Excitons in Organic Semiconductors

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Abstract

Current Master thesis is devoted to the research in photophysics of organic semiconductors. The thesis comprises two parts: "Phosphorescent Iridium complexes OLEDs” and "Exciton diffusion length measurement in polymers.”

The first part of the thesis contains the results on organometallic Ir(III) complexes. Being phosphorescent materials, they could significantly improve the efficiency of the light-emitting devices. A blend of poly(9-vinylcarbazole)(PVK) and an n-type semiconductor 2-(4- tert-Butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazol (PBD) was used as a host matrix for phosphorescent organometallic complexes. The procedure of the white LED fabrication based on FIrpic (sky-blue emitting complex) and Btp2Ir(acac)(red emitting complex) has been elaborated. Newly synthesized red emitting Ir complexes containing carbazolyl acetylacetionate ligands were benchmarked. Their performance in the light-emitting devices was compared to the performance of the commercially available Btp2Ir(acac) complex emitting in the same spectral range. The novel complexes were shown to be up to 30% more efficient.

The second part of the thesis is devoted to the experiments on the exciton diffusion length measurement in the narrow band gap polymers that showed high efficiencies in the bulk heterojunction solar cells: poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b’]-dithiophene)-alt-4,7-(2,1,3-b-(2,1,3-benzothiadiazole) and poly[(4,4’-bis(2-ethylhexyl)dithieno[3,2-b:2’,3’-d]silole)-2,6-diyl-alt-(4,7-bis(2-thienyl)- 2,1,3-benzothiadiazol-2-thienyl)- 2,1,3-benzothiadiazole]-5,5’diyl. The exciton diffusion length in the materials has been estimated based on the results of the time resolved photoluminescence in ultra-thin films of various thicknesses. The values obtained for the diffusion length are below 10 nm that is typical for organic polymers.
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Part I

Phosphorescent Iridium Complexes OLEDs
Chapter 1
Introduction

Upon giving a brief introduction into the field of π-conjugated materials, the operating principle of an organic light emitting diode (OLED) is presented. An overview of photometry and colorimetry, techniques used for an LED characterization, is provided. Finally, the motivation and the goals of the research project are discussed.

1.1 Basics of π-conjugated materials

All organic compounds in general, and conjugated polymers in particular, are carbon based. The electronic configuration of the carbon atom in its ground state is 1\(s^2\)2\(s^2\)2\(p^2\). Four electrons at the outer shell can form hybridized orbitals. During \(sp^3\) hybridization 4 equivalent \(sp^3\) orbitals are formed in tetrahedral configuration, while in the case of \(sp^2\) hybridization 3 hybrid \(sp^2\) orbitals lying in a plane are formed with one \(p\) orbital being perpendicular to it. In the case of \(sp\) hybridization 2 \(sp\) orbitals are created and two \(p\) orbitals remain unchanged.

The skeletons of the hydrocarbons are built up from tetrahedral (\(sp^3\)), trigonal planar (\(sp^2\)), or linear (\(sp\)) hybridized carbon atoms. The hybridization type could be determined by a number of \(\sigma\) bonds the atom forms. If a carbon atom makes two \(\sigma\) bonds then it is \(sp\) hybridized, in the case of three and four single bonds the hybridization types are \(sp^2\) and \(sp^3\), respectively [1].

The nature of the semiconductive behavior of conjugated polymers lies in the alternation of single and double bonds between the carbon atoms. In a chain of the carbon atoms the single bonds are formed by the \(sp^2\) hybrid orbitals, while the double bonds contain one bond formed by \(sp^2\) orbitals and the other one formed by \(p_z\) orbitals. The \(sp^2\) orbitals lie in the plane forming the backbone of the polymer, \(p_z\) orbitals are perpendicular to the plane. The \(p_z\) orbitals form an electron cloud above the molecular plane leading to the bonding \(\pi\) orbital which is the highest occupied molecular orbital (HOMO) and the antibonding \(\pi^*\) orbital which is the lowest occupied molecular orbital (LUMO). The HOMO and LUMO are as well referred to as the frontier orbitals. The HOMO-LUMO gap is basically determining the optical properties of an organic material. The gap is reduced with the increased conjugation length. The mechanism of the charge conductivity is similar to inorganic materials: the LUMO acts as an analog of the conduction band and the HOMO as an analog of the valence band. Typically, organic materials are p-type conductors [2]. The simplest example of a conjugated polymer is polyacetylene illustrated in Fig. 1.2.
Figure 1.1. $sp^2$ hybridization in a carbon atom and an example of the simplest molecule with a double bond: ethylene.

Figure 1.2. The chain of the carbon atoms with the alternating single and double bonds and an energy band structure: HOMO(conduction band) and LUMO(valence band).
There is a wide range of applications of \( \pi \)-conjugated materials in optoelectronics: organic light emitting diodes, solar cells, field-effect transistors, organic memories, organic lasers, etc. If compared to their inorganic counterparts, the organic materials have a number of advantages: low cost for a large scale production, a possibility to be processed from the solution (doctor blading, ink jet printing), flexibility, and others. Some devices based on the organic materials are already available on the market (for instance OLED displays). However, there are still some drawbacks of the organic materials to be overcome by the further research, the most severe of them are low efficiency and short lifetime of the devices.

### 1.2 Luminescence in organic materials

Luminescence is the phenomenon of light emission at the relatively low temperatures (not to be confused with the thermal radiation, for instance black body radiation or radiation of an incandescent bulb, that is not luminescence). Luminescence could be classified depending on the factor that initiates it: chemoluminescence (as the result of a chemical reaction), electroluminescence (in response to the current passing through the material), photoluminescence (the absorption of light and concomitant re-emission), etc.

The phenomenon of luminescence could be understood if a quantum mechanical description is applied. Due to the fact that the electrons and the holes are fermions, their spin number is half-integer \( s = \frac{1}{2} \). There are two possible values of the spin projection on the axis of quantization \( z \): \( s_z = \pm \frac{1}{2} \), or spin up and spin down. The spin parts of the wavefunctions of the particles could be written in Dirac notation: \(| \uparrow \rangle \) and \(| \downarrow \rangle \). Since the exciton is formed by two particles: an electron and a hole, there are four eigenstates of the exciton: non-degenerate singlet state with the spin \( S = 0 \)

\[
\frac{1}{\sqrt{2}} (| \uparrow \downarrow \rangle + | \downarrow \uparrow \rangle)
\]  

(1.1)

and a triply degenerate triplet state with the spin \( S = 1 \)

\[
| \uparrow \uparrow \rangle,
\]  

(1.2)

\[
\frac{1}{\sqrt{2}} (| \uparrow \downarrow \rangle - | \downarrow \uparrow \rangle),
\]  

(1.3)

\[
| \downarrow \downarrow \rangle,
\]  

(1.4)

with the sub-states having the spin projections \( S_z = +1, 0, -1 \) respectively [3]. The state multiplicity is defined as \( 2S + 1 \).

If the luminescence occurs from an excited singlet state it has a short lifetime and is called fluorescence. Triplet states have much longer lifetimes, and lead to phosphorescent emission.

A typical Jablonski diagram for an organic molecule [4] is shown in Fig. 1.3. The ground state of the molecule is a singlet state \( S_0 \), while the excited states could be either singlets or triplets with the lowest excited triplet state \( T_1 \) lying below the lowest excited singlet state \( S_1 \).

Singlet-triplet transitions are forbidden in the dipole approximation, thus the incident light could excite only singlet states. Consider the excitation of the lowest singlet state
Upon excitation, $S_1$ could radiatively relax to the ground state $S_0$, emitting a photon or via the process of intersystem crossing (ISC) exhibit a transition to the triplet state $T_1$. The transition $T_1 - S_0$ is a spin forbidden transition and could potentially result in phosphorescent emission. The rate of the ISC compared to the radiative lifetime of $S_1$ is a determining factor in further evolution of the system. If the ISC is weak, the transition $S_1 - T_1$ is highly improbable and the excitation relaxes to the ground state through $S_1 - S_0$ transition. However, provided the intersystem crossing is strong, $S_1 - T_1$ transition becomes more probable than $S_1 - S_0$ resulting in consequent excitation pathway $S_1 - T_1 - S_0$.

