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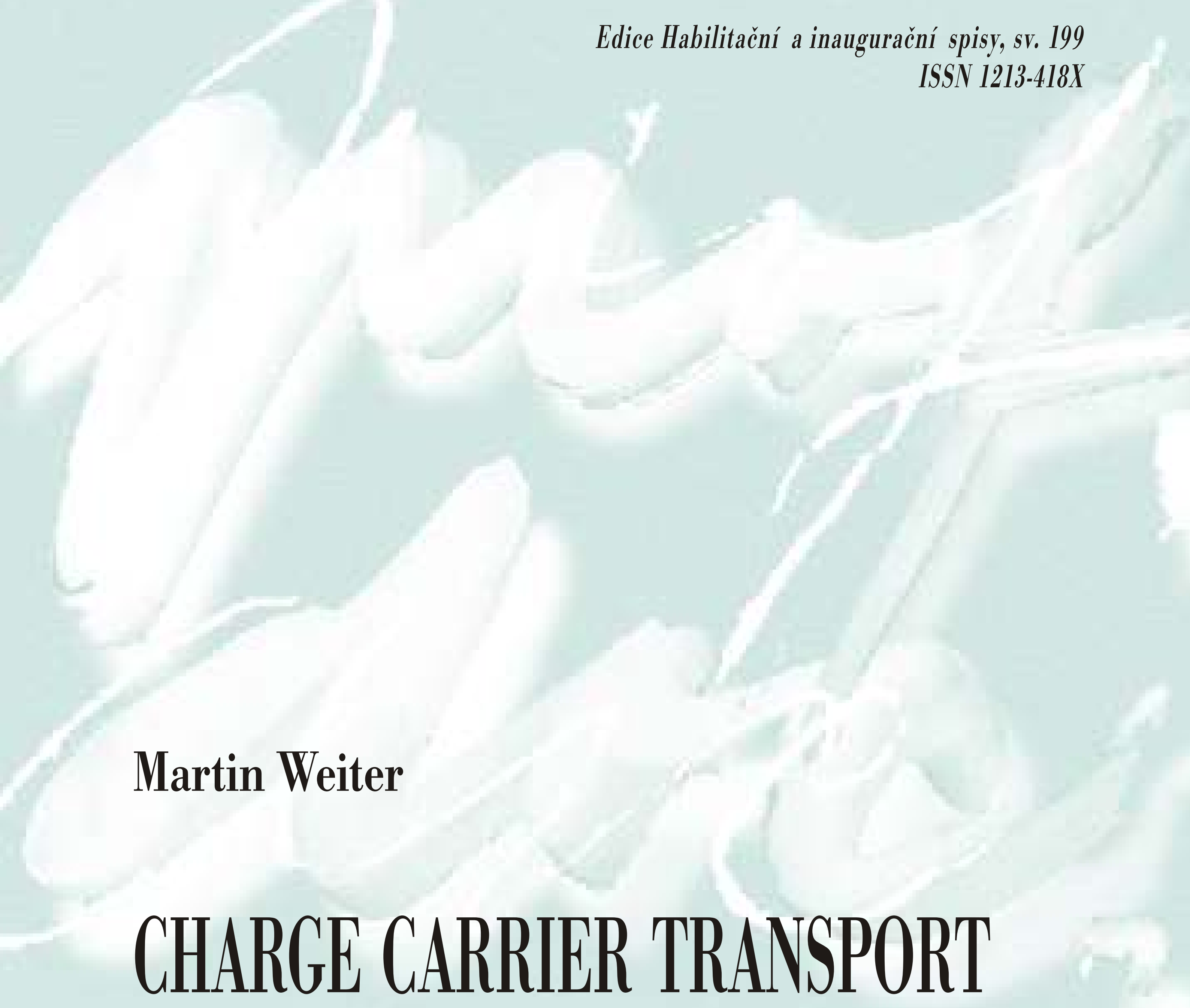

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CHARGE CARRIER TRANSPORT AND PHOTOGENERATION IN DISORDERED ORGANIC SEMICONDUCTORS

BRNO UNIVERSITY OF TECHNOLOGY
Faculty of Chemistry
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Charge carrier transport and photogeneration in disordered organic semiconductors

Transport nosičů náboje a fotogenerace v neuspořádaných organických polovodičích

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V Brně dne 7. listopadu 2005

1 INTRODUCTION

Submitted thesis contains a 11 articles published in recognized international scientific journals with average impact factor 1.24 and two articles accepted for publication. The articles have been published since 1996, but most of them (9 papers) have been published during the last two years. In spite of short time elapsed from their publication a citation response to some of them was notified. In this short version of habilitation thesis a considerable results published in the papers are summarized.

All the submitted papers discuss optoelectronic properties of organic disordered semiconductors in general, the charge carrier transport and photogeneration in particular. Organic semiconductors have attracted much attention over the past fifteen years for their potential applications in optoelectronic devices like large area flat displays, photodetectors, solar cells and transistors. Short review of state of the art in the field of organic semiconductors is given in Chapter 2. In Faculty of Chemistry we have been studying organic semiconductors since 1995 when we focused on preparation and characterization of polysilylenes. Polysilylenes are well known as quasi-one-dimensional Si-backbone polymers with alkyl or aryl groups as side chains. They have attracted much attention, because they exhibit various interesting properties, e.g. photoconductivity, relatively large hole mobility, thermochromism and large non-linear optical effects. The results of my work from this period are summarized in Chapter 4.3. The year 2002 can be regarded as turning point in organic semiconductor research at our faculty because of the two following reasons. At first the research group investigating polysilylenes was reorganized. The second impulse was my nine months stay at Phillips University in Marburg, Germany in the framework of European research project LAMINATE (Large Area Molecular-electronics). Participation in this project gave me the opportunity to collaborate with excellent European research teams. After my return back we succeeded in establishing working group that has concentrated on polymeric semiconductors and other intelligent responsible organic materials. Nowadays our working group consists of four research academic workers, three PhD. students and four diploma and bachelor students.

Articles included in habilitation thesis have predominantly experimental character and contain the result of research implemented at Brno University of Technology, Faculty of Chemistry and also partially during my stay at Phillips University in Marburg. Articles with the significant portion of author work were selected for this thesis. Nevertheless, a majority of the research results published in these articles could not be realized without strong cooperation of the author with cooperating institutions, e.g. Institute of Macromolecular Chemistry in Prague, Phillips University in Marburg, Germany, Wroclaw University of Technology in Poland and many others, which is reflected in the list of co-authors of proposed articles and is also consistent with the fact, that modern research requires collaboration and teamwork.

2 ORGANIC SEMICONDUCTORS

2.1 THE DAWN OF ORGANIC ELECTRONICS

Organic materials are poised as never before to transform the world of circuit and display technology. Nowadays various polymers and polymer composites are used in xerography and laser printers, electroluminescent diodes and flat displays, the functional polymers are applied even in the logical circuits, which give rise to a new branch – ‘Plastic Logic’. Using organic light-emitting devices (OLEDs), organic full-color displays may replace liquid-crystal displays (LCDs) for use with laptop and even desktop computers. Such displays can be deposited on flexible plastic foils eliminating the fragile and heavy glass substrates used in LCDs, and can emit bright light without the pronounced directionality inherent in LCD viewing, all with efficiencies higher than can be obtained with incandescent light bulbs. New polymer materials are able not only to substitute the expensive crystalline semiconductors in these devices, but their specific properties originate the principle new devices and technologies.

