseconds to polymer segments that are randomly oriented with respect to the initial segment. The electron and the hole quickly become separated onto neighboring chains. From our measurements three life times can be obtained using a third order exponential decay function: $14 \pm 5$ ps, $\sim 370$ ps, and 1 $\mu$s. The third life time (1 $\mu$s) was chosen to this value to account for the offset at $t<0$, due to long lived species. The first life time is attributed to the decay or diffusion to other chains of the polaron excitons. The second life time is attributed to the singlet radiative decay time.

The life time of the photoluminescence is measured and presented in the Appendix. From a bi-exponential fit to the results two life time components are obtained: 71 ps, which is close to the experimental resolution and 271 ps. So it is suggested that the measured second life time of the bleaching (370 ps) is the singlet radiative decay time which also governs the photoluminescence. At longer times after photoexcitation, the charge carriers become separated more
upon diffusion, such that their wavefunctions no longer overlap and the decay becomes nonradiatively.

The life time of the longer-lived species can not be easily measured with the present experimental set-up. However, by varying the repetition rate of the pump pulses, an indication of the long life times can be obtained. These long lived species are identified as triplet excitations in the steady state PIA measurement.

Figure 4.13: Time dependence of the photoinduced bleaching of P3HT pumped at 585 nm (10.8 mW), at room temperature.
Measurement of the pump-probe signal of the P3HT sample as function of the repetition rate of the cavity dumper is shown in figure 4.15. Decreasing the repetition rate shows a decrease of the offset at $t<0$. When the laser pump pulses repeat quickly, the created charge carriers that decay slowly do not have time to decay all, resulting in an accumulation of charged excitations on the polymer chains, due to multiple excitation pulses. When the repetition rate is reduced a factor of 10, 10 percent of the photoexcitations present at 250 ns (the pulse repetition time) are left. When the repetition rate is reduced a factor of 20, still 6 percent of the photoexcitations are left. Thus, a nonexponential decay is observed on a time scale of microseconds to milliseconds, consistent with decay in this time scale measured in other studies as discussed in section 4.2.1.

Probing the photoexcitation at 720 nm, does not give any signal on the picosecond time scale. This is expected, since the steady state PIA spectrum shows only a very small photoinduced absorption at this wavelength, see figure 4.2. On the micro/millisecond time scale still some absorption is observed as a constant background as shown in figure 4.16. This is in contrast to the measurement of the photoabsorption at this wavelength of the blend, which will be discussed below.
Figure 4.15: Time dependence of the photoinduced bleaching of P3HT at room temperature, pumped at different pulse repetition rates.

Figure 4.16: Time dependence of the photoinduced absorption of P3HT at 720 nm at 300 K. Pumped at 12.8 mW.
Influence of the chopper frequency

Varying the chopper frequency, while keeping the repetition rate at 4 MHz, shows a similar result (see figure 4.17). The offset at t=0 ps of the pump-probe signal increases exponentially with decreasing chopper frequency. At low chopper frequency (30-130Hz), the signals become very noisy. This is because of fluctuations in the laser beam, which can also be observed visually. At high chopper frequency, the increase of the signal relative to its offset is due to limitations of the photodetector. Therefore, the chopper frequency is kept between 200 and 700 Hz.

![Figure 4.17: Time dependence of the photoinduced bleaching of P3HT at 300 K, pump beam (15 mW) chopped at different frequencies.](image)

Temperature dependence of the decay

The photoinduced bleaching is also measured at 77 K. Comparison of the measurements at 77 K and 300 K is shown in figure 4.18. From the figure it is observed that up to 100 ps there is no significant difference in the decay kinetics ($\tau_1=14\pm5$ ps), consistent with measurements in [28]. For longer times the difference becomes significant, the life time was fitted to $\sim600$ ps at 77 K and to $\sim370$ ps at 300 K.

The temperature independence on the small time scale, indicate that the decay dynamics of the polaron exciton is not due to multiple trapping. If the polaron exciton gets trapped, then its life time should be longer at low temperatures. Since, at room temperature, it has enough energy to get out of the trap. Instead it is suggested in [31] that the photogenerated excitons recombine upon diffusion to the boundaries of the conjugated chain segments. The recombination centers are randomly distributed due to the different conjugations lengths.
of the individual chains. This leads to the nonexponential decay.

For times $>100$ ps, a strong dependence of the temperature is observed. The long time decay at 77 K is slower than at 300 K. This suggests that the long lived excitations do get trapped. It is suggested that upon diffusion to the longest chains, the long lived excitations get trapped there due to their low mobility.