The rate of the ISC is determined by the spin-orbit coupling. As it is known from the quantum mechanics, the spin-orbit interaction is strong in the atoms with heavy nuclei, for example in the transition metals [5].

When the system is excited via electron-hole recombination, all four states, one singlet and three triplets are populated with the same probability. Thus 25% of the formed excitons are $S_1$ while 75% are $T_1$. In the case of electrical excitation of a fluorescent material only 25% of the excitons are emissive, while in the case of the phosphorescent material this number could be up to 100%. Thus, phosphorescent materials have high quantum yield and are attractive for the efficient light sources.

### 1.3 Organometallic complexes

Among the phosphorescent materials, organometallic complexes are especially promising for application in the light emitting devices.

The organometallic complexes are composed of a metal ion surrounded by the organic ligands. Typically the ion is a transition metal ion: iridium, ruthenium, palladium, rhenium, europium, etc.

Optoelectronic properties of the complexes are largely determined by the frontier orbitals (the HOMO and the LUMO). The following types of excitations are distinguished [6]:

1. ligand-centered excitations, for example $\pi - \pi^*$
2. metal-centered excitations, for example $d - d^*$
3. metal-to-ligand charge transfer excitations, for example $d - \pi^*$

Out of them, metal-to-ligand charge transfer states are of particular interest. The mixing of a ligand state with a state of the metal ion introduces an enhanced spin-orbit character to the transition and consequently results in the high phosphorescence yield.

1.4 OLEDs

For the organic materials the electroluminescence was first reported in 1960s for anthracene single crystals [7, 8] and in 1990s for polymers [9, 10, 11].

Electroluminescence in organic materials occurs upon injection of the negative charges (electrons) and the positive charges (holes) into the material, a creation of bound excited state (exciton), and its radiative decay. The electrons are injected from a low workfunction material called a cathode and the holes from a high workfunction material called an anode.

An organic light emitting diode (OLED) is a device based on the phenomenon of the electroluminescence. In a simplified configuration the device consists of a light emitting organic layer sandwiched in between the electrodes. The energy levels of such a structure are shown in Fig. 1.4.

A typical IV curve for an OLED is depicted in Fig. 1.5. The threshold voltage is defined as a point of change in the IV curve steepness. Above the threshold voltage, the barriers for charge injection from the electrodes into the organic material are overcome and the current flows through the device. Below the threshold voltage the current is attributed to leakage.
1.5 Introduction to photometry and colorimetry

1.5.1 Photometry

The field of optics that deals with the description of light in terms of the perceived brightness is called photometry. Our eyes are not equally sensitive to all the wavelengths of the visible light. The sensitivity is higher to the green light than to the red or blue. In some practical applications the physiological response level is of crucial importance and the description in terms of energetic parameters then becomes completely irrelevant. Different levels of the sensitivity to the different wavelengths are taken into account by the procedure of weighting of the energetic parameters by so-called luminosity function (sometimes also referred to as the visual sensitivity function or the luminous efficiency function).

One distinguishes two different regimes when the eye is adapted to the bright light (photopic vision) or to the dark conditions (scotopic vision). Typically the photometry is based on photopic vision. The CIE 1931 standard [13] photopic luminosity function is presented in Fig. 1.6. Basic SI photometry units are collected in Table 1.1.

![Figure 1.6. Photopic luminosity function of the CIE 1931 standard.](image)

<table>
<thead>
<tr>
<th>Value</th>
<th>Symbol</th>
<th>SI unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Luminous energy</td>
<td>$Q_v$</td>
<td>$Lm \times s$</td>
</tr>
<tr>
<td>Luminous flux</td>
<td>$F$</td>
<td>$lm = cdsr$</td>
</tr>
<tr>
<td>Luminous intensity</td>
<td>$I_v$</td>
<td>$cd = lm/sr$</td>
</tr>
<tr>
<td>Luminance</td>
<td>$L_v$</td>
<td>$lux = lm/m^2$</td>
</tr>
<tr>
<td>Illuminance</td>
<td>$E_v$</td>
<td>$lux = lm/m^2$</td>
</tr>
</tbody>
</table>

Table 1.1. SI photometry units.

1.5.2 Colorimetry

As it is known from the physiological studies, there are four types of the sensor cells in the retina of the human eye that are responsible for vision: one type of the rod cells and 3 types of the cone cells (see Fig. 1.7 a, b). The rod cells function in the dim light condition and are mainly responsible for the scotopic vision, while the cone cells are active at the brighter light conditions [14].

Since there are three types of the cone cells S, M, L with the sensitivity peaks in different wavelength ranges: small (420-440 nm), middle(530-550 nm), and long (560-580 nm) respectively, color sensation is attributed mainly to them. The normalized sensitivity of the different types of the cone cells is shown in Fig. 1.7 c.

In the efforts to construct a mathematical model of color perception several color systems have been proposed. They all are based on the three stimuli approach. Up to date the most widely used is the one described in the CIE 1931 standard [13].
The CIE 1931 XYZ color space is a standard adopted in 1931 by the International Commission on Illumination (traditionally abbreviated as CIE what derives from its French name ‘La Comission Internationale de l’Éclairage’). The standard is based on the so-called standard $2^\circ$ photopic observer with the corresponding color matching functions $x(\lambda)$, $y(\lambda)$, $z(\lambda)$ shown in Fig. 1.8(b). The color matching functions could be thought of as the spectral sensitivity curves of three linear light detectors.

The tristimulus values for a signal with the spectral distribution $I(\lambda)$ are defined in the following way:

$$X = \int_0^\infty \bar{x}(\lambda)I(\lambda)d\lambda$$  \hspace{1cm} (1.5)
The color is then determined by the normalized values:

\begin{align}
x &= \frac{X}{X + Y + Z}, \\
y &= \frac{Y}{X + Y + Z}, \\
z &= \frac{Z}{X + Y + Z} = 1 - x - y,
\end{align}

out of which any two of three (for instance x and y) remain independent. Non-normalized value Y is responsible for the overall perceived intensity. Hence, the derived color space is frequently referred to as the xyY color space.

For the sake of visual representation, each color is depicted on the plane of xy parameters referred to as the chromaticity diagram. All the possible coordinates of the spectra are located within the shape shown in Fig. 1.8(a). The points at the outlet curve of the shape represent monochromatic radiation of a certain wavelength. The point (0.33,0.33) corresponds to the white light.

1.6 Motivation and goals

Nowadays the OLED technology is widely used in the displays of the desktop and handheld electronic devices. In the nearest future, highly efficient solid state lighting will completely replace inefficient incandescent bulbs.

Organometallic compounds possess an enormous potential for being utilized as phosphorescent emitters in the OLEDs. They can lead to fourfold efficiency improvement compared to the devices based on purely organic fluorescent materials.

Our goal is to investigate the performance of organometallic iridium complexes in the PVK (poly(9-vinylcarbazole)) polymer matrix: to develop a phosphorescent white OLED fabrication technology, and to benchmark novel red emitting compounds that contain carbazolyl acetylacetonate ligands and are potentially well miscible in PVK.
Chapter 2

Experimental

2.1 Materials and fabrication

In order to investigate the performance of the phosphorescent iridium complexes in OLEDs, the devices with the structure represented in Fig 2.1 were fabricated.

As a host material for phosphorescent complexes poly-9 vinylcarbazole (PVK) was selected. Chemical structure of the PVK polymer is shown in Fig. 2.2(a). The backbone of the PVK is non-conjugated while the side groups are π-conjugated carbazolyl units.

The PVK has a relatively high band gap with the HOMO of -5.8 eV and the LUMO of -2.2 eV, the triplet energy of PVK is 2.5 eV [15]. Due to this fact, it is an attractive material to be used as a host for various phosphorescent complexes emitting in the visible spectral range. The PVK of average molecular weight \( M_w \sim 1,100,000 \text{u} \) was purchased from Sigma-Aldrich and used without further purification.