Organic electronics are already entering the commercial world. Major electronics firms such as Philips and Pioneer, and smaller companies such as Cambridge Display Technology, Universal Display, and Uniax, are developing the low cost and sometimes surprisingly high performance organic electronic and optoelectronic devices. Large-scale multicolor displays together with organic flexible integrated circuits are now commercially available. It is possible that soon, portable and lightweight roll-up OLED displays will cover our walls, replacing the bulky and power-hungry cathode ray tube that has been the television standard for 50 years. Given the need for very low-cost (but not always high-performance) circuits for everything from smart cards carrying personal information, to building entry cards, to inventory control, it is reasonable to assume that within 10 years, the square footage of organic circuitry might exceed that of silicon electronics, though one expects that silicon transistors would still vastly outnumber and outperform those fabricated from organic materials [1].

Organic semiconductors have been the subjects of scientific investigation for the past 50 years. During most of that time, these materials were considered to be merely a scientific curiosity. Traditionally, the study of semiconducting organic materials focused on small organic molecules in the crystalline state. Several molecular crystals like naphthalene and anthracene were found to display the semiconducting properties known from their inorganic counterparts [2, 3]. For example, photoconductivity in organic crystals [4, 5] and electroluminescent devices based on anthracene crystals [6] have been demonstrated in the early 1960s. However, due to their poor semiconducting characteristics, organics were mostly considered as materials with little potential for applications. The first highly conducting organic polymer, chemically doped polyacetylene, was reported in 1977 [7]. Although initially these doped conducting polymers were unstable in air, brittle, and difficult to process, new generations of these materials are stable and easily processable from a wide variety of solvents. The electrical conductivities now range from those typical for insulators ($< 10^{-10}$ S/cm), to those typical of semiconductors such as silicon ($\sim 10^{-5}$ S/cm), to those greater than 10^4 S/cm (nearly that of copper, $5 \cdot 10^5$ S/cm) [8]. Applications of these polymers, especially polyanilines, have begun to emerge. These include coatings and blends for electrostatic dissipation and electromagnetic-interference shielding, conductive layers for opto-electronic polymer devices, and anticorrosion coatings for iron and steel [9].

The interest in undoped organic semiconductors, both polymers and small molecules, revived at the end of the 1980s. Poly(phenylenevinylene) (PPV) has been one of the most studied polymers at this time. This intense research led to the discovery of the polymer-based light emitting diode (LED) [10] in 1990 by the Cambridge group in England. At the same period the high-performance electroluminescent devices made of multilayer of vacuum-sublimed dye films at Eastman Kodak [11], field-effect transistors made from polythiophene [12, 13] and from small conjugated oligomers [14, 15] were demonstrated. This was a breakthrough improvement since it made it possible to combine the good mechanical and processing properties of polymers with semiconducting behavior (providing processibility under well established techniques, such as spin or dip coating). From that time, the potential use of the organic semiconductors for the construction of optoelectronic devices has stimulated considerable interest. Most of the materials currently used in electroluminescent diodes or in photocopying machines are now commercially available from different suppliers, for different quantities and qualities (Covion, Syntec, American Dyes, H.W. Sands, Sigma Aldrich, …). A number of reviews on organic semiconductors focusing the basic physics [16–20], synthesis and properties [21,22], device operation and materials [23–26] and also general reviews [27], polymer specific reviews [28] and molecular engineering review [29] have been published. Detailed reviews can be also found in scientific books [30–37].

In spite of great progress that has been made, there is still much to be understood about the underlying science that controls the properties of the organic electronic devices. Organic materials have often proved to be unstable and when exposed to air, water, or ultraviolet light, their electronic properties can degrade rapidly. Making reliable electrical contacts to organic thin films is difficult and the metal-polymer interface is a matter of intensive study [38–40]. The low carrier mobilities characteristic of organic materials [41, 42] obviates their use in high-frequency (greater than 10 MHz) applications. These shortcomings are compounded by the difficulty of both purifying and doping the materials. Finally, in many types of organic semiconductors, the processes connected with the photogeneration and transport of charge carriers under the influence to electric field are still not well understood and are open to conjecture. The better understanding of these basic phenomena can enhance speed and efficiency of organic electronic devices, which is the fundamental motivation for our work. Before discussing the results, let us first discuss some basic physical aspects of organic semiconductors.

2.2 ELECTRONIC STRUCTURE

In *inorganic semiconductors* the morphology and electronic structure is generally characterized by their strong covalent and ionic bonding between atoms in the lattice. Bloch's theorem is a direct consequence of the periodicity and describes the electrons and holes by wavefunctions which are extended in space with quantum states defined by the momentum. The absence of the ordered atomic structure in *organic semiconductors* necessitates a different theoretical approach. The description of these materials is developed from the chemical bonding between the atoms instead, with emphasizes on the short range bonding interaction rather than the long range order. In inorganic semiconductors the charge transport can easily take place through a strong exchange interaction of overlap atomic orbitals in closed-packed structure, whereas in organic semiconductors the bonding between molecules is mainly due to Van der Waals forces and is therefore rather week, and also the overlap of molecular electron exchange is small. This implies the transport bands in molecular solid, i.e. valence and conduction bands are narrow. Typical bandwidths range from 10 to 100 meV [3, 35]. As a consequence, the mean free paths of charge carriers are of order of the lattice spacing. This renders coherence effects in transport unimportant except at low temperatures. Another consequence of weak intermolecular interactions is a relatively easy formation of disordered structures, giving rise to formation of electronic localized states in the band gap, capable of localizing charge carriers. The transport of carriers via localized states (hopping) predominates over the transport in the bands. The low relative permittivity, which is a consequence of the molecules retaining their electronic identity, leads to coulombic effects being important. Typical values for an organic solid are 3 to 4 compared, for instance, with 11 for silicon.

Polymers, oligomers, dendrimers, dyes, pigments, liquid crystals, organo-mineral hybrid materials, all organic semiconductors share in common part of their electronic structure. It is based on conjugated π electrons. By definition, a conjugated system is made of an alternation between single and double bonds. The essential property which comes out from conjugation is that the π electrons are much more mobile than the σ electrons; they can jump from site to site between carbon atoms with a low potential energy barrier as compared to the ionisation potential. The π electron system has all the essential electronic features of organic materials: light absorption and emission, charge generation and transport.

Electronic properties of polymers can be described in terms of semiconductor physics [43]. The particular framework of one dimensional periodic media is well suited to the basic understanding of an isolated polymer chain [44]. Polymers are bonded by strong covalent bonds. As π-orbitals overlap is weaker than σ-orbitals overlap, the energy spacing (band gap) between bounding and antibounding molecular orbitals is larger for the π–π^* difference than for the σ –σ^* one. One can thus, in a first approach, limit the band study to the π–π^* molecular orbitals. Those are respectively the HOMO (for Highest Occupied Molecular Orbital) and LUMO (for Lowest Unoccupied Molecular Orbital), in terms of molecular physics. They are also the usual valance (VB) and conduction bands (CB) of semiconductor physics, respectively. The simplified energy band model of an organic semiconductor is presented in Fig. 2.1.