![Figure 4.18: Comparison of the time dependence of the photoinduced bleaching of P3HT at room temperature and at 77K.](image)

**Power dependence of the signal**

A measurement of the pump probe signal as function of the pump power is shown in figure 4.19. The signal increases with increasing pump power. However, it can be seen that only the offset increases, whereas the fast decaying part of the signal is almost unchanged with varying pump powers. Also, it can be observed that at a very low pump power, the pump probe signal is very small. Thus, more long lived excitations are created at higher pump powers. The slow decay component (at $t<0$ ps) is saturated at powers between 10 en 20 mW, whereas the fast component is saturated at 4 mW. Thus, less power is needed to saturate the fast component, which suggests that fewer chain segments are involved with the fast decay. An alternative explanation would be that the saturation power for the slow decay is higher than the saturation power for the fast decay. This is contrary to the usual case where a fast decay corresponds to a higher saturation power.
Figure 4.19: (a) Time dependence of the photoinduced bleaching of P3HT at 300 K, measured at different pump powers (b) Signal at t=80 ps (squares) and the ratio of fast decay to the slow decay components of the signal (triangles), as function of the pump power (at 300 K). The fit is to the square root of the pump power.
Wavelength dependence of the signal

The decay dynamics of the photoinduced bleaching at different pump wavelengths is compared in figure 4.20. It is observed that at 620 nm the offset is smaller than at shorter wavelengths. This is due to the smaller absorption by the sample and the lower intensity of the laser beam at this wavelength. After fitting, for all the excitation wavelengths the same decay rate \((\tau = 9.2 \pm 0.7\,\text{ps})\) is measured.

![Figure 4.20: Time dependence of the photoinduced bleaching of P3HT at 300 K, measured at different pump wavelengths.](image)

**Figure 4.20:** Time dependence of the photoinduced bleaching of P3HT at 300 K, measured at different pump wavelengths.

### 4.4.2 P3HT:PCBM

All measurements on the blend have been done at high excitation density, unless mentioned otherwise.

**Decay dynamics**

In figure 4.21 the decay of the absorption of P3HT:PCBM is shown at 585 nm. The figure shows a photoinduced bleaching (PB) \((\Delta T/T > 0)\). Again a multi-exponential decay of the bleaching is observed. The PB was measured with the probe beam polarized perpendicular and parallel to the pump beam. It can be observed that for the parallel polarized beam, the noise in the signal is much higher. This is due to the fact that two lock-in amplifiers are used to suppress stray light of the intense pump beam. The probe beam is chopped at 30 Hz and the pump beam at 1330 Hz. Since the laser output is not stable but fluctuating around low frequencies (30 Hz), the noise in the signal is enhanced by the first lock-in amplifier. A third order exponential fit to the data gives \(\tau_1 = 5.7 \pm 0.8\)
Figure 4.21: Time dependence of the photoinduced bleaching of P3HT:PCBM at 300 K, measured for polarization of the probe beam perpendicular (dashed) and parallel (dotted) to that of the pump beam. To allow for comparison, the data is normalized.

ps, $\tau_2 = 542 \pm 24$ ps, and $\tau_3$ is taken 1 $\mu$s. Compared to the photoinduced bleaching of the pristine P3HT, a difference of the signal strength at $t=0$ ps is observed, which is in contrast to the steady state PIA measurements. However, it should be stressed that the strength of the signal is very dependent on the overlap of the pump and probe beams. Comparing the decay times and the corresponding coefficients of the pristine P3HT and the blend, it is observed that for the blend the fastest decay component is dominant, and for the pristine the slowest decay component. In figure 4.22 the decay on the nanosecond time scale is compared. The faster decay of the photoinduced bleaching observed in the blend, suggests that, after photoexcitation, the LUMO of the blend is occupied for a shorter time than the LUMO of the pristine P3HT. This is due to back transfer of the charge separated electrons. The second time, 542 $\pm$ 24 ps, is almost twice that of the measured life time of the photoluminescence of P3HT. Thus, this life time can not be attributed to the singlet excited state. The third time is attributed to the charge separated excitations (polarons).

Alternatively, the decay of the P3HT:PCBM can be fitted using a power law function $\Delta t^{-\alpha}$, where $\alpha = 0.15 \pm 0.01$ ps is obtained. The fit is shown in figure 4.22. Plotting both axes on a logarithmic scale, gives a nearly straight decay curve.
Figure 4.22: Comparison of the decay on the nanosecond time scale of the blend and the pristine P3HT at 77 K, shown in a linear, a logarithmic and a double logarithmic plot.
Temperature dependence of the decay

The dependence of the decay on the temperature is measured in figure 4.23. It can be observed that there is no significant difference between the decay dynamics at 300 K and 77 K during the first 500 ps. On larger timescales the temperature dependence is evident from the fact that the offset is higher at low temperature, what indicates that at low temperature the photoexcitations decay slower. As was the case for the pure P3HT this suggests existence of traps. This may be explained as follows: after electron transfer to the fullerene, a hole is left on the polymer. Only after diffusion of the hole, the hole and the electron can recombine. Thus, the recombination rate at low temperatures is expected to be slower. The large oscillations at t=0 will be discussed in the next section.