![Figure 2.1. (a) Structure of the PVK OLED device. (b) Energy levels of the materials used in the device.](image)

The electrodes were chosen in a way that their Fermi levels match the HOMO and the LUMO of the polymer in order to facilitate the injection of charges at the interfaces. ITO (indium tin oxide) with a 60 nm layer of PEDOT:PSS (poly(3,4-ethylenedioxythiophene) : poly(styrenesulfonate)) as a hole transport material was used as an anode. The chemical...
structure of PEDOT:PSS is shown in Fig. 2.2(b). The cathode comprised 5nm Ba layer covered by 100nm Al layer. In the configuration of the device chosen there was an 0.6 eV barrier for the electron injection and 0.6 eV barrier for the hole injection.

As the majority of the organic polymers, PVK is a hole conducting material with poor electron conductivity. In order to use the material for the organic LEDs, an ambipolar device that requires both electrons and holes for its operation, the polymer has to be doped by an n-type conductor.

A widely used dopant for PVK is 2-tert-butylphenyl-5-biphenyl-1,3,4 oxadiazol (PBD). The performance of the recently synthesized materials NDI-8 and NDI-F as the n-type dopants for the PVK OLEDs was also tested. The chemical structures of PBD, NDI-F, and NDI-8 are shown in Fig. 2.2.

The Fermi levels of the electrodes, and the HOMO and the LUMO levels of the PVK polymer and some dopants are depicted in Fig. 2.1 (b). Doping by PBD which has the LUMO level at 2.7eV (compared to 2.2eV for PVK) not only improves the electron conductivity but also facilitates the electron injection from the cathode. HOMO and LUMO levels of the phosphorescent dopants lie within the band gap of the PVK:PBD matrix, this fact leads to the charge trapping mechanism of the exciton formation on the phosphorescent dopant sites.

Several phosphorescent metalloorganic Ir complexes were used in the research: commercially available bis[(4,6-difluorophenyl)-pyridinato-N,C 20] iridium(III) (picolinate) (Flr-
pic) and bis(2-(2'-benzo-thienyl)pyridinatoN,C 3') iridium(III) (acetylacetonate) (Btp2-Ir(acac)), and newly synthesized IrCZ1 and IrCZ2.

![Chemical structures of FIrpic(a) and Btp2Ir(acac) (b).](image)

The structures of FIrpic and Btp2Ir(acac) are provided in Fig. 2.3. FIrpic is a sky-blue emitting complex, while Btp2Ir(acac) is emitting in red. Both compounds were purchased from American Dye Source company and used without further purification.

![Chemical structure of IrCZ1 (a) and IrCZ2 (b).](image)

Red emitting complexes IrCZ1 and IrCZ2 were obtained from the Functional Polymers Group, University of Wuppertal. Their chemical structures are shown in Fig. 2.4. The complexes are equipped with the ligands containing carbazolyl units.

Light emitting diodes were fabricated under the clean room conditions. Glass substrates with the ITO (indium tin oxide) areas were cleaned using a standardized cleaning procedure. Upon cleaning, a 60 nm layer of PEDOT:PSS was spin cast from the aqueous solution in air. The samples were baked in the oven at 140° C during 10 min to remove
water, and then transferred into an oxygen and water free glove box with the nitrogen atmosphere. An active layer was applied by the spincoating, aiming at the thicknesses in the range of 75-85 nm. The films were annealed on a hot plate at 110° C during 30 min. The cathode layers of Ba(5 nm) and Al (100 nm) were evaporated on top of the polymer under high vacuum conditions. After the fabrication, the devices were transferred, without contacting air, into the nitrogen glovebox for measurements.

2.2 IV-photocurrent, and electroluminescence spectra measurements

Current-voltage characteristics of the light emitting diodes were acquired with Keithley 2400 source meter. The applied bias was scanned in a range from -2 to 10 V with the step of 0.1V, time delay 0.3 s per step. The light output was measured by the silicon photodiode mounted directly above the sample. The Electroluminescence spectra were measured by the Ocean Optics USB 2000 fiber optic spectrometer for the applied bias of 10 V.

2.3 Luminosity measurements

The luminosity of the devices was measured using a Minolta LS-110 luminance meter. The bias applied to the devices was kept at the constant value of 10 V. The measurements were performed in the nitrogen atmosphere to prevent degradation of the devices. In order to reliably estimate the device performance at least three devices were measured for each composition of an active layer. Every device was measured at three time moments: immediately after turn on, in 30 seconds, and in one minute. The obtained values of the luminous efficiency were averaged out and the measurement errors were estimated as a root mean square deviation from the mean value. Power efficiency was calculated from the luminous efficiency values assuming that the emission of the devices is governed by the Lambertian law [16].

2.4 Photoluminescence spectra and time resolved spectroscopy

The photoluminescence measurements were performed on a separately fabricated set of films spincast on quartz substrates. Upon fabrication, the samples were mounted into the cryostat for optical measurements and kept in dynamic vacuum. The films were excited by the second harmonic (380 nm) of a Ti-Sapphire laser delivering 150 fs pulses. The photoluminescence decays were measured using a Hamamatsu streak camera working in a single sweep mode. The steady state photoluminescence spectra were measured with an ImageEM Hamamatsu CCD detector.
Chapter 3

Results on n-type dopants

In order to choose a highly efficient n-type dopant for the phosphorescent OLEDs the performance of PBD in PVK OLEDs was compared to the performance of the NDI-F and NDI-8 molecules, which showed high performance in the organic field effect transistors [17].

The PVK OLED devices doped with NDI-F or NDI-8 at a ratio of 70:30 wt% exhibited lower current and significantly lower light output than the devices doped with PBD. The IV curves and the light output of the devices is represented in Fig. 3.1.

The PVK:PBD OLEDs were performing with high stability. The IV curves and the light output for a number of scans are shown in Fig. 3.2. A hysteresis in both the IV curve and the light output was observed for the first scan while absent for the subsequent scans. This phenomenon could be explained by an irreversible filling of the charge traps present in the polymer [18].

The emission from the PVK is in the blue spectral range with the emission maximum at 440 nm. The electroluminescence spectra of the devices for different applied biases are shown in Fig. 3.3. Substantial light output was observed under the applied biases of 10 V and higher, however for the bias of the order of 13-15 V the devices were destroyed. Due to these reasons, an operating bias of 10 V has been chosen.

The turn on voltage of the devices was equal to 3 V. Two operating modes were observed: the leakage current mode for low voltages and the diffusion current for the voltages above the turn-on voltage.
Figure 3.1. Performance of the PVK devices with different n-type dopants (for the weight ratio 70:30): PBD, NDI-8, NDI-F: IV curves (a), light output(b).

Figure 3.2. The IV curves and the light output for PVK:PBD devices for three first scans.

Figure 3.3. Electroluminescence spectrum for PVK:PBD devices under different applied biases.
Chapter 4

Results on white OLEDs

In order to obtain a recipe for a two component phosphorescent white OLED, the devices with different ratios of red and blue phosphorescent dopants were fabricated and characterized.

The concentration of the FIrpic dopant was chosen at the level of 10wt% and kept unchanged. The concentration of the red dopant was varied in a wide range with the purpose to achieve white light emission.

The shapes of the IV and photocurrent curves for the OLEDs doped with FIrpic and Btp2Ir(acac) did not differ from those for undoped PVK:PBD OLEDs (see Fig. 3.2). Thus the phosphorescent dopants do not influence significantly the charge injection.

![Color coordinates of the fabricated devices represented on the CIE 1931 chromaticity diagram](image)

Figure 4.1. Color coordinates of the fabricated devices represented on the CIE 1931 chromaticity diagram
Doping & CIE 1931 x & CIE 1931 y

<table>
<thead>
<tr>
<th>Doping</th>
<th>CIE 1931 x</th>
<th>CIE 1931 y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped</td>
<td>0.18</td>
<td>0.19</td>
</tr>
<tr>
<td>10% FIrpic</td>
<td>0.23</td>
<td>0.45</td>
</tr>
<tr>
<td>10% FIrpic, 0.05% Btp2Ir(acac)</td>
<td>0.29</td>
<td>0.41</td>
</tr>
<tr>
<td>10% FIrpic, 0.2% Btp2Ir(acac)</td>
<td>0.46</td>
<td>0.37</td>
</tr>
<tr>
<td>10% FIrpic, 1% Btp2Ir(acac)</td>
<td>0.62</td>
<td>0.34</td>
</tr>
</tbody>
</table>

Table 4.1. CIE 1931 x and y coordinates of the fabricated devices.