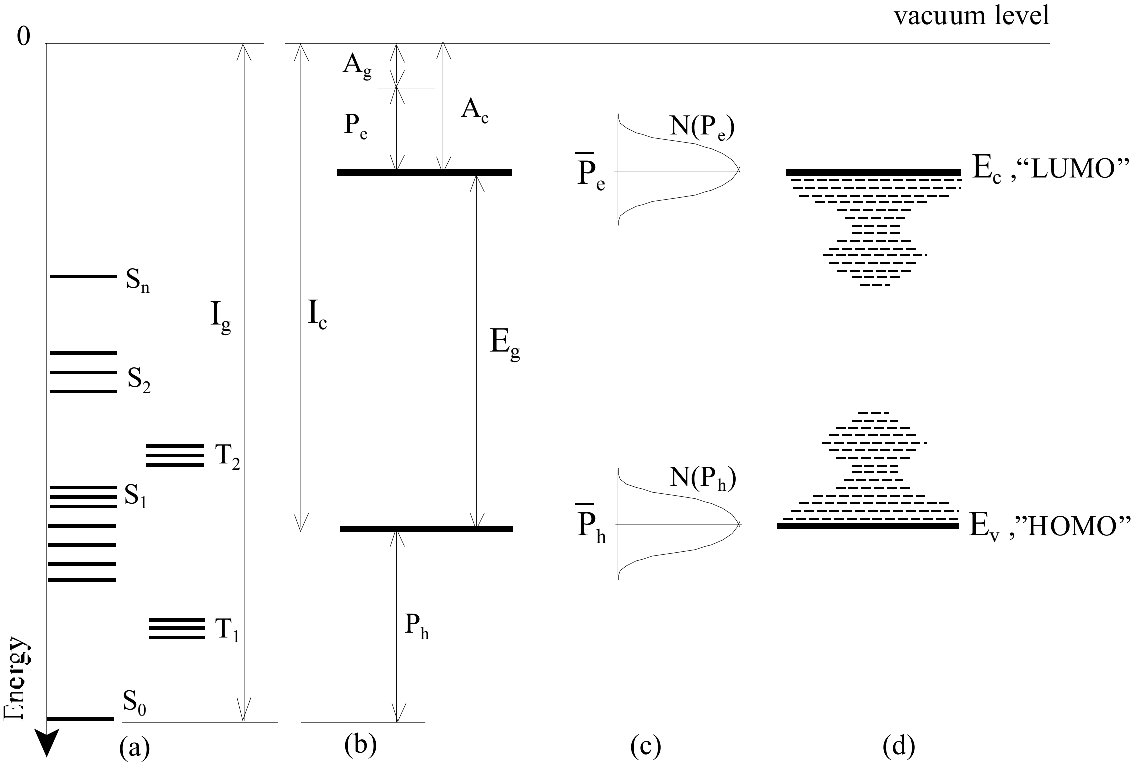

Fig. 2.1 *A simplified scheme of energy levels in (a) an isolated molecule and a solid (b)-(d). Vibrational levels associated with the ground state and with excited singlet (S) and triplet (T) states of a molecule (a) have not been shown in (b) for clarity. A and I denote the electron affinities and ionization energies, respectively; the subscript g and c refer to the isolated molecular and condensed phase, respectively;* P_e *and* P_h *is energy of electronic polarization of the solid by electron and hole, respectively.*

On the left side of the figure (part a) an energetic scheme of an isolated molecule is shown. It consists of vibrational levels of Rydberg serie associated with the ground state and with excited singlet and triplet states of the molecule. The ground state level is determined by the ionization potential I_g of the molecule. An energetic scheme of the solid polymers is depicted in Fig. 2.1 (b-d). In a solid polymers the energy levels are shifted, since the ionization potentials I_c of the solid differ from I_g by the electronic polarization energy of holes P_h. The position of the valence band, associated with I_c , can be located by a photoelectron or photoemission spectroscopy. Typical values for the ionization potential I_c are between 5 and 6 eV. The location of the conduction band as well as the band gap E_g is not amenable to direct optical probing. A useful estimate is, however, provided by the approximate relation $E_g=I_g - A_g -(P_h+P_e)$, where A_g is the ionization energy and electron affinity in the gas phase, respectively, and the P_e and P_h is the electronic polarization energies of a positive and a negative charge carrier in the solid. While P_h is the difference between the ionization energy in the gas phase and solid, respectively, P_e cannot be measured directly but has to be calculated. The zero-order approximation $P_h=P_e$ gives a typically value about 1.3 eV.

In real molecular solids there are a lot of irregularities which rise from defects in the structure. Therefore, the polarization energies are dispersed, the situation is shown in Fig. 2.1 (c). The dispersion of polarization energies influence the energetic distribution of electron states (see Fig. 2.1(d)), which can be described by Gaussian distribution:

$$g(E) = \frac{N_\mathrm{t}}{\sigma\sqrt{2\pi}} \exp\left\{-\frac{(E-E_\mathrm{t})^2}{2\sigma^2}\right\}, \tag{2.1}$$

where E is the energy, N_t is the concentration of localized states, E_t is the energetic position and σ is the energy width (mean square value) of the Gaussian distribution.

2.3 CHARGE TRANSPORT

Charge carrier transport in organic semiconductor materials – where electronic transfer integrals are expected to be small, electron-phonon coupling strong, and scattering of charge carriers very efficient – is an important topic. Understanding of the basic transport mechanisms in this special class of electronic materials is not only of fundamental academic interest, but also bears great technical relevance in that more professional knowledge may help to increase transport efficiency with the consequences of increased device speed, reduced power loss and avoidance of excessive heating in organic electronic devices. Electronic transport is described by the (local) electric field-induced directional velocity component, $\langle \boldsymbol{v} \rangle$, of the mobile charge carriers, which is associated with a current density $\boldsymbol{j}$:

$$\boldsymbol{j} = \mathrm{e}n\langle \boldsymbol{v} \rangle \tag{2.2}$$

where e is the electronic charge unit and n the local charge carrier density. The latter can be altered (in principle) by doping, injection, or photo-generation. The relation between $\langle \boldsymbol{v} \rangle$ and the applied electric field $\boldsymbol{E}$ is usually linear for not too high fields (reflecting Ohm's law):

$$\langle \boldsymbol{v} \rangle = \mu \boldsymbol{E} \tag{2.3}$$

and it is obvious that μ, the charge carrier mobility, is the fundamental electronic transport quantity that is specific of a given semiconductor material.

The low coupling between the molecules in the solid state ensures that the carriers in these materials are strongly localized on a molecule. From the simplified point of view, transport occurs via a sequence of charge transfer steps from one molecule to another. To describe the transport, several basic theories of electronic transport have been suggested [2, 36], the most important are one-dimensional band transport model of quasi-free charge carriers and variety of one-dimensional polaron-band and polaron-hopping models with different kind and degree of electron–phonon coupling. For typical hopping transport, mobility should be thermally activated in one or another way, for typical band transport, in contrast, mobility should be ‘‘thermally deactivated’’, e.g. decrease with rising temperature.

Nevertheless, in a great number of polymeric organic materials the contemporary theory of conduction is based on the assumption that due to weak intermolecular interaction, charge carriers are strongly localized and the variable *range hopping* is the dominant charge transport mechanism [45]. According to this theory charge transport occurs by thermally activated hopping through a manifold of localized states with a Miller-Abrahams asymmetric hopping probability ν_{ij} [46]:

$$\nu_{\mathrm{ij}} = \nu_0 \exp\left(-2\gamma a \frac{\Delta R_{\mathrm{ij}}}{a}\right) \exp\left(\frac{-E_{\mathrm{p}}}{2kT}\right) \times \left\{ \begin{matrix} \exp\left[-\left(\frac{E_{\mathrm{j}} - E_{\mathrm{i}}}{kT}\right)\right]; & E_{\mathrm{j}} > E_{\mathrm{i}} \\ 1; & E_{\mathrm{j}} < E_{\mathrm{i}} \end{matrix} \right\}. \qquad (2.4)$$

In Eq. (2.4), ν_0 is a frequency prefactor, γ an inverse wave function decay constant, a the average lattice constant, R_{ij} the intersite distance between sites i and j and E_{p} is the polaron binding energy. By virtue of the intermolecular nature of the structural distortion, E_{p} is a well-defined energy, specific for a given transport molecule. The concept of variable-range hopping suggests that the rate-limiting step in charge transport is jumps of equilibrated carriers, occupying deeper states, to shallower sites that play a role of transport states. According to the Miller–Abrahams equation (2.4), the carrier jump rate strongly decreases with increasing both the distance and energy difference between starting and target sites. A combination of the distance and energy difference, that provides the highest jump rate, is determined by the temperature, the carrier localization radius $1/\gamma$, and the shape of the electron density of states (DOS) distribution. Transport energy of hopping in Gaussian density of state distribution was studied by Hartenstein and Bässler [47], [48] by Monte-Carlo simulation techniques. In the case of weak intersite coupling relevant for organic systems it was found that there is a broad distribution of transport energy values and that its maximum decreases with decreasing temperature in qualitative agreement with the concept of variable-range hopping. Both Monte-Carlo simulation and analytic consideration have shown that a carrier will most probably jump from a currently occupied state to a hopping site that belongs to the so-called *effective transport level* of the energy E_{tr} [49]. Latterly, a model of hopping charge carrier transport in a doped disordered organic semiconductor [50] was suggested by Arkhipov. It is shown that the doping efficiency can be high in such materials even if the activation energy for dopant formation is comparatively large.