![Graph showing the temperature dependence of the decay.](Image)

**Figure 4.23:** Time dependence of the photoinduced bleaching of P3HT:PCBM, measured at different temperatures.

Intensity and wavelength dependence of the signal

The decay dynamics of the photoinduced bleaching at different pump wavelengths is compared in figure 4.24. Here the same observation is made as was the case for the pristine P3HT: the decay rate is the same at the different wavelengths. The change in signal strength is due to the different maximum obtainable intensities and the absorption at the chosen wavelengths. It should be noted that for this measurement the excitation density was less than for the corresponding measurement of the pristine P3HT, which may explain the smaller change in offset. The relative small offset of the signal suggests that at this excitation density, fewer long lived photoexcitations are created.
Figure 4.24: Time dependence of the photoinduced bleaching of P3HT:PCBM at 300 K, measured at different pump wavelengths. Low excitation density.

4.4.3 Decay dynamics at 1.72 eV of P3HT:PCBM

The decay dynamics probed at 1.72 eV (720 nm) is very different than that of the pristine P3HT. This decay is measured multiple times, for both low and high excitation densities, at low (77 K) and high (300 K) temperature, see figure 4.25. A fit to the measurements gives a life time of 2.5±0.5 ns for the decay at 300 K. The decay at 77 K could not be fitted properly, since it extends in the micro/millisecond time scale.

The photoinduced absorption at 1.72 eV may be attributed to the P3 transition of the polarons. When the separation between the positive polarons on the P3HT gets small enough, their wavefunctions overlap, and the P3 transition is allowed, which may account for the photoinduced absorption at 1.72 eV. This is discussed in section 4.2.1. The long decay times imply that the recombination of the polarons is inhibited. This can be understood by comparison with the 1.72 eV probe measurement of the pristine P3HT, where no signal was observed. The mechanism leading to the creation of a strong photoinduced absorption at 1.72 eV is the transfer of the excited electrons on the P3HT chains to the PCBM. Electron transfer takes place within 1 ps. In figure 4.26, it can be observed that the photoinduced absorption signal is created within the experimental resolution after overlap of the pulses (the cross-correlation of the pump and probe beams is ~10 ps). The back-transfer of the electron is inhibited since it is trapped at the PCBM molecule. Recombination of the electron on the PCBM and the hole (positive polaron) on the P3HT will take place only after diffusional motion of the charge carriers.

For some cases, when the C60 is close to the polymer chain, the recombina-
Figure 4.25: Time dependence of the photoinduced absorption of P3HT:PCBM at 720 nm, measured at 300 K and 77K (low excitation density). By using a microscopic objective, a high excitation density was achieved.

tion takes place, which may explain the 2.5 ns life time.

However, an alternative explanation is possible. The time between dissociation of the exciton and the charge transfer onto the PCBM molecule, may be depending on the concentration of the PCBM molecules, the trapping of the charge separated excitations and the specific polymer. During that time, polaron pairs may be formed between the positive polaron and the not yet transferred negative polaron on the polymer. Thus, the PP$_2$ transition of the polaron pair may also account for the observed PIA at 1.72 eV.
4.4.4 Nonlinear optical phenomena

The photoinduced absorption measurement of P3HT:PCBM, pumped at 585 nm and probed at 720 nm, shows a sudden decrease in the photoinduced absorption when the pump and the probe pulses overlap, see figure 4.26. This feature is seen best at the high excitation density. It is not photoluminescence, since the photoluminescence of P3HT:PCBM is several orders less in magnitude than the photoinduced absorption. It may be stimulated emission or Raman gain. The luminescence of P3HT:PCBM is maximum around 720 nm, see figure A.11, but very weak. In a study of pristine P3MT [28], a similar feature is observed (at 1.71 and at 1.79 eV) and considered to be due to Raman gain. The corresponding Raman shifts (1450 and 2100 cm⁻¹) were attributed to the C=C and C≡C stretching modes. In our case, the shift is 3228 cm⁻¹. That is too large to be a C-H stretching mode. Thus, Raman gain is ruled out. Since this feature is not observed in pristine P3HT, it must be contributed to the PCBM.

An other feature is observed only at low excitation density, for the photoinduced bleaching of the blend, see figure 4.27: an oscillatory structure in the photoinduced bleaching is observed when the pump and the probe pulses overlap in time at the sample. This oscillation may be due to the coherent interaction of the weak probe pulse with the polarization induced by the intense pump pulse [28]. At high excitation density this feature is not observed, instead, a sharp bleaching peak is observed, which may be due to hole burning.