The electroluminescence spectra of the devices were measured at an applied bias of 10 V. The color of the light emission in the CIE 1931 color space was calculated for each device using the eqs. 1.8 and 1.9. Corresponding points depicted on the CIE 1931 chromaticity diagram are shown in Fig. 4.1 and CIE1931 x and y coordinates of the devices are given in Table 4.1. Addition of the red emitting dyes leads to a gradeate decrease in the intensity of the electroluminescence originated from FIrpic, and the increase in red emission from Btp2Ir(acac). In the intermediate range of concentrations white light emission can be acheived.

Figure 4.2. Spectra of the devices doped with 10% of FIrpic and different amount of Btp2Ir(acac): 0%, 0.05% , and 1%.

At the concentration of 0.05 % of Btp2Ir(acac) dopant the devices exhibited a warm white color of light emission with the CIE 1931 coordinates (0.29, 0.41). All the corresponding CIE 1931 xy coordinates for the devices doped with FIrpic and Btp2Ir(acac) were geometrically located on a line in the CIE1931 xy plane. The color of light emission corresponding to the different points on the line can be achieved by varying the ratio of the dopants.

In Fig. 4.1(b) the normalized electroluminescence spectra for the red(10% FIrpic, 1% Btp2Ir(acac)), blue (10% FIrpic, 0% Btp2Ir(acac)) and white (10% FIrpic, 0.05% Btp2Ir(acac)) devices are shown.
Chapter 5

Results on red-emitting Ir(III) complexes

This chapter contains the results on the benchmarking of new phosphorescent Ir complexes IrCZ1 and IrCZ2, a commercially available complex IrBtp2(acac) has been chosen as the basis for comparison.

The performance of the complexes in the OLEDs with PVK:PBD (weight ratio 70:30) as a host matrix was investigated. The devices with the molar concentrations of 4, 8, 12 and 16 dopant molecules per 1000 PVK monomer units were fabricated for each type of the dopant. The dependence of the efficiency on the dopant concentration was studied.

5.1 The influence of annealing

The investigation of the annealing step influence on the performance of the devices was done. Two badges of the OLEDs doped with IrCZ1 were fabricated: with the annealing of polymer layer at 140\degree C and without annealing. Significant improvement of the device performance was observed upon annealing. The comparison of the IV curves and light output for not annealed and annealed devices is shown in Fig. 5.1.

![IV curves](image1)

![Light output](image2)

Figure 5.1. Performance of annealed versus not annealed devices: (a) IV curves and (b) light output.
The increase of half an order of magnitude for current and photocurrent was observed.

Figure 5.2. AFM images of not annealed (a,c) versus annealed (b,d) PVK:PBD layer doped with IrCZ1 (4:1000) at different length scales.

The AFM study of the active layer surface showed the impact of the annealing on the surface morphology. The AFM images of the annealed and not annealed layers are represented in Fig. 5.2.

The RMS roughness of the not annealed and the annealed samples were 0.22 nm and 1.75 nm, respectively, averaging over the area of $10 \times 10\mu m$, and 0.11 nm and 0.21 nm, respectively, averaging over the scan area $1 \times 1\mu m$. The gain in current upon the increase in the roughness of the active layer could be explained by a higher cathode-polymer contact area leading to more electrons being injected into the active layer.
5.2 Luminosity of the devices

All the devices fabricated have shown the luminosity of the order of 500-700 cd/m². The absolute values of the luminosity varied significantly (about 60 cd/m²) for different devices of the same active layer composition. There are several factors that could be contributing to this: variations in thickness of the active layer, variations in the morphology of the active layer, and time degradation of the devices during the measurement procedure.

5.3 Time stability of the devices

Time degradation of the devices was studied for the LEDs with the surface area $10^{-5} cm^2$, active layer doped with 12 dopant molecules per 1000 monomer units of PVK for different types of dopants. The applied bias was equal to 10V.

![Figure 5.3](image)

Figure 5.3. Time degradation of working devices: (a) current(solid line) and luminosity(dashed line), (b) luminous efficiency.

The current and the luminance for each device were measured at three moments: immediately after turn-on, in 30 seconds and in 60 seconds. The decay curves for the current and the luminosity are shown in Fig. 5.3 a. Both current and luminosity exhibited a decay in time, however the luminosity remained proportional to the electric current what could be seen from the time behavior of the luminous efficiency determined by the ratio of the luminosity and the current. The fact of the stability in the efficiency value gives an opportunity to characterize the devices on the basis of the efficiency rather than on the absolute values of current or luminance.

Since the measurements were performed in nitrogen atmosphere, as well as the fabrication was done under oxygen and water free conditions, degradation of the working OLEDs due to the oxidation is eliminated. Potential explanations to the degradation are the electrochemical reactions occurring in the active layer due to high chemical reactivity of the excited states or the electric field assisted migration of ions from the electrodes.
5.4 Efficiency

The efficiency of an OLED is a parameter that relates the electrical energy conversion into light. Luminous efficiency $L_{eff}$ is a parameter that is traditionally used to characterize the OLEDs and is calculated according to the formula:

$$L_{eff} = \frac{L_v A}{I}, \quad (5.1)$$

where $L_v$ is the luminance and $A$ is the area of the device, and $I$ is the current passing through the device.

Taking into account that OLED is emitting as a Lambertian source it is possible to calculate the power efficiency directly from the luminous efficiency:

$$P_{eff} = \frac{2\pi}{V} L_{eff}, \quad (5.2)$$

where $V$ is an applied bias, and the factor of $2\pi$ is determined by the solid angle of the emission of an OLED. The dependences of the luminous and the power efficiencies on the concentration of the dopant for different dopants is shown in Fig. 5.4(a). Each data point on the plot is an average result for at least 4 devices, 3 measurements per device: immediately after turn on, in 30 seconds and in a minute. The error bars represent a root mean square deviation from the mean value.

![Figure 5.4. Luminous and power efficiency of the devices compared to photocurrent efficiency.](image)

IrCZ1 and IrCZ2 complexes show better performance than the conventional Btp2Ir(acac) complex. The best performance was observed for the molar concentrations 8-10 dopant molecules per 1000 monomer units of PVK. Both cabarzolyl containing complexes were performing at the same level of luminous efficiency of about $4 cd/A$ compared to $3 cd/A$ for the conventional complex.

Due to the fact that in the experiments the light output of the devices was measured not only by means of luminance meter but also by a solid state photodetector during the IV scans, it is possible to introduce another value that describes the efficiency, namely the
ratio of the photocurrent of the photodetector $I_{ph}$ to the current $I$ applied to the device at a fixed operating bias:

$$E_{ph} = \frac{I_{ph}}{I}$$

(5.3)

This dependence is represented in Fig. 5.4 (b) and has a similar trend with the dependence represented in Fig. 5.4 (a). Each point is a result of the measurements of at least 4 devices, 1 measurement per device. Only one measurement per device was performed since the degradation of the OLEDs during the IV scans was negligible. Comparing Fig. 5.4 (a) and Fig. 5.4 (b) we conclude that the results on the photocurrent efficiency corroborate the results on the luminous efficiency.

### 5.5 Electroluminescence and photoluminescence

For the chosen concentrations of the dopants both the photoluminescence and the electroluminescence spectra exhibit no dependence on the dopant concentration. The emission of the PVK in the samples with the dopants was practically absent. The absence of the emission from the PVK in the photoluminescence experiments is a sign of the fast and efficient energy transfer from the PVK matrix to the phosphorescent dopants. The absence of the PVK emission in the electroluminescence experiments tells about the efficient charge trapping at the dopant sites [19].

![Figure 5.5](image)

Figure 5.5. (a) Photoluminescence (dashed line) and electroluminescence (solid line) of the PVK:PBD layer doped with phosphorescent Ir complexes at the concentration 8 dopant molecules per 1000 PVK monomer units. (b) Time resolved photoluminescence of phosphorescent Ir complexes in PVK:PBD polymer matrix.