The canonical technique for determining the charge transport properties of photoconductors is the *time-of-flight technique*. In this technique, a flash of light generates a sheet of charge carriers close to one electrode of a parallel plate capacitor. Under an applied electric field E, the carriers move to the opposite electrode. The transit time t_{t} at which the carriers reach this electrode at distance L is then a direct measure of the carrier mobility

$$\mu = \frac{L}{t_{\mathrm{t}} F}. \qquad (2.5)$$

A problem with disordered materials is that the photocurrent transients are often dispersive, i.e., the velocity of the sheet of carriers decreases as the sample is traversed. In that case the mean arrival time of the carriers, and consequently the carrier mobility, depends on the dimensions of the sample and the mobility does not respect a genuine material parameter. Time-of-flight studies of disordered organic semiconductors show both dispersive and nondispersive transients, depending on, e.g., chemical purity, layer thickness or temperature (see e.g. [41] for review).

2.4 PHOTOGENERATION OF CHARGE CARRIERS

In *inorganic semiconductors*, the photogeneration of charge involves the excitation of an electron from the valence band into the conduction band. Due to the delocalized nature of the electronic states and screening efects, the Coulomb interaction within the resulting electron-hole pair is weak and the carriers are either free or form very weakly bound excitons of the Mott-Wannier type [51]. In *molecular systems*, the primary optical excitations are localized on a single molecule. Due to this fact, and due to the low dielectric constant in organics, the Coulomb interaction between the electron in the LUMO and the hole in the HOMO is strong and the exciton is of the Frenkel type. Since the HOMO and LUMO vary for different molecules, the excitons may relax in the course of a random walk to molecules where the energy is low, this process is known as spectral diffusion. This results in a red shift of the emission spectrum with respect to the absorption spectrum.

The binding energy of an optical excitation, E_{exc}, is a key parameter for the understanding of the opto-electronic properties of organic solids in general and of organic semoconductors in particular [52, 53]. It determines the energy of the dissociation of an excitation of either singlet or triplet character into a pair of free charges and the reverse process, that is, the recombination of an electron–hole pair yielding an excitation which can decay radiatively or non-radiatively. If E_{exc} is large, photogeneration of charge carriers is an endothermic, i.e. inefficient process. Obviously, in a photovoltaic device, one would like E_{exc} to be as small as possible, whereas in a light emitting diode (LED) it is the opposite. E_{exc} also determines whether conjugated polymers behave more like inorganic quasi-one-dimensional semiconductors or, rather like organic solids [3, 54].

In *conjugated polymers*, the π-conjugated system extends over the whole polymer chain, thus allowing for delocalized states in one direction. Therefore conjugated polymers were initially regarded as one-dimensional semiconductors. In their pioneering work Su, Schrieffer, and Heeger [55] studied the interaction of an excitation with an ideal one-dimensional lattice, neglecting Coulomb interactions and disorder effects. They found that, in addition to direct electron and hole excitations across the semiconductor band gap, the one-dimensional system may support a host of exotic carrier types like solitons (topological defects without charge, with spin 1/2), polarons (electrons and holes, self-trapped by carrier-lattice interactions), soliton-polarons (charged topological defects without spin, self-trapped by carrier-lattice interactions), bipolarons (two carriers with charge of the same sign, bound by lattice distortion), and polaron-excitons (two carriers with charge of the opposite sign, bound by lattice distortion) [55]. In this one-dimensional semiconductor picture, the red shift between absorption and emission is attributed to the creation of self-trapped polarons after the initial generation of free carriers. The energy shift is then a measure for the self-localization energy of the polaron. One of the major arguments in favor of the one-dimensional semiconductor picture for conjugated polymers has been the coincidence of the onset of photoconductivity with the onset of optical absorption [56], which indicates the absence of a sizeable exciton binding energy. On the other hand, spectroscopic studies of conjugated polymers show many features that are characteristic for disordered molecular systems [57]. Among these studies are site-selective fluorescence experiments [58], where the emission spectrum is monitored as a function of excitation in a narrow spectral window, and time-resolved photoluminescence experiments [59]. Both the spectral and time dependence of the emission indicate that the primary excitation in a conjugated polymer is a neutral exciton localized on a molecule, executing an incoherent random walk between molecules. The molecules may be identified with segments of the polymer chain, separated by mechanical and chemical defects (twists, kinks, impurities, crosslinks …). Additional experimental proof for this molecular picture is formed by the observation of luminescence quenching by high electric fields [60, 61] (attributed to the dissociation of strongly bound excitons) and the recent demonstration that the photoconduction near the absorption edge is mostly of extrinsic origin, resulting from exciton dissociation at electrodes [62]. The intrinsic photoconduction commences at much higher energies, in accord with the molecular exciton picture.

Thus, there is a conceptually very different approach to the problem of exciton dissociation. Among these is the notion that photoionization is tractable in terms of Onsager theory [3, 63] which gives the efficiency of photo-dissociation φ of the exciton as a power series of the electric field E and temperature T:

$$\varphi = \varphi_0 \exp\left(\frac{-r_\mathrm{C}}{r_0}\right)\left[1+\frac{r_\mathrm{C}\mathrm{e}E}{2!k_\mathrm{B}T}+\ldots\right], \tag{2.5}$$

where $r_\mathrm{C} = e^2/4\pi\varepsilon k_\mathrm{B}T$ is the critical distance below which Coulomb energy is larger than kinetic energy, r_0 the ‘thermalisation distance’ and k_B is the Boltzman constant. Onsager theory implies that intrinsic photogeneration is a multi-step process, the initial event being either the autoionization of a higher excited optical Franck-Condon singlet state yielding a Coulombically bound geminate electron-hole pair (GP) or direct charge transfer [64]. Subsequently the pair can recombine geminately or fully dissociate in the course of temperature and field assisted diffusive escape process. The spectroscopically accessible energy difference between the lowest charge transport state and the singlet excited of the parent molecule plays a key role in that process. In conventional molecular crystals it is as large as about 0.5 eV [64]. This precludes thermal dissociation of the vibrationally relaxed singlet excitation unless that excitation is generated near an electrode which can act as a acceptor of one of the charge comprising the initial exciton. Tacitly, it has always been implied that in a bulk system the initial event that generate GPs is exothermic, i. e. not requiring any temperature or field assistance. It was also believed that the commencement of photoconductivity right at the onset of optical absorption is a signature of those materials behaving like an inorganic semiconductor in which the optical and electrical gap are identical [52, 65]. Meanwhile there is abundant evidence against these notions. Most experimentalists [66, 67] and theoreticians [68-70] concur that the binding energy of a singlet exciton, i.e. the energy needed to split an exciton to a Coulombically unbound charges, is no less than 0.5 eV. The ubiquitous increase of the photoconductive yield at about 1 eV above the absorption threshold [66, 71] is analogous to the behavior of conventional molecular crystals such an anthracene. It indicates that the excess electronic energy can be used to overcome the Coulombic binding energy of a Frenkel-type neutral exciton via either autoionization or dissociation while the excited chain segment is still vibrationally "hot" [71]. There is clear evidence, though, that also vibrationally relaxed excitons can dissociate, provided that the required excess energy is supplied by either a strong electric field or a sensitizer. The realization of the former case has been proven by (i) field quenching of the fluorescence [60], (ii) transient absorption under an electric field that can monitor the correlated decrease of the population of S_1

excitons and the growth of the polaron signal [72] and (iii) transient photoconductivity in a ladder-type poly(para-phenylene) (MeLPPP) that is characterized by an exceptionally low degree of disorder and high degree of chemical purity [73]. At times, it is difficult to distinguish both phenomena. It is open to conjecture what the rate-determining step for generation of mobile carrier is. It is the primary field dependent dissociation of a singlet exciton into a Coulombically bound geminate electron-hole pair (GP) or is it its subsequent escape from its initial potential? At our previous works we try to delineate characteristic features of both processes and the results are described in the next chapter and related papers.