In literature, polymer-fullerene blends have been studies for their strong incoherent nonlinearity $\chi^{(3)}_{\text{inc}}$. In these blends dynamic holography with good diffraction efficiency is shown and attributed to the electron transfer. In the
Figure 4.27: Oscillation in the time dependence of the photoinduced bleaching of P3HT:PCBM.

next chapter a four-wave mixing experiment to measure the nonlinear phenomena is described.
4.5 Conclusions

The decay of the photoinduced bleaching of P3HT has been measured. A multi-exponential decay is observed. From the measurements, three lifetimes are obtained using a third order exponential decay function: $14 \pm 5$ ps, $\sim 370$ ps, and $1 \mu$s. The third lifetime ($1 \mu$s) was chosen to represent the lifetime of the triplet state. The first lifetime is attributed to the decay or diffusion of the photoexcitations to other chains. The second lifetime is attributed to the singlet radiative decay time. The lifetime of the triplet state cannot be easily measured with the present experimental set-up.

The decay of the photoinduced bleaching of P3HT:PCBM has been measured. A third order exponential fit to the data gives $\tau_1 = 5.7 \pm 0.8$ ps, $\tau_2 = 542 \pm 24$ ps, and $\tau_3$ is taken $1 \mu$s.

It is observed that for pristine P3HT the slowest decay component is dominant, while for the blend the fastest decay component is dominant. The faster decay of the photoinduced bleaching observed in the blend is attributed to back transfer of the charge separated electrons. The long-lived species that are left are assumed to be polarons.

Probing the pristine P3HT at 720 nm, does not give any signal on the picosecond time scale. This is expected, since the steady state PIA spectrum shows only a very small photoinduced absorption at this wavelength. For the blend, the photoinduced absorption at 720 nm arises from charged excitations on the polymer chain, due to electron transfer to the fullerene. A decay time of $2.5 \pm 0.5$ ns was measured for the photoinduced absorption signal at 720 nm, which is probably due to back transfer of the charge separated electrons to the ground state. We discussed several possibilities for the nature of the charged excitations, which dominate the PIA spectrum around 720 nm.
Chapter 5

Four-wave mixing

5.1 Introduction

In semiconducting polymer/fullerene blends, the photoinduced absorption can be significantly enhanced over those in either of the component materials due to the photoinduced charge transfer. The change in the absorption coefficient $\Delta K$ and the refractive index $\Delta N$ can be measured by four-wave mixing.

In four-wave mixing two laser beams are used to create a grating. When two beams are focussed on the same area, they interfere. The interference produces a spatially periodic light intensity distribution which changes the optical properties of the material. The spatial modulation of the optical properties acts as a diffraction grating. Because of the photoinduced charge transfer, the interference of the light induces a space charge grating, which leads to the modulation of the refractive index $\Delta N$. The metastability of the photoinduced charge transfer enables control of the grating decay dynamics by varying the concentration of acceptors in the blend [4], and the photoinduced charge transfer enhances the magnitude of the modulated changes in the complex index of refraction at certain wavelengths.

The absorption modulation $\Delta K$ arises from an excited state of the blend. The absorption coefficient at the probe wavelength is spatially modulated by the induced absorption. If the probe beam is strongly modulated, a large diffracted signal results. Therefore, the probe wavelength should be chosen near the peak of the excited state absorption, such that the probe wave is fully transmitted in absence of the grating, but is strongly diffracted by the grating.

Studies [4, 34, 3] show that the early-time diffraction efficiency in the near-IR is dominated by a combination of phase (from $\Delta N$) and amplitude (from $\Delta K$) gratings which arise from the complex $\chi^{(3)}_{\text{exc}}$ which, in turn, originates from the excited-state absorption. Absorption from the charge separated excited state leads to enhanced density of photocarriers with high absorption cross sections. Spectral windows appropriate for NLO applications can be determined from steady-state PIA measurements.
5.2 Theory

In literature, often the modulation of the absorption coefficient $\Delta K$ and the refractive index $\Delta n$ are combined to a complex refractive index

\[ \tilde{n} = n + iK/(2k_C), \quad (5.1) \]

\[ \Delta \tilde{n} = \Delta n + i\Delta K/(2k_C), \quad (5.2) \]

where $k_C$ is the absolute value of the wave vector of the light for which the optical properties are measured. The complex refractive index is related to the complex optical frequency dielectric constant $\epsilon$ and the susceptibility $\chi$ by

\[ \tilde{n}^2 = \epsilon = 1 + \chi, \quad (5.3) \]

\[ \Delta \tilde{n} = \Delta \epsilon/(2\epsilon^{1/2}) = \Delta \chi/(2(1 + \chi)^{1/2}). \quad (5.4) \]

Thus, an optical grating responds to a spatial modulation of any of the quantities $\tilde{n}$, $\epsilon$, or $\chi$.