The electroluminescence and the photoluminescence spectra for the active layers of the devices at the concentration of the phosphorescent dopants of 8 dopant molecules per 1000 monomer units of PVK are provided in Fig. 5.5 (a).

The electroluminescence spectra are red shifted with respect to the photoluminescence spectra. It is typical for the materials with charge trapping mechanism of the exciton formation at the dopant sites. The shift between the electroluminescence and the photoluminescence maxima is 20 nm for IrCZ1 and IrCZ2, and 10 nm for Btp2Ir(acac).
Time resolved photoluminescence profiles are represented in Fig. 5.5 (b). New carbazolyl complexes have shown significantly shorter photoluminescence decays compared to the conventional complex: $1.2\mu s$ versus $5.1\mu s$. A shorter phosphorescence decay time for the carbazolyl containing complexes is an explanation to their highly efficient performance in the devices. Shorter radiative lifetime decreases the probability of non-radiative decay of the triplet state.
Chapter 6

Conclusions

Based on the results presented above we conclude that the PVK polymer doped with the PBD n-type conductor is a good matrix to be utilized as a host for phosphorescent Ir complexes in the organic LEDs. Recently synthesized naphthalene diimide derivatives NDI-F and NDI-8 exhibited lower than PBD performance as the n-type dopants in the PVK LEDs. Wide bandgap of the PVK allows to use different organometallic complexes and to achieve phosphorescent emission in all the wavelengths of the visible light.

The annealing step is essential for the fabrication of the PVK:PBD OLEDs. It leads to the increase in the electrical current and light output of the devices by half an order of magnitude. The AFM studies revealed that upon annealing the roughness of the doped polymer layer is significantly increased. A larger contact area of the rough active layer with the cathode is an explanation of the higher performance of the annealed devices. The differences in the current under the same applied bias for annealed and not annealed devices.

The procedure of the phosphorescent white OLEDs fabrication has been developed. White LEDs could be produced based on the commercially available complexes: red emitting IrBtp2(acac) and sky-blue emitting FIrpic, with the concentration of FIrpic and Btp2Ir(acac) 10% and 0.05% respectively. The CIE 1931 xy coordinates of the white light emitted by the device were equal to (0.29, 0.41). This color could be characterized as yellowish white.

The research on the recently synthesized red emitting phosphorescent iridium complexes IrCZ1 and IrCZ2 have shown that they perform more efficiently in PVK:PBD polymer matrix than commercially available Btp2Ir(acac), demonstrating a similar emission spectrum. The photoluminescence decay times of the carbazolyl complexes are five times shorter than of the conventional one. Shorter phosphorescence lifetimes are favorable for highly efficient light emitting devices due to the reduction in the relative probability of the non-radiative decay.
Part II

Exciton Diffusion Length Measurement in Polymers
Chapter 7

Introduction

7.1 Motivation

Optoelectronic devices based on the organic materials are nowadays attracting a lot of attention due to their numerous advantages compared to the devices based on the conventional inorganic materials: low weight, mechanical flexibility, easy fabrication methods, and low cost. Organic light emitting diodes are already available on the market. Poor efficiency of the organic solar cells currently prevents their commercialization. Low performance of the organic solar cells is mainly attributed to the short exciton diffusion length, low charge mobility and morphology effects [20]. In order to improve the performance of the organic solar cells fundamental physics of the excitons and charges in the organic materials should be understood better.

The goal of the current project is to measure the exciton diffusion length in narrow band gap polymers PCPDTBT and Si-PCPDTBT. These materials are showing superior performance in the bulk heterojunction solar cells. Si-PCPDTBT has the highest up to date reported efficiency amongst low band gap polymers (5.2% for Si-PCPDTBT) in the blends with [6,6]-phenyl C71-butyric acid methyl ester (C70-PCBM) [21].

7.2 Excitons in organic materials

In conjugated polymers charge neutral optical excitations are described as strongly bound Frenkel excitons [22]. The excitons are usually localized on a single polymer chain [23, 24]. The exciton is created upon a photon absorption by the material. Fast vibrational relaxation process occurs on the time scale shorter than 100fs [25]. The exciton then migrates in the polymer density of states by hopping with the rate of the order of 10ps [26, 23, 27]. The polymer density of states is broadened due to the disorder in the material. The exciton migration in the Gaussian density of states is represented in Fig. 7.1. At the room temperature fast downhill migration is followed by thermally activated hopping. Due to the downhill migration process the time-resolved photoluminescence spectra are redshifted with time after the excitation by a femtosecond laser pulse [28]. The exciton transfer between the polymer segments occurs presumably by the Förster-type energy transfer process.

A typical lifetime of an exciton in the organic polymers is of the order of a nanosecond or shorter. The average distance the exciton moves in the material during its lifetime
Figure 7.1. The exciton diffusion process in the Gaussian density of states at low temperatures (a) and at the room temperature (b) [29].

is called an exciton diffusion length. In the organic polymers the typical values for the exciton diffusion length are in the range of 5-15 nm [30, 31].

The exciton could decay either non-radiatively, or radiatively by emitting a photon. In addition to the radiative or non-radiative decay, the exciton might end up in being quenched. Two main mechanisms of the exciton quenching are distinguished: the charge transfer and the energy transfer to a molecule of a quencher.

Figure 7.2. Two exciton quenching mechanisms: (a) charge transfer [32] and (b) energy transfer.

Quenching by the charge transfer mechanism is represented in Fig. 7.2(a). The dissociation of the exciton occurs by the electron transfer from the LUMO of the donor to the LUMO of the acceptor, that lies below the LUMO of the donor. The hole remains at the HOMO of the donor molecule. After the dissociation the recombination process occurs by
the electron back transfer to the HOMO of the acceptor within the time of \( \sim 1 \mu s \) [32]. The fullerene molecules show high electron affinity resulting from the deep LUMO level of \(-4.3\text{eV}\). Therefore the fullerenes are nice electron acceptors and perfect exciton quenchers by charge transfer mechanism [33].

The energy transfer from an excited donor molecule to an acceptor molecule is represented in Fig. 7.2(b). It occurs as a non-radiative process through the dipole-dipole coupling: the donor molecule emits a virtual photon that is absorbed by the acceptor molecule. This mechanism is also referred to as the Förster resonance energy transfer. The process typically occurs at the donor-acceptor separation distances of below 10 nm.

The exciton hopping process resembles a random walk and could be theoretically modelled by the diffusion equation. The exciton diffusion length \( L_D \) and the lifetime \( \tau \) are connected via the exciton diffusion coefficient \( D \):

\[
L_{D,\alpha} = \sqrt{\alpha \tau D},
\]

where the factor \( \alpha \) depends on the dimensionality and is equal to unity for a one-dimensional diffusion.

### 7.3 Overview of the exciton diffusion length measurement method

Several methods of the exciton diffusion length measurement have been so far reported in the literature. Among them: photocurrent spectrum method [34], exciton-exciton annihilation [35], and the method of photoluminescence quenching.

In the photocurrent spectrum method the solar cell from the material under investigation is fabricated. The exciton diffusion length is extracted from the photocurrent measurements. The drawback of this method is a complicated model, in addition a number of problems arises from the usage of metal electrodes (e.g., reflections, not complete quenching by metal).

The exciton annihilation method extracts the exciton diffusion length from the time resolved photoluminescence measurements performed at different excitation powers. For substantial densities of the excitons the annihilation process becomes efficient. The annihilation turns out to be diffusion limited. The drawback of the model is that it relies on the estimated exciton diffusion radius. Another drawback of the method is the usage of high excitation powers that could lead to the degradation of the sample.

There are several variations of the exciton quenching method. The samples with the quenchers could be prepared either as a blend of the polymer and the quencher or as a bilayer structure with a layer of the exciton quencher and a layer of the polymer [31]. Fullerene derivatives are typical materials that are used as the quenchers in these experiments.