It is well known that photodissociation can be highly efficient in two component donor-acceptor systems, as evidenced by the photovoltaic response of several systems. For instance, a polyfluorene copolymer backbone and a perylene-substituted side chains [74] and also a hexa-peri-hexabenzocoronene derivative:perylenediimide blend system [74]. The obvious conclusion is that the dissociation must strongly depend on the concentration of the sensitizing, i.e. electron accepting moiety. Organic photovoltaics currently lag behind the inorganic one because of low solar energy conversion efficiency about 1-3 %. To improve the efficiency, the combination of nanomaterials and polymer substrates were employed. These hybrid organic-inorganic consist of light-absorbing polymers in contact with semiconductor nanocrystals, fullerenes or nanostructured metals [76-79]. The nanomaterilas affect electro-optical properties of the conducting polymer, which include assisting in absorption of red and near -IR photons, a significant part of the solar spectrum.

3 LIST OF ARTICLES INCLUDED IN HABILITATION THESIS

Articles are arranged according to date of their publication.

W1. Handlíř, R., **Weiter, M.,** Schauer, F. Methods of Electron Structure Spectroscopy in Molecular Organic Solids Based on Transient Photoconductivity with Space Charge. *Chemical Papers,* 1996, vol. 50, no. 4, pp. 199–205. ISSN 0366-6352. IF[*] 0,226

W2. Handlíř, R., Schauer, F., Nešpůrek, S., Kuřitka, I., **Weiter, M**. and Schauer, P. Metastable states in poly(methylsilylene) induced by UV radiation and electron beam. *Journal of Non-Crystalline Solids*, 1998, vol. 227–230, pp. 669–672. ISSN 0022-3093. IF 1,563

W3. Schauer, F., **Weiter, M**. Rigorous modeling of recombination under double injection in amorphous films – an example of the stiff problem. *IS&T Journal of Imaging Science and Technology*, 1999, vol. 43, pp. 413–419. ISSN 8750-9237 IF 0,582

W4. Horváth, P., Schauer, F., Kuřitka, I., **Weiter, M.**, Salyk, O., Dokoupil, N., Nešpůrek, S. and Fidler, V. Luminescence in organic silicons prepared from organic precursors in plasma discharges. *Monatshefte für chemie, Chemical Monthly*, 2001, vol. 132, no. 1, pp. 177–183. ISSN 0026-3672 IF 0,886

W5. **Weiter, M.,** Bässler, H., Gulbinas, V., Scherf, U. Transient photoconductivity in a film of ladder-type poly-phenylene: Failure of the Onsager approach. *Chemical Physics Letters*, 2003, vol. 379, pp. 177–182. ISSN 0009-2614 IF 2,438

W6. Markham, J., P., J., Samuel, I., D., W., Burn, S., Lo, P., **Weiter, M.,** Bässler, H. Charge transport in highly efficient iridium cored electrophosphorent dendrimers. *Journal of Applied Physics,* 2004, vol. 95, pp. 438–445. ISSN 0021-8979 IF 2,171

W7. **Weiter, M.**, Arkhipov, V., I., Bässler, H. Transient photoconductivity in a thin film of a polyphenylenevinylene type conjugated polymer. *Synthetic Metals*, 2004, vol. 141, pp. 165 – 170. ISSN 0379-6779 IF 1,303

W8. Nešpůrek, S., Sworakowski, J., Combellas, C., Wang, G., **Weiter, M.** A molecular device based on light controlled charge carrier mobility. *Applied Surface Science*, 2004, vol. 234, iss. 1–4, pp. 395–402. ISSN 0169-4332 IF 1,284

W9. **Weiter, M.**, Bässler, H. Transient photoconductivity and charge generation in thin films of pi-conjugated polymers. *Journal of Luminescence,* 2005, vol. 112, iss. 1–4, pp. 363-367. ISSN 0022-2313 IF 1,314

W10. Salyk, O., Broža, P., Dokoupil, N., Herrmann, R., Kuřitka, I., Pryček, J., **Weiter, M.** Plasma polymerisation of methylphenylsilane. *Surface & Coatings Technology,* 2005, vol. 200, iss. 1–4, pp. 486–489. ISSN 0257-8972 IF 1,432

W11. **Weiter, M.,** Vala, M., Nešpůrek, S., Sworakowski, J., Salyk, O., Zmeškal, O. Reversible formation of charge carrier traps in poly(phenylenevinylene) derivative due to the

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[*] IF: Impact factor

phototransformation of a photochromic additive. *Molecular Crystals and Liquid Crystals*, 2005, vol. 430, pp. 227–234. ISSN 1058-725X IF 0,446

W12. Toman, P., Nešpůrek, S., **Weiter, M.**, Vala, M., Sworakowski, J., Bartkowiak, W., Menšík, M., Photoswitching in polymers with photochromic dipolar species. *Nonlinear Optics, Quantum Optics*, accepted

W13. Vala, M., **Weiter, M.,** Rajtrová, G., Nešpůrek, S., Toman, P., Sworakowski, J. Photochromic properties of spiropyranes in polymeric p-conjugated matrices. *Nonlinear Optics, Quantum Optics*, accepted

4 RESULTS

With respect to the studied materials and used experimental methods achieved results should be divided to the three related categories:
- π-conjugated polymers,
- molecular switching systems,
- polysilylene based organic semiconductors.

Last category is represented by the papers concerning numerical modelling of experimentally studied phenomena.

4.1 Π-CONJUGATED POLYMERS

[articles W5, W6, W7, W9]

As it was described in chapter 2.4, the discussion on the precise nature and dynamics of excited states in conjugated polymers – one dimensional semiconductors with strong electron-phonon interaction versus disordered molecular solids with strong Coulomb interaction – is still very much alive.