The experimental set-up for the production of laser-induced gratings is sketched in figure 5.1. Light from a pump laser is split into two beams $A$ and $B$ with wave vector $k_A$ and $k_B$, electric field amplitudes $A_A$ and $A_B$, and intensities $I_A$, $I_B$. The two beams intersect at an angle $\theta$ at the sample and create an interference pattern, of which the grating vector $q$ is

\[ q = \pm (k_A - k_B) \quad (5.5) \]

The spatial period $\Lambda$ is $\Lambda = \frac{2\pi}{q}$ where $q = |q|$. $\Lambda$ can be expressed in terms of the pump wavelength $\lambda_p$ and the angle $\theta$

\[ \Lambda = \frac{\lambda_p}{2\sin(\theta/2)}. \quad (5.6) \]

Light-induced gratings can be probed with a third laser beam with intensity $I_C$ and a wavelength $\lambda_C$, equal to or different from that of the excitation beams. The gratings diffracts some of the probe light into various directions.
The characteristics of the diffraction process are strongly dependent on the sample thickness \( d \). If \( d \) is of the order of the grating period \( \lambda \) or smaller, the grating is called thin, otherwise it is called thick.

For a thin grating, constructive interference is possible at arbitrary directions \( \alpha \) of the probing beam, see figure 5.2a. The direction of the diffracted beam can be calculated using

\[
\lambda \left[ \sin(\phi_m + \alpha) - \sin(\alpha) \right] = m\lambda_C, m = 0, \pm 1, \pm 2, \ldots, \tag{5.7}
\]

where \( \alpha \) is the angle of incidence. Thus the component \( k_{mx} \) of the wave vector \( k_m \) of the diffracted wave is given by the corresponding component \( k_{Cx} \) of the wave vector \( k_C \) of the incident probe beam plus some integer multiple of the grating constant \( q \)

\[
k_{mx} = k_{Cx} + mq, m = \pm 1, \pm 2, \ldots \tag{5.8}
\]

A thick grating can only be probed efficiently if the Bragg condition

\[
k_m - k_C = mq, m = \pm 1, \pm 2, \ldots \tag{5.9}
\]

is obeyed [13], see figure 5.2b.

![Figure 5.2: Characteristics of diffraction at (a) thin and (b) thick gratings.](image)

When the probe beam traverses the grating area, it creates a periodic polarization

\[
\Delta P_{C,1} = \Delta \chi_{ij} A_{C,j}. \tag{5.10}
\]

The amplitude \( A_1 \) diffracted into the first order \((m = \pm 1)\) from the grating is, to a first approximation, proportional to the refractive index or susceptibility modulation amplitude \( \Delta n \) or \( \Delta \chi \), which is proportional to the material excitation.

The detection of the grating involves four beams: the two pump beams at frequency \( \omega_p \), the probe beam, and the diffracted beam, both at frequency \( \omega_C = \omega_D \). To describe the interaction between the four beams, linear theory cannot be used, since the polarization \( P \) is no longer proportional to the electric field \( E \) applied. Instead we have to consider \( P \) as a functional of \( E \). \( P \) can be expanded into a power series of \( E \), by writing \( \chi \) in the form

\[
\chi = \chi^{(1)} + \chi^{(2)}E + \chi^{(3)}E^2 + \ldots \tag{5.11}
\]
Then the polarization takes the form
\[ P = \epsilon_0(\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + ...), \] (5.12)
where the superscript of \( \chi \) denotes the order. Rewriting this expression in tensorial notation gives
\[ P_l(\pm\omega_p \pm \omega_p \pm \omega_C \pm \omega_D) = \epsilon_0[\chi_{ij}^{(1)} A_j + \chi_{ijkl}^{(2)} A_j A_k + \chi_{ijklm}^{(3)} A_j A_k A_l]. \] (5.13)

Now we look at contribution to the polarization \( P_D(\omega_D) \) at the frequency \( \omega_D \) of the diffracted beam. The second order term involves the combination of two field amplitudes and hence the sum or difference of the available frequencies: \( 2\omega_p, \omega_p \pm \omega_C, 2\omega_C, 0 \). Thus, this term cannot contribute at \( \omega_D \). The third order term gives a contribution for the combination \( \omega_p - \omega_p + \omega_C = \omega_C = \omega_D \). The source term with \( \omega_D \) radiates a new wave \( A_D \) which builds up monotonically if the respective wavevectors are equal:
\[ k_D = k_A - k_B + k_C. \] (5.14)

This equation is called the phase-matching condition in nonlinear optics. It corresponds to the first order Bragg-condition (equation 5.9 with \( m=1 \)). Neglecting higher order terms, because they are smaller, the polarization \( P_D \) can be written as
\[ P_{D,i} = \epsilon_0(\chi^{(1)} A_{D,j} + \chi^{(3)} A_{C,j} A_{A,k} A_{B,i}). \] (5.15)

This equation can be reduced to the change \( \Delta \chi_{ij} \) of the linear susceptibility for the probe beam
\[ P_{D,i} = \epsilon_0(\chi_{ij} A_{D,j} + \Delta \chi_{ij} A_{C,j}), \] (5.16)
with
\[ \Delta \chi_{ij} = \chi^{(3)} A_{A,k} A_{B,i}. \] (5.17)

### 5.3 Experiment and results

The set-up for the four-wave mixing experiment is largely the same as the pump-probe instrumentation described in section 4.3. For non-degenerate four-wave mixing experiments the same set-up was used, for degenerate four-wave mixing experiments, the setup was slightly modified: the main beam was split into three separate beams, the strongest two beams were used to create the grating, the weakest was used to probe the grating, see figure 5.3. For the degenerate four-wave mixing experiment, two lock-in amplifiers were used to avoid detection of the strong pump beams.