The major drawback of the measurement in the blend is that the concentration of the quenching sites could not be determined precisely since the quencher molecules might potentially form the clusters instead of being mixed with the polymer at the molecular level. The theoretical model in this case is also quite complicated. The heterostructure approach does not have these problems, however there is a problem to fabricate the samples having sharp polymer-fullerene interface layers. This problem could be successfully solved by using the crosslinkable fullerene derivatives [31].
Figure 7.3. The structure of the samples for the exciton diffusion length experiments: (a) neat polymer films and (b) bilayered samples with the fullerene quenching layer.

The photoluminescence measurements could also be performed either in the steady state mode or in the time-resolved mode [36], and the exciton diffusion length extracted either from the absolute photoluminescence intensity values or from the normalized photoluminescence time decay profiles, respectively. The measurement of the absolute intensity values encounters a number of experimental problems (callibration of the detector, precise alignment of the setup, stability of the excitation power). The time resolved method overcomes all these obstacles.

In addition to the quenching at the fullerene-polymer interface, the polymer-vacuum interface of a film can as well quench the photoluminescence due to the formation of a dense skin layer during the spincoating procedure [37].

We will measure the exciton diffusion length by means of time resolved photoluminescence in thin films and heterostructures with the quenching layer (Fig. 7.3). The exciton diffusion length will be extracted by fitting the data with the theoretical model.
Chapter 8

Theoretical background

8.1 Formulation of the problem

Current chapter contains the theoretical background of the exciton diffusion length measurement method in the thin polymer films and the heterostructures with the quenching layer. The geometry of the problem is represented in Fig. 8.1. The polymer film of the thickness $L$ is located on top of the quartz substrate or on top of the quenching layer. We choose the axis $x$ perpendicular to the film surface, with the origin on the top surface of the polymer film.

The sample is excited by a femtosecond laser pulse. In our model we assume that the change in the pulse energy upon traversing the sample is negligibly small. The pulse intensity is however quite low and the photochemical reactions and nonlinear processes (e.g. exciton annihilation) do not occur. Interference effects are also not taken into account since the films are significantly thinner than the wavelength of the laser light. As well, we assume that the laser pulse acts instantaneously. This assumption is justified by the fact that the duration of the laser pulse is significantly shorter than typical lifetimes of the excitons in organic materials. Provided all the conditions mentioned above are fulfilled, we conclude that the initial density of the excitons created by the laser pulse (at time moment $t = 0$) could be assumed homogeneous.

After the excitation is over, the excitons start to move in the sample performing a random walk. The duration of this process is an intrinsic lifetime of the exciton in the bulk material. Finally the excitons decay either radiatively by emitting a photon or nonradiatively. Upon reaching an interface, the excitons can also be quenched. In the model the exciton migration in the material is described by the diffusion equation for the time and coordinate dependent exciton density function $n(\vec{r}, t)$.

8.2 Diffusion equation

Since the geometry of the problem is one dimensional we use the diffusion equation dependent only on the direction $x$ perpendicular to the surface of the sample.
Let \( n(x,t) \) be the coordinate and time dependent density of excitons function. The one dimensional exciton diffusion equation reads as follows

\[
\frac{\partial n}{\partial t} = -\frac{n}{\tau} + D \frac{\partial^2 n}{\partial x^2} + G(x,t) - S(x)n, \tag{8.1}
\]

where \( G(x,t) \) is the generation term, \( S(x) \) is the quenching term, and the parameters \( \tau \) and \( D \) denote the exciton lifetime and the diffusion coefficient, respectively.

Due to the fact that the femtosecond laser pulse creates the population of the excitons in the sample during the time interval much shorter than the exciton lifetime, and during which the excitons could not diffuse to a noticeable distance, the generation term can be dropped out from the equation and taken into account as the initial conditions. In the case when the exciton quenching occurs only at the interfaces we can also drop the quenching term in eq. 8.1 and thus obtain a reduced diffusion equation

\[
\frac{\partial n}{\partial t} + \frac{n}{\tau} = D \frac{\partial^2 n}{\partial x^2}. \tag{8.2}
\]

This equation, together with the initial condition and the boundary conditions, will be used hereinafter.

### 8.3 General solution

A partial solution of the reduced diffusion equation (eq. 8.2) has a form of the product of the coordinate dependent function \( X(x) \) and the time dependent function \( T(t) \):

\[
n_m(x,t) = X_m(x)T_m(t). \tag{8.3}
\]

According to the theory of partial differential equations the general solution of the eq. 8.2 is represented as a sum of the partial solutions

\[
n(x,t) = \sum_m n_m(x,t). \tag{8.4}
\]

The substitution of the partial solution eq. 8.3 into eq.8.2 leads to:

\[
\frac{T'(t)_m}{T(t)_m} + \frac{1}{\tau} = D \frac{X''(x)_m}{X(x)_m} = -\lambda_m^2,
\]

where \( \lambda_m \) are the eigenvalues of the problem. By introducing a new parameter \( \kappa_m^2 = \frac{\lambda_m^2}{D} \) and solving eq. 8.5 we obtain the explicit expressions for the \( X_m(x) \) and \( T_m(t) \) functions

\[
T_m(t) = \exp\left(-\left(\frac{1}{\tau} + D\kappa_m^2\right)t\right), \tag{8.6}
\]

\[
X_m(x) = A_m \sin(\kappa_m x) + B_m \cos(\kappa_m x), \tag{8.7}
\]

where \( A_m, B_m, \) and \( D_m \) are constants.
8.4 Initial condition and boundary conditions

In order to solve the diffusion equation we need to formulate the initial condition and the boundary conditions for the exciton density function \( n(x, t) \). Assuming the laser pulse populates the polymer film with the homogeneous density of the excitons we have the initial condition

\[
n(x, t = 0) = N_0 \text{ for } x \in (0, L).
\] (8.8)

In the case of a perfectly quenching interface the exciton density at the interface is equal to zero:

\[
n(x = x_{\text{interface}}, t) = 0,
\] (8.9)

and for an absolutely non-quenching interface the boundary condition is defined as follows

\[
\frac{\partial n(x = x_{\text{interface}}, t)}{\partial x} = 0.
\] (8.10)

Depending on the variation of the type of quenching on the top and the bottom interface, 3 limiting cases are possible:

1. none of the interfaces is quenching
2. one interface is quenching
3. two interfaces are quenching

We are going to construct the solutions of the diffusion equation for each single cases mentioned above.

8.5 Diffusion equation solution

8.5.1 Two non-quenching interfaces

In the case when both interfaces at \( x = 0 \) and at \( x = L \) are non-quenching the boundary conditions are as follows:

\[
X'_m(x = 0) = 0,
\] (8.11)
\[
X'_m(x = L) = 0.
\] (8.12)

This gives us a solution

\[
n(x, t) = N_0 \exp\left(-\frac{t}{\tau}\right),
\] (8.14)

or by integration over \( x \)

\[
n(0)(t) = N_0 L \exp\left(-\frac{t}{\tau}\right).
\] (8.15)

Analyzing eq. 8.16 we conclude that if the quenchers are absent, the time decay of the photoluminescence is mono-exponential with the time constant \( \tau \) that is equal to the photoluminescence decay time in the bulk. Time integration of 8.16 gives the number of photons emitted by the film:

\[
N(0) = N_0 L \tau,
\] (8.16)
8.5.2 One quenching interface

Assuming that the interface at \( x = L \) is quenching we have the boundary conditions:

\[
X'_m(x = 0) = 0, \quad (8.17)
\]

\[
X_m(x = L) = 0. \quad (8.18)
\]

The exciton density at the point \( x \) in the time moment \( t \) is determined by the following expression

\[
n(x, t) = \sum_{m=0}^{\infty} \frac{4N_0}{(2m + 1)\pi} (-1)^{m+1} \cos \left( \frac{\pi}{2L} (2m + 1)x \right) \exp \left[ -\left( \frac{1}{\tau} + \frac{D(2m + 1)^2\pi^2}{4L^2} \right) t \right]. \quad (8.19)
\]

Integration of eq. 8.19 over the film thickness gives the time dependence of the photoluminescence

\[
n(1)(t) = \sum_{m=0}^{\infty} \frac{8N_0}{(2m + 1)^2\pi^2} \frac{L}{\pi} \exp \left[ -\left( \frac{1}{\tau} + \frac{D(2m + 1)^2\pi^2}{4L^2} \right) t \right]. \quad (8.20)
\]

Integrating eq. 8.20 over time we get

\[
N_1 = N_0L\tau \left( 1 - \frac{\sqrt{\tau D}}{L} \tanh \left( \frac{L}{\sqrt{\tau D}} \right) \right). \quad (8.21)
\]

Thus, the introduction of the quenching interface leads to the multiexponential time decay and the overall decrease in photoluminescence intensity.