At our previous works [W5, W7, W9] we concentrate on the basic processes connected with the photogeneration of charge carrier: dissociation of a singlet exciton into a Coulombically bound geminate electron-hole pair (GP) and on its subsequent escape from its initial potential. We try to delineate characteristic features of both processes and determine the rate-limiting step for charge carrier generation. A photoconductive Time of Flight method was utilized for this study, accompanied by femtosecond absorption spectroscopy and numerical modelling. We focus on the charge carrier generation in methyl-substituted poly-phenylene (MeLPPP) and in phenyl-substituted poly-phenylenevinylene-type copolymer (PhPPV) The structure formulas of these

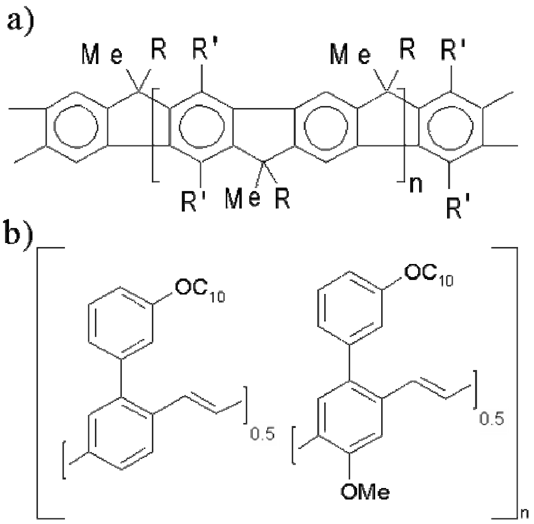

Fig. 4.1 Chemical structure of investigated polymers a) MeLPPP, b) PhPPV.

polymers are shown in Figure 4.1. Some PhPPV samples were doped with 1% (by weight) by trinitrofluorene (TNF) as an electron acceptor. The thickness of the layer was typically 100 nm for MeLPPP and 150 nm for PhPPV respectively. In order to prevent hole injection the ITO was covered by a semitransparent aluminium layer. Top thick Al-layer served as a top electrode. Transient photocurrents were observed upon excitation by a 5 ns laser flash of frequency doubled NdYag laser at photon energy 3.49 eV (355 nm). The sample was mounted in a cryostat, which allowed cooling down to 150 K.

The charge generation was measured as a function of electric field, temperature, photon dose and polarity of irradiated electrode. Fig. 4.2a shows photocurrent transients in MeLPPP film at an incident photon dose of 40 μJ/pulse and at different external electric fields. The rise time is determined by the RC time constant of the circuit that was about 30 ns. At times shorter than 1μs and at low electric fields the current features a plateau in a double logarithmic representative. At higher fields an algebraic decay followed by an almost exponential decay at $t > 1$ μs is observed. Fig. 4.2b shows complementary data on a PhPPV film at electric field of $3.5 \cdot 10^5$ V/cm and

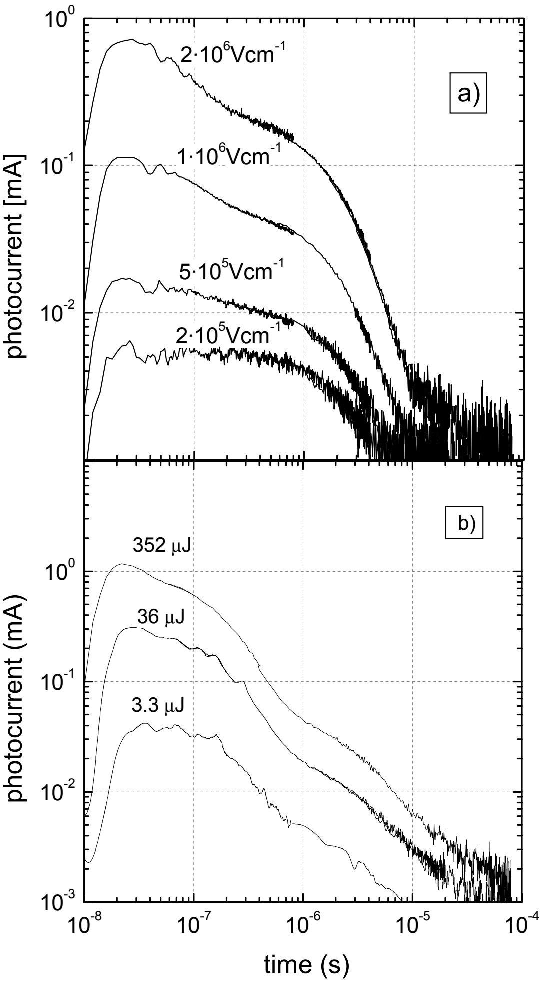

Fig. 4.2. Transient photocurrents measured a) on MeLPPP at diffrerent electric field at incident photon dose 40 μJ/pulse, b) on PhPPV at different photon dose at electric field $3.5 \cdot 10^5$ Vcm^{-1}.

different light intensities. Data representation in double logarithmic scale reveals a non-exponential decay extending into the 10 μs regime. The shape of the *j(t)* time dependence is virtually invariant with light intensity. The number of collected charges Q was calculated by integration of the current. The quantum yield of the photogeneration was calculated as the ratio of *Q* and the number of absorbed photons. Fig. 4.3 compares the quantum yield in undoped and doped PhPPV films and in MeLPPP film at the same incident light intensity.

A transient current can be either transport or generation limited. From previous results is known that electron transport has never been observed in these materials in Time of Flight experiment indicating that electrons are trapped within the time scale of the experiment. In MeLPPP films hole transport is trap-free yielding a hole mobility of $2 \cdot 10^{-3}$ $cm^2V^{-1}s^{-1}$ with an exceptionally weak temperature and field dependence. This is a consequence of the low degree of structural disorder. It turns out that at the lowest electric field in Fig. 4.2a, the expected transit time of holes is 25 ns, i. e. about 3 orders of magnitude shorter than the duration of the photocurrent pulse. Obviously, the observed transient photocurrent must be controlled by charge carrier generation rather than by their transport. This concurs with the fact that the duration of the signal is virtually independent at the electric field. Based upon a value of $\mu = 2 \cdot 10^{-6}$ cm^{-2}/Vs for mobility of holes in PhPPV one could estimated the mean transit time of holes at Fig. 4.2b to be 4...40 μs. This could, indeed, be comparable to the measured duration of the current transient implying it to be entirely transport limited. However, not observing any significant shortening the current pulse at higher fields cast doubt in this assignment. It is known that in energetically random dielectric such a film of PhPPV the motion of charges is associated with dispersion. It may well be that in a sample as thin as 150 nm the effective hole mobility is higher. In any event, the observed current transient is a convolution of time dependent charge carrier generation, transport and discharge.

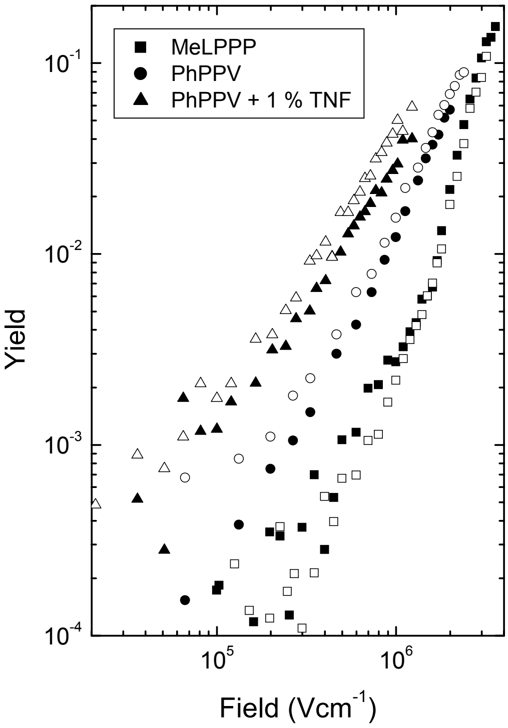

Fig. 4.3 A comparison of the photogeneration yield for investigated polymers.

Since the measured current transient must involve dissociation after pulse excitation the dissociating entity has to be a metastable electron-hole pair produced from a short lived initial optical absorption. However, it is open to conjecture what the rate-determining step for generation of mobile carrier is. It is the primary field dependent dissociation of a singlet exciton into a Coulumbically bound geminate electron-hole pair (GP) or is it its subsequent escape from its initial potential? In order to distinguish the above possibilities requires additional experimental information. In the case of MeLPPP this was field-modulated picosecond transient absorption of charge carriers and excitons simultaneously. By comparing the field dependence of the evaluation of the transient absorption of geminately bound positive polarons with the microsecond transient photocurent signal we could ascertain that it must be the field-assisted initial dissociation event which is rate controlling [W5].