The first sample that was used was Rhodamine 6G solved in ethylene glycol. The unfocussed pump and a probe beams were overlapped at the sample, however, no pump-probe signal or diffracted beam were detected. Since Rhodamine 6G has a maximum absorption at 530 nm, and absorbs much less at the available wavelengths (570-610 nm), it was replaced by a second dye: DODCI.
Figure 5.3: Schematic diagram of the set-up used for the four-wave mixing experiment.
Figure 5.4: Signal obtained at the position of the diffracted beam, using two lock-in amplifiers. At 300 K, pump beams power=6 mW, probe beam power=1 mW.

DODCI is used as a saturable absorber for the Rhodamine 6G, therefore, this dye has a maximum absorption at the available wavelengths. Again no signal was detected.

Since the signal could be very small, the beams were focussed the sample by a lens (focal length 4 cm) and the sample itself was replaced by a thin film: P3HT:PCBM (1:1 wt%) dropcasted on a sapphire substrate. The larger focus results in a higher excitation density, which would result in a larger change in ΔN and correspondingly a larger diffracted fourth beam. P3HT:PCBM was chosen, for P3HT absorbs around the available pump wavelength (585 nm). Using the equations described in the theory, the period of the grating was calculated to be 2.5 μm, much greater than the sample thickness, 55 nm. Thus, constructive interference was possible at arbitrary directions of the third (probe) beam. The first order diffracted beam was calculated to be at 25.5° from the transmitted beam.

A pump-probe signal was found, and optimized by overlapping the pump and the probe beams on the sample, as described in section 4.3. Subsequently pump-probe measurements were made. These measurements are described in section 4.4. By using two lock-in amplifiers, a signal was detected that showed the characteristics of a nonlinear absorption, see figure 5.4. However, since no decay is measured it was assumed that the signal is just to weak to be detected. Strong scattering at the sample caused a lot of stray light of the strong pump beams. In particular the interference between the stray light of both pump beams yielded a signal which was much larger than the diffracted wave.

Thus, to get rid of the straylight due to the pump beams, the wavelength of the probe was changed into 720 nm. At this wavelength the P3HT:PCBM would not absorb. By placing a monochromator and a color filter in front of the detector, the stray light of the pump beams was blocked. To ensure a large
$\Delta N$ the excitation density was enlarged by replacing the lens by a microscopic objective, as described in section 4.3. However, due to the small aperture of the objective, the set-up had to be modified such that the pump and the probe beams could simultaneously enter the aperture. This created a new problem, because after crossing at the sample, the beams were made parallel again, and could not be separated, thus stray light of the probe beam is detected. By measuring the power of the stray light, an estimate of the intensity of the diffracted beam can be made: the power of the stray light was measured to be \(~1\, \text{nW, thus the power of the diffracted signal is smaller than} \sim 1\, \text{nW, a factor} 10^6\text{ smaller than the transmitted probe beam.}

During the experiment, it became clear that the used sample, P3HT:PCBM, did not absorb as much as the pristine P3HT at 585 nm. UV/Vis absorption measurements show that upon mixing the P3HT and the PCBM, the absorption maximum shifts to smaller wavelengths. This measured by [17] on P3HT:C$_{60}$ blends, see figure 5.5. Therefore, a new sample was acquired, PTPTB:PCBM (1:1 wt%) spincoated on a glass substrate. First, PTPTB:PCBM was chosen, because it has a maximum absorption around 600 nm, see figure 5.6. Second, it was spincoated on the substrate, instead of dropcasted, which resulted in a more regular film and thus less scattering. However, the diffracted signal could again not be detected. In the next section, examples from literature are given and ways of improving the current set-up are discussed.

**Figure 5.5:** UV/Vis absorption spectra of P3HT:C$_{60}$, with varying amounts of added C$_{60}$ (from [17]).
5.4 Discussion

The main reason that no measurements could be made is the low peak intensity of the output of the used laser system. Since the change in polarization is \( \sim I_{\text{pump}} \), see equation 5.17, the grating can be enhanced when higher intensities are available. The pulse energy in our experiments was typically 2.5 nJ. The energy density obtained after focussing by the microscopic objective was 2.8 \( \mu \text{J mm}^{-1} \). This is very well comparable to the energy densities used in similar experiments in literature [4, 35, 34]. However, the peak power of the output of our system is \( \sim 10^4 \) times smaller, due to the picosecond pulse width and the low power of the output of the laser system, versus the femtosecond pulses and high power of other systems.