8.5.3 Two quenching interfaces

When both interfaces of the film are quenching, the boundary conditions are as follows

\[
X_m(x = 0) = 0, \quad (8.22)
\]

\[
X_m(x = L) = 0. \quad (8.23)
\]

The exciton density at the point \( x \) in the time moment \( t \) is determined by the following expression

\[
n(x, t) = \sum_{k=0}^{\infty} \frac{4N_0}{(2k + 1)\pi} \sin \left( \frac{(2k + 1)\pi}{L} (2k + 1)x \right) \exp \left[ -\left( \frac{1}{\tau} + \frac{D(2k + 1)^2\pi^2}{L^2} \right) t \right]. \quad (8.24)
\]

Integration over the thickness yields in time dependence

\[
n(2)(t) = \sum_{k=0}^{\infty} \frac{8N_0}{(2k + 1)^2\pi^2} \frac{L}{\pi} \exp \left[ -\left( \frac{1}{\tau} + \frac{D(2k + 1)^2\pi^2}{L^2} \right) t \right]. \quad (8.25)
\]

The number of the photons emitted is determined by

\[
N(2) = N_0L\tau \left( 1 - \frac{2\sqrt{\tau D}}{L} \tanh \left( \frac{L}{2\sqrt{\tau D}} \right) \right). \quad (8.26)
\]
8.6 Quenching efficiency

The relative quenching efficiency for a film is defined as unity minus the ratio of the number of the photons emitted by the film to the number of the photons emitted by the non-quenching film of the same thickness[36].

\[ Q = 1 - \frac{\int_0^L \int_0^\infty n(x,t) dx \, dt}{\int_0^L \int_0^\infty n_{\text{non-quenching}}(x,t) dx \, dt}, \quad (8.27) \]

For a film without quenchers \( Q = 0 \). In the case of one or two quenching interfaces we have:

\[ Q_{1,2} = 1 - \frac{N_{(1),(2)}(L)}{N_{(0)}(L)}, \quad (8.28) \]

The substitution of eqs. 8.21 and 8.26 into eq.8.27 yields in the expressions for one quenching interface and two quenching interfaces respectively [37]:

\[ Q_1(L, L_D) = \frac{L_D}{L} \tanh \frac{L}{L_D}, \quad (8.29) \]

\[ Q_2(L, L_D) = \frac{2L_D}{L} \tanh \frac{L}{2L_D}. \quad (8.30) \]

In both cases the only fitting parameter is the diffusion length \( L_D = \sqrt{\tau D} \).

There is another way to obtain the expressions 8.29 and 8.30. If we consider the PL decay profiles normalized in such a way that \( n(t = 0) = 1 \), the normalization of eqs. 8.16, 8.20, and 8.25 is equivalent to the substitution \( N_0 = 1/L \). The usage of the normalized time decay profiles allows to overcome the experimental problems with the measurement of the absolute values of light intensity. As well instead of hypothetical non-quenching reference sample with the same thickness \( L \) it is possible to use a thick drop-cast sample for which the influence of the interfaces is eliminated. The quenching determined from the experimental time resolved spectroscopy data is calculated according to the following expression:

\[ Q(L) = 1 - \frac{\int_0^\infty n_{\text{normalized}}(t) \, dt}{\int_0^\infty n_{\text{dropcast}}(t) \, dt}, \quad (8.31) \]
Chapter 9

Experimental

9.1 Materials and fabrication

Photophysical properties of the polymers PCPDTBT and Si-PCPDTBT with the chemical structures shown in Fig. 9.1 were investigated. The only structural difference between two polymers is the silicon bridge in Si-PCPDTBT instead of the carbon bridge in PCPDTBT.

Figure 9.1. Chemical structures of (a) PCPDTBT polymer (poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b’]-dithiophene)-alt-4,7-(2,1,3-b-(2,1,3-benzothiadiazole)) and (b) Si-PCPDTBT polymer (poly[(4,4'-bis(2-ethylhexyl)dithieno[3,2-b;2',3'-d]silole)-2,6-diyl-alt-(4,7-bis(2-thienyl)-2,1,3-benzothiadiazol-2-thienyl)-2,1,3-benzothiadiazole)-5,5’diyl] (c).

The solution of PCPDTBT polymer in chlorobenzene with the concentration of 10 mg/ml was prepared. In contrast to PCPDTBT, Si-PCPDTBT showed lower solubility in chlorobenzene and could only be dissolved at 90°C in ortho-dichlorobenzene, which is a stronger solvent. The solutions were filtered with 5µm PTFE filters. The solution of the fullerene derivative F2D with the concentration of 10mg/ml was prepared.

Quartz substrates with the roughness below 1nm purchased from Valley Design Corp.
were used. The F2D layer was spincast from the solution onto a quartz substrate. An F2D molecule is equipped with the side chains containing diacetylene moieties that are able to polymerize (see Fig. 9.1(c)), the crosslinking reaction occurs at 250°C and results in completely insoluble in chlorobenzene or ortho-dichlorobenzene film of poly(F2D) [31]. The F2D films were annealed on a hot plate at 270°C during 30 min resulting in a poly(F2D) film of 10-15 nm thickness. Neat polymer films of PCPDTBT and Si-PCPDTBT of various thicknesses in the range of 5-90 nm were spincast on top of the polymerized fullerene layer or on top of the quartz substrate. All the fabrication steps described above were performed in the water and oxygen free glovebox kept under nitrogen atmosphere.

9.2 Spectroscopy

The time resolved photoluminescence experiments were performed on the samples mounted into the cryostat for optical measurements. The mounting procedure was done in the nitrogen atmosphere in order to prevent the contact of the samples with the air and their oxidation. The cryostat was pumped to high vacuum ($1.510^{-6}$ mbar). The samples were excited by a 20MHz train of 150fs laser pulses delivered by the first harmonic of Ti:sapphire laser (765 nm). Photoluminescence decays were measured using a Hamamatsu streak camera operating in a synchroscan mode. The steady state photoluminescence spectra were measured by a Hamamatsu CCD detector. The excitation power was varied in the range from 19 to 100µW.

Spectroscopy in the solution was performed in the 1mm thick cuvettes using the same excitation parameters as for the thin film samples. Solutions were diluted up to the concentrations as low as 0.01mg/ml.

Steady state absorption spectra were acquired using Perkin Elmer Lambda 900 absorption spectrometer. During the absorption measurements the samples were kept in nitrogen in order to prevent photooxidation.

9.3 AFM and thickness measurements

Atomic force microscopy was performed using Digital Instruments - Veeco Nanoscope IV Multimode AFM setup. The images were acquired in the tapping mode. Budget Sensors Tap 300-G AFM tips with the resonance frequency 300 kHz and the force constant of 40N/m were used.

In order to measure the film thickness, the samples were scratched with a blade and the AFM scan performed in the scratch area. The film thickness was extracted from the AFM image profiles.
Chapter 10

Results and discussions

10.1 Morphology

The roughness of the samples for the exciton diffusion length measurement must be as minimal as possible in order to reduce the experimental error. The values of the polymer film RMS (root mean square) roughness below 1 nm are desirable.

In order to reduce the roughness of the spin cast films, specially polished quartz substrates with the roughness below 1 nm were used. The roughness of 10nm thick (poly)F2D layer was of the order of the roughness of the substrate.

The AFM scans performed on the polymer layers revealed the roughness of the order of 2nm for PCPDTBT and of the order of 4nm for Si-PCPDTBT for the films having the thicknesses in the range of 5-80 nm. The AFM images of the polymer layer surfaces are represented in Fig. 10.1.