In the case of PhPPV the situation is different. Previous spectroscopic and cw-photoconduction work on PhPPV without and with controlled doping with TNF showed that neat PhPPV contains about 0.04 % of dopants which quench about 50% of excitations forms on electron hole pairs on TNF and PhPPV already. Intentional doping by 1% TNF can therefore increase the photogeneration of charge carriers by about a factor of 2 only, in agreement with Fig. 4.3. This proves that in this case the field assisted step for photogeneration must be the subsequent escape of the pair, i.e. an exciton, from its coulombic well while the initial event is exciton diffusion towards to the sensitizes following charge transfer efficiency close of unity. Since this process is exothermic it does not require an electric field. Additional support for this argument is that in PhPPV the photoresponse is larger than in MeLPPP and is associated with a weaker field dependence although the field quenching of prompt fluorescence in MeLPPP and PhPPV turns out to be virtually identical. This implies that the exciton binding energy in both systems has also to be the same indicating that the amount of intrinsic field-assisted exciton breaking has to be the same, too [W7].

The field and temperature dependence of the photogeneration yield in the PhPPV film doped with 1% TNF can be fitted by a recent theory by Arkhipov et al. that differs from the conventional Onsager description [80]. The parameter is the relative effective mass of the hole on a polymer chain. It turns out that a perfect fit is obtained for $m_{eff}/m_0 \approx 2$. Such a value of m_{eff}/m_0 for a π-conjugated polymer is at variance with theory [81] and electro-reflection experiments on single crystalline poly-diacetylenes featuring a Franz-Keldysh effect. On the other hand, there is experimental evidence that even the on-chain charge carrier mobility, probed via microwave techniques is of the order of 0.1 $cm^2V^{-1}s^{-1}$, i.e. comparable with that of molecular crystals at 295 K. This implies that m_{eff}/m_0 must be of the order of unity. We conjecture that the low value of the effective mass applies only upon instantaneous generation of a charge, i.e. at times shorter than the electron-phonon time [W7].

Additional probe of longer-lived geminate e-h pairs was done using double shot technique. The question is whether or not there are geminate pairs that can be dissociated optically by a second laser pulse rather than decay by geminate pair recombination. After the reexcitation of the sample by the second laser pulse, the unusually substantial photoresponse is observed. The obvious source of this enhanced photogeneration must be the dissociation of the GPs produced by the first pulse. Since the dissociation of GPs is field enhanced, the concentration of undissociated GPs has to be much higher at lower intensities of electric fields. The slope gradient of the time dependence of the delayed photocurrent maximum (Figure 4.4) at low field intensities, which correspond with lifetime of the bound GPs, proves this notion. This is also in accordance with the previous delayed fluorescence experiments on PhPPV that showed that delayed fluorescence in time scale up to microsecond originates from the radiative decay of GPs. On the other hand the concentration of free carriers increases with increasing field. Thus the influence of the recombination at increasing intensities of electric field of bimolecular recombination is enhanced, as it is demonstrated by the decreasing slope and following increase of the delayed photocurrent maximum (see Fig. 4.4) [W9].

We have reported a detailed study of charge transport in electrophosphorescent organic semiconductors. The materials studied were dendrimers closely related to *fac* tris(2-phenylpyridine) iridium [Ir(ppy)$_3$] which is widely used in OLEDs. We find that we can fine tune the mobility by dendrimer generation, and that the transport dynamics can be related to the structural configuration of the dendrimers. In addition, we have investigated both the field and the temperature dependence of these unique materials. The TOF indicates that energetic disorder can account for the general transport properties in these materials. As the disorder of 100 meV corresponds well with that measured for some molecularly doped polymers and some of the more disordered conjugated polymers. The transport is weakly dispersive at room temperature, and a transition to nondispersive transport is seen at elevated temperatures. A measured transition temperature T_c of 293 K is much higher than that measured for conjugated polymers. This may be

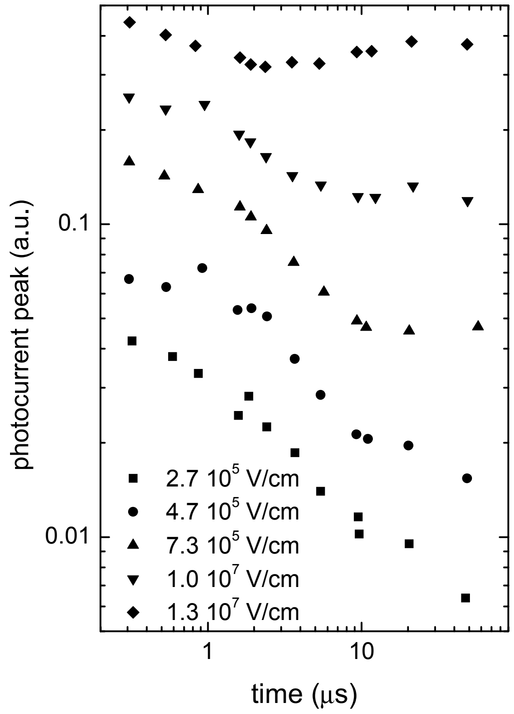

Fig. 4.4 Time dependence of the maximum of the second peak of the photocurrent at different electric field intensities. The energy of the first pulse at 3.49 eV was 35 μJ/pulse, the energy of the second pulse at 2.74 eV was 0.7 μJ/pulse.

due to specific properties of the metal complex core or disorder introduced by the morphological properties of the dendrimer. We show that by increasing the generation of the dendrimer, we simply lower the mobility and do not increase the level of disorder in the film, as reflected in identical levels of tail broadening for the first- and second-generation material. By increasing the generation, we are able to improve the balance of charge carriers and are able to create efficient single layer LEDs. In addition, even higher efficiencies can be obtained in a bilayer structure, with the dendrimer architecture having a large impact on the performance of the device [W6].

4.2 MOLECULAR SWITCHING SYSTEMS

[W8, W11, W12, W13]

The published articles included in this category were realized in the framework of the project *Light driven molecular current switch* subsidized by Czech Science Foundation, which is solved by author. The fundamental parts of experimental work were done in Faculty of Chemistry, Brno University of Technology in cooperation with Institute of Macromolecular Chemistry in Prague (Dr. Toman, Prof. Nešpůrek) and Wroclaw University of Technology in Poland (Prof. Sworakovski).

The aim of the project is to suggest new molecular photoelectronic devices based on interactions between conjugated macromolecules and photochromic materials. Proposed device (switch, modulator) is based on light controlled modulation of charge transport along main chain of the polymer. Switch consists of molecular wire (σ- and π-conjugated polymers) which side chains contain reversible photochromic moieties. The chemical structure of the side chains strongly affects electron structure of the polymer, the energy of the gap and optical properties above all. Very often the dipole moment of the metastable form of photochromic system is higher than that of the stable form, and this feature allows control of the polymer chain conjugation, and hence a change in the on-chain mobility of charge carriers. Thus, a molecular switch is based on the principle of controlled electrical conductivity of the polymer. The research activities are focused in theoretical and experimental study of the model molecular systems suitable for the construction of new devices transforming the optical signal to electrical response. The goal of the characterization is to find the suitable material with optimized structure for current switch.