The diffraction efficiency \( I_D/I_C \) depends on the thickness of the sample. This is described by

\[
I_D/I_C = \eta = \frac{\pi \Delta n d}{\lambda_C} = \left( \frac{\pi \Delta n d}{\lambda_C} \right)^2 + \left( \frac{\Delta K d}{4} \right)^2.
\]  

(5.18)

This formula is only valid if the interference between the pump beams is an ideal plane grating. If the following conditions are met, this grating is very close to an ideal one:

1. the minimum width of the interaction zone must be large compared to the grating period,
2. the overlap length of the two beams in z-direction must be large compared to the sample thickness \( d \),
3. the attenuation of the exciting beams must be negligible within the sample.

The first condition is met since the overlap width is 20 \( \mu \text{m} \), greater than the grating period 2.5 \( \mu \text{m} \). The second condition is met, since the angle between the pump beams is small, 20.2°. Finally, the third condition is met, since the absorption of the samples at the pump wavelength is small (OD<0.4).
From equation 5.18, it is concluded that the diffraction efficiency can be enhanced by increasing the sample thickness and changing the probe wavelength to a region where the photoinduced change in the absorption is highest. However, in thick samples, the excitation intensity is not constant through the sample depth, this complicates the interpretation of measurements of intensity dependent dynamics.

An analysis for thin holographic gratings in [3], in which refractive index gratings arising from the induced absorption are neglected, found that

$$E_d = E_0 \frac{\sigma_d N_0 P z}{4} \exp\left(-\frac{\sigma_e N_0 P}{2} z\right) \approx \chi_{inc}^{(3)} E_p^2 E_0,$$

(5.19)

where $\sigma_e$ represents the absorption cross section of the excited state at the probe wavelength, $N_0$ is the ground state population, and $P$ is the fraction of the ground state population which has been depleted, $E_d$ is the amplitude of the diffracted (fourth) beam, $E_0$ is the probe beam amplitude and $E_p$ is the pump beam amplitude. Thus, increasing amplitude of the pump beam will increase the diffraction efficiency further. The $\chi_{inc}^{(3)}$ obtained from charge transfer blends is 2-3 orders of magnitude larger than nonresonant coherent $\chi^{(3)}$ values typical of conjugated polymers ($10^{-10}$ esu) [3].

When increasing the pump beam intensity is not possible, another means of detecting the small diffracted beam among the scattered light is given in [13], which involves phase-sensitive detection (heterodyne detection).
Chapter 6

Recommendations

To gain more insight in the dynamic behavior of the photoinduced charged excitations in polymer/fullerene blends the current experimental set-up should be improved in a number of ways:

1. higher laser intensity, or
2. heterodyne detection: for a strong holographic grating and the successful detection of the diffraction beam
3. femtosecond resolution: to measure the forward electron transfer time
4. white light continuum for probing in a spectral region of 400-1000 nm: to be able to follow the photoexcitation at different spectral regions
5. lower repetition rates: to measure the complete decay of the charged excitations
6. higher stability of the power and the direction of the laser beam: to measure a weak signal more easily and to produce better looking results
7. higher quality samples: to reduce scattering and thus to be able to measure weak signals.

With the current set-up it is not possible to determine the nature of the photoinduced charge carriers. For this a different type of measurement is required, such as PA-detected magnetic resonance.

An indirect measurement of the forward electron transfer time can be made by measurements on a sample consisting of C₆₀ layer, an inert layer and a polymer layer.
Bibliography


Appendix A

Appendix

A.1 Life time measurements of the photoluminescence of OPV3 in toluene

![Graph showing lifetime measurement of photoluminescence of OPV3 in toluene](image)

**Figure A.1:** Life time measurement of the photoluminescence of OPV3 solved in toluene OD=0.04, excited at 305 nm, excitation density is 0.1 mW/mm².

In the figure it is shown how the experimental apparatus is calibrated, using the time calibrator: every 10 ns it generates a peak, which can be seen in the time spectrum. From this measurement the life time for both the PL at 458 and 500 nm is found to be 1.54±0.01 ns.

A.2 Life time measurements of the photoluminescence of different samples.

In this section the result of the time-resolved photoluminescence measurements of different samples are presented. The measurements were recorded at room temperature. All samples were excited at 305 nm, the excitation density was 0.5 mW per mm². The optical density of the solution was ~0.1 for all samples. In figure A.2, the structure of the studied samples are shown. The abbreviations
T, P, Ph, An and Al, stand for thiophene, pyrrole, phenyl, aniline and aldehyde, respectively.

Figure A.2: The structures of (a) TPT (b) Ph-TPT-Ph (c) Ph-An-2Al.

**TPT solved in toluene**

The life time of the photoluminescence at 458 nm of TPT solved in toluene is measured to be 0.49 ns (see figure A.3).

![Figure A.3: Life time measurement of the photoluminescence of TPT solved in toluene.](image)

**Ph-AN2-Al solved in toluene**

The life time of the photoluminescence at 500 nm of TPT solved in toluene is measured to be 2.15 ns (see figure A.4).