![AFM images of polymer layer surfaces](image)

Figure 10.1. Typical morphology of the surface of PCPDTBT polymer film (a) and Si-PCPDTBT polymer film (b).

The roughness of PCPDTBT films is still acceptable for the method however the roughness of the Si-PCPDTBT is quite high and makes the results of the photoluminescence quenching experiments for the films below 10 nm unreliable. High values of the roughness

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1 All the roughness values presented in this section are mentioned for the 10 × 10µm scan area
could be attributed to the large number of the pinholes in the film as well as to the crystallinity of Si-PCPDTBT. The attempts to further improve the morphology of the silole bridged polymer films by varying the spincoating program parameters or by spincoating on a hot substrate did not succeed.

10.2 Steady state spectra

Typical absorption and steady state photoluminescence spectra for the films of PCPDTBT and Si-PCPDTBT polymers are shown in Fig. 10.2. The maxima of the absorption spectra for both materials are around 770nm. The photoluminescence of the films was excited close to the absorption maxima by the laser radiation of 780 nm. The photoluminescence spectra are red shifted with respect to the absorption spectra. The photoluminescence peaks are around 900 nm for both compounds.

![Figure 10.2. Photoluminescence and absorption spectra of PCPDTBT (a) and Si-PCPDTBT (b).](image)

Different from the experiments on the thin films of the PPV (poly(p-phenylene vinylene)) polymer [37], no systematic shift of the absorption or photoluminescence spectra for PCPDTBT and Si-PCPDTBT has been observed. This means that the spectral shift with the thickness is either absent or is below the resolution of the experimental methods used. The peculiarities of PCPDTBT and Si-PCPDTBT are high absorption and low photoluminescence intensity. The spectral resolution of the absorption spectroscopy was low for the thick films (30-80 nm) due to almost zero transmission of the samples in a wide spectral range. During the photoluminescence experiments the intensity of the signal from the samples was weak. In order to reduce the noise level and gain in the collected intensity the entrance slit of the detector was widely open leading to a drop down in the spectral resolution.

10.3 Time resolved photoluminescence experiments

Time resolved spectroscopy was performed on the diluted solutions, neat polymer films, and polymer-fullerene heterostructures of PCPDTBT and Si-PCPDTBT polymers. The
time decay profiles were obtained by the integration of the time resolved spectra over all the emission spectrum.

The experiments on the photoluminescence of the solution of the PCPDTBT solution in chlorobenzene with the concentration of 0.05 mg/ml revealed monoexponential decay with the time constant of 202 ps. The photoluminescence decay time of Si-PCPDTBT dissolved in ortho-dichlorobenzene at the same concentration was significantly longer and equal to 584 ps. No change in the lifetimes was observed upon further dilution. The photoluminescence decay profiles for the solutions of the diluted solutions of low band gap polymers are shown in Fig. 10.3.

Figure 10.3. PL decay profiles of the diluted (0.05 mg/ml) solutions of PCPDTB and Si-PCPDTB polymers

Figure 10.4. PL decays of the neat polymer films (a) and heterostructures (b) of PCPDTBT polymer for various thickness.

Photoluminescence decay curves obtained by the integration over all the emission spec-
trum for neat polymer films and heterostructures with various thicknesses of the polymer layer are represented in Fig. 10.4 (a) for PCPDTBT polymer and in Fig. 10.5(a) for the Si-PCPDTBT polymer.

![Figure 10.4](image)

Figure 10.4. PL decays of the neat films and heterostructures of PCPDTBT polymer for various thickness.

![Figure 10.5](image)

Figure 10.5. PL decays of the neat films (a) and heterostructures (b) of Si-PCPDTBT polymer for various thickness.

![Figure 10.6](image)

Figure 10.6. Thickness dependence of the PL decay time in PCPDTBT polymer films and heterostructures (a) and Si-PCPDTBT polymer films and heterostructures (b).

Thinner films exhibited shorter decay times. The photoluminescence decay times of PCPDTBT varied from 150 ps for 80 nm thick sample to 70 ps for 5 nm thick sample. For Si-PCPDTBT the values of the decay time varied from 323 ps for the 49 nm sample to 66 ps for the 10 nm sample. The decay times for the dropcast samples were 186 ps for PCPDTBT and 305 ps for Si-PCPDTBT. The increase in the photoluminescence lifetime for the ultrathin samples with the thickness below 10 nm compared to the samples of the 10nm thickness could be explained by the high roughness of the films. The results of the experiments on the films with thicknesses below 10 nm are not reliable.
The photoluminescence decay profiles for the heterostructures with the fullerene quenching layer are shown in Fig.10.4(b) for PCPDTBT polymer and in Fig.10.5(b) for the Si-PCPDTBT polymer. The heterostructures with 10nm F2D layer showed the photoluminescence with approximately the same lifetimes as the neat polymer films of the same thickness.
10.4 Quenching efficiency and the exciton diffusion length

In order to calculate the exciton diffusion length in the materials the model for the exciton diffusion with the interface quenching described in Chapter 8 was applied. Normalized PL decay profiles were fitted with the exponential decay functions. Relative quenching efficiencies with respect to thick dropcast sample were estimated according to eq. 8.31.

The precision of the method is strongly limited by high values of the polymer films roughness (of the order of 2 nm for PCPDTBT and 4 nm for Si-PCPDTBT). Time resolution of the streak camera (about 5ps) also contributes to the experimental error.

The thickness dependences of the photoluminescence quenching efficiency calculated from the photoluminescence decays of the PCPDTBT and Si-PCPDTBT samples are represented in Figs. 10.7 and 10.8 respectively. The photoluminescence is quenched more efficiently in thinner films. This leads to the conclusion that the photoluminescence quenching in the samples is a surface dependent phenomenon.

![Graphs showing quenching efficiency vs. polymer film thickness]

Figure 10.7. Experimental data on the thickness dependence of quenching efficiency and the best fit for (a) pristine polymer films and (b) heterostructures of PCPDTBT polymer.

No additional quenching was observed for the heterostructures with fullerenes with respect to the neat polymer films of the same thickness. Possible explanations to this could be the following:

1. The photoluminescence quenching due to the electron transfer from the PCPDTBT and Si-PCPDTBT polymers to the polymerized F2D layer indeed does not occur, which is in contradiction with the results on high performances of the polymer-PCBM solar cells.
2. The fullerene layer was too thin to quench the luminescence efficiently
3. The polymer-substrate interface unlike in the experiments with PPV [37] is already quenching without the fullerenes

In order to answer the question why the additional quenching in the heterostructures was not observed, further experiments should be performed. However, if the polymer-substrate interface for some reason is already good exciton quencher, then we can apply
the model with one quenching interface even for the measured data to extract the exciton diffusion length. Thus we obtain the values of 4 and 7 nm for the carbon and silicon bridged polymers, respectively. The reason for such a quenching could be interactions with OH groups, which are always present on the quartz substrates after the cleaning procedure.

Recently, it has been reported that the free interface can act as exciton quencher in PPV [37]. Although we have not seen the experimental evidences that the studied materials also have quenching polymer-vacuum interface, we provide the modeling of the data, which accounts two quenching interfaces. In this case the numbers are twice smaller than for the case of one quenching interface, 2 and 3.5 nm for carbon and silicon bridged polymers, respectively.

Thus, if we assume that excitons get efficiently quenched at the polymer-substrate interface, then the exciton diffusion length in the studied materials would be between 2 and 4 nm for the carbon bridged, between 3.5 and 7 for silicon bridged polymers. Those values are typical for conjugated polymers. In this case the superior performance of the studied materials in solar cells can not be explained by unusually large exciton diffusion length.
Chapter 11

Conclusions

The time-resolved photoluminescence experiments performed on thin neat polymer films of PCPDTBT and Si-PCPDTBT show strong dependence of the photoluminescence decay time on the film thickness. The fit with the theoretical model of the exciton quenching at one interface results in the exciton diffusion lengths of 4 nm for PCPDTBT and 7 nm for Si-PCPDTBT.

The experiments on the heterostructures with 10 nm of the crosslinkable fullerene layer showed no photoluminescence quenching by the fullerenes. The reason to this is still unclear, and in order to elucidate it, more experiments are needed.
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Bibliography