**Ph-TPT-Ph solved in toluene**

The life time of the photoluminescence at 500 nm of Ph-TPT-Ph solved in toluene is measured to be 0.79 ns (see figure A.5).
Figure A.4: Life time measurement of the photoluminescence of Ph-AN2-Al solved in toluene.

Figure A.5: Life time measurement of the photoluminescence of Ph-TPT-Ph solved in toluene.
A.3 Life time measurements of the PL of OPV3-C$_{60}$ and OPV4-C$_{60}$

The life times of the PL of OPV3-C$_{60}$ is measured at different wavelengths, see figure A.6. The life time of the photoluminescence at 420 nm is fitted in the time interval between 0.7 and 1.7 ns, for all other wavelengths it is fitted in the time interval between 0.7 and 4.7 ns. The errors in the fit are 0.07 ns. The fitted life times in these intervals are shown in the inset of figure A.6.

![Graph](image)

**Figure A.6:** Life time of the luminescence of OPV3-C$_{60}$ excited at 395 nm, measured at different wavelengths.

The life times of the PL of OPV4-C$_{60}$ is measured at different wavelengths, see figure A.7. The life time of the photoluminescence at 740 and 715 nm is fitted in the time interval between 0.7 and 6.5 ns, for all other wavelengths it is fitted between 0.7 and 4.7 ns. The fitted life times in these intervals are shown in the inset of figure A.7.
Figure A.7: Life time the luminescence of OPV4-C\textsubscript{60} excited at 395 nm, measured at different wavelengths.

A.4 Steady-state fluorescence spectra of OPV3-C\textsubscript{60} and OPV4-C\textsubscript{60}

In figure A.8 the measured steady-state fluorescence spectra of OPV3-C\textsubscript{60} and OPV4-C\textsubscript{60} solved in toluene are shown. At 450 nm the Raman scattering of the toluene is observed.
A.5 Time-resolved photoinduced absorption measurements of PTPTB:PCBM

In figure A.9 the results of the time-resolved PIA measurements of PTPTB:PCBM are shown. Observed is a multi-exponential decay of the photoinduced bleaching, at 585 nm and at 720 nm. The decays are fitted to a third order decay. For the 585 nm bleaching, the decay times $\tau_1 = 81 \pm 4$ ps and $\tau_2 = 673 \pm 21$ ps are found. For the 720 nm bleaching, the decay times $\tau_1 = 29 \pm 7$ ps and $\tau_2 = 507 \pm 28$ ps are found. As the third time, $\tau_3$, 1 $\mu$s was chosen to account for the long lived species. Compared to the measurements on P3HT:PCBM, a stronger photoinduced bleaching is observed and a longer rise time of the photoinduced bleaching ($\sim 5$ ps versus $\sim 2$ ps). Also, the noise in the signal is less, which is due to the larger thickness of the sample.
Probed at:
- 585 nm: \( t_1 = 81 \pm 4 \) ps, \( t_2 = 673 \pm 21 \) ps
- 720 nm: \( t_1 = 29 \pm 7 \) ps, \( t_2 = 507 \pm 28 \) ps

Figure A.9: (a) Life time measurement of the photoinduced bleaching of a PTPTB:PCBM (1:1) film at 585 nm and 720 nm (b) Magnification of the first 20 ps of the PB at 585 nm. Pump wavelength=585 nm, pump power=11 mW, excitation density=2.5 nJ/mm\(^2\), repetition frequency=4 MHz
A.6 Time-resolved photoluminescence measurements of P3HT and P3HT:PCBM

In this section, preliminary measurements of the photoluminescence spectra and the lifetime of the photoluminescence of P3HT and P3HT:PCBM are presented. The spectra are shown in figure A.11. The peak at 806 nm is due to the laser beam that was frequency doubled to obtain a 403 nm pump beam. Very weak photoluminescence of the P3HT:PCBM, and also of the pristine P3HT, is measured. The lifetime of the photoluminescence at 720 nm is measured. A bi-exponential decay of the photoluminescence is observed, the fast component is around the experimental resolution (70 ps): for P3HT $\tau_1 = 71 \pm 2$ ps and $\tau_2 = 271 \pm 5$ ps, for P3HT:PCBM $\tau_1 = 72 \pm 2$ ps and $\tau_2 = 1211 \pm 71$ ps. However, the coefficient for this last lifetime is much smaller. Thus, the PCBM quenches the photoluminescence.

Figure A.10: Photoluminescence spectra of a P3HT and a P3HT:PCBM (1:1) film, excited at 403 nm, 0.17 mW per 2 mm$^2$, at 300K.
Figure A.11: Decay of the photoluminescence of a P3HT and a P3HT:PCBM (1:1) film, excited at 403 nm, 0.17 mW per 2 mm², at 300K.
Appendix B

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