The results reported in [W8] demonstrate a possibility of a reversible formation and annihilation of charge carrier traps in molecular materials consisting of photoconducting polymer containing photochromic species. Both the dark conductivity and photoconductivity of poly(methylphenylsilylene) with admixed spiropyran are reversibly modified due to the formation and annihilation of dipolar traps. To find a molecular system suitable for optoelectrical switching, kinetics of photochromic reaction of spiropyran dissolved in a poly(phenylenevinylene) derivative MEH-PPV was studied by optical and impedance spectroscopy [W11]. The rates and characteristic parameters of the photochromic processes detected from changes in the capacitance by impedance spectroscopy qualitatively followed the parameters of photochromic changes detected optically. It was conclude that photochromic transformation of spiropyran produced charge carrier traps affecting the electrical properties of the polymer matrix, capacitance and photoconductivity in particular. Therefore the detailed kinetic studies of the photochromic reaction of spiropyrane in poly(methyl methacrylate) and in π-conjugated photoconductive polymer matrices based on poly(p-phenylene vinylene) derivatives were done [W12]. The polymer matrix strongly influences the reaction rate, lifetime of coloured species and the value and distribution of activation energies of the bleaching process. It was also found that the activation energy depends on the intensity of light used for photochromic conversion and the exposure time. Photochromic reaction is influenced by energy transfer processes between the conjugated chain and photochromic additive. These observations were supported by quantum chemical calculations [W13]. The calculations showed that the presence of dipolar species in the vicinity of the polymer chain shifts the polymer transport levels and consequently increase the energetic disorder of chain hopping states. It was shown that the increasing disorder destroys the resonance between energies on adjacent sites, and therefore limits the charge carrier motion.

4.3 POLYSILYLENE BASED ORGANIC SEMICONDUCTORS

[W2, W4, W10]

In contrast to conventional conjugated polymers, polysilylene polymers exhibit the σ-electron delocalization along the polymer chain with catenated Si-Si bonds. In our working group in Faculty of Chemistry the polysilylenes were of considerable research interest, especially the poly(methylphenylsilylene) (PMPSi). The comparison of traditionally prepared one-dimensional PMPSi [W2] with non-traditionally prepared three-dimensional PMPSi was presented. Films were investigated by photoluminescence (PL) and electroluminescence (EL) methods with support of UV VIS and IR absorption spectroscopy. The aim of the work of our group in Faculty of Chemistry was to find material for large area light-emitting displays operating at low drive voltage. The linear polysilylenes prepared by standard technique exhibit excellent properties as transport and photosensitivity for electronic applications. On the other hand, some undesirable properties as degrability by UV radiation, low mechanical resistance and solubility were observed. To improve the mentioned properties we use the unconventional polymerization methods such as vacuum evaporation technique [W4], radio frequency plasma polymerization [W4, W10] and microwave electron cyclotron resonance plasma enhanced chemical vapor deposition [W4, W10].

A photoluminescence and electroluminescence methods were used to investigate physical properties and to optimize PMPSi films prepared by different deposition techniques including plasma deposition and vacuum evaporation. The detailed characterization of electroluminescence in spin-coated PMPSi was done. The characterization of non-traditionally prepared three-dimensional PMPSi thin films gave partial successful results. We achieve suitable electronic properties at samples, such as the higher resistivity against the degradation by light and against ageing. Some types of samples also exhibit the emission spectrum similar to that of spin-coated samples. However, the electroluminescence emission intensity is still low.

4.4 NUMERICAL MODELLING

[W1, W3]

New numerical method for modelling a charge transport, transient photoconductivity and electroluminescence with respect to distribution of localised states (DOS) in disordered solids was suggested. Model is based on rigorous mathematical treatment in contrast to simulations usually published in this area, which are based on stochastic Monte Carlo method. The main advantage of suggested method compared to the conventional methods is that it is always stable irrespective of the time step chosen and that it is independent on the number of examined charge carriers. The principal input parameter of the model is distribution of DOS.

Using a model, the influence of DOS to the transient photoconductivity was examined. It was shown, that the traps in distribution of localized states have the predominant influence on the transient photoconductivity of disorder solids. Thus, the transient photocurrent reflects the DOS and can be used with advantage for their determination. For this purpose a posttransient photocurrent analysis method was adapted. The method is based on Fourier transform of the transient photocurrent. Based on this transform a numerical procedure for the evaluation of DOS was built. Using the method and numerical modelling it was demonstrate that the posttransient analysis method is suitable for reconstruction of DOS from transient photocurrent in organic materials. The accuracy of posttransient analysis method in the determination of energy position and concentration of localized states was examined with favourable results for experimental work [W1].

Suggested model was used for the elucidation of the transient space-charge-limited double injection after the onset of generation of excess carriers. The main subject of the study was the recombination paths in a model material with respect to electroluminescence in diode-like structures. The modelling gave results concerning the emission zone, energy positions of predominant recombination states and the balance of electron to hole contributions to the recombination currents [W3].

5 SUMMARY

The submitted habilitation thesis deals with the study of charge carrier transport and photogeneration in organic disordered semiconductors. These phenomena were studied by experimental methods and numerical modelling especially in π-conjugated polymers, molecular switching systems and in polysilylene based organic semiconductors.

In π-conjugated polymers it was shown that there two processes occurring in the bulk of conjugated polymer that can give rise to photogeneration. One of them is the field assisted dissociation of excitons into geminate pairs that subsequently can separate fully. This is a generic process but requires a strong electric field. The other one is sensitized photogeneartion at either non-intentional or intentional dopants that can act as electron scavengers. In neither case the Onsager description is applicable because in the intrinsic case the field assistance in the primary event of exciton breaking into geminate pair is disregarded in the Onsager formalism, while in the other case geminate pair disssociation is aided by the finite energy of the charge carrier (hole) that resides on a segment of the conjugated polymer next to the counter charge. The field and temperature dependence of the photogeneration yield was fitted by a recent theory by Arkhipov et al. that differs from the conventional Onsager description.

A detailed study of charge transport in highly efficient iridium cored electrophosphorescent dendrimers was reported. We found out that we can fine tune the mobility of charge carriers by dendrimer generation, and that the transport dynamics can be related to the structural configuration of the dendrimers.

The charge carrier transport in conjugated polymers containing suitable photochromic species was studied in details. It was shown that in these materials the photochromic reaction should eventuate in changes of their electrical properties such as conductivity. Due to charge-dipole interactions of photochromic additive, dipolar traps are formed in the vicinity of polar species dispersed in a non-polar material. Besides the trap formation, an increase of the width of distribution of hopping transport states should be observed. Both effects result in a decrease of the charge carrier mobility. In this way it is possible to use the photochromic process for a reversible formation of charge carrier traps and, consequently, for a mobility modulation. Thus, an optical signal can be transformed into an electrical one and a polymeric optron can be, in principle, constructed.

In many types of organic semiconductors, the processes connected with the photogeneration and transport of charge carriers under the influence to electric field are still not well understood and are open to conjecture. The better understanding of these basic phenomena can enhance the progress in molecular electronic and organic electronic devices based on the materials which exhibit a unique combination of properties: the electronic and optical properties of metals and semiconductors in combination with the processing advantages and mechanical properties of polymers.

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ABSTRACT

Tématem předkládaná habilitační práce je studium transportu nosičů náboje a fotogenerace v organických neuspořádaných polovodičích. Tyto jevy byly studovány experimentálními metodami a metodami numerického modelování zejména v π-konjugovaných polymerech, molekulárních spínacích systémech a v organických polovodičích na bázi polysilylenů.

Při studium fotogenerace v π-konjugovaných polymerech jsme ukázali, že zde existují dva objemové procesy, které vedou ke generaci nosičů náboje. Prvním z těchto procesů je elektrickým polem asistovaná disociace excitonů na vázaný pár elektron díra, který následně může plně disociovat. Tento proces je nejběžnějším způsobem disociace excitonů, ale vyžaduje velkou intenzitu elektrického pole. Druhým procesem je fotogenerace nosičů náboje na příměsích, které mohou sloužit jako elektronové akceptory. Žádný z těchto procesů nelze popsat doposud používanou Onsagerovou teorií fotogenerace. V prvním případě je to z důvodu, že Onsagerova teorie opomíjí elektrickým polem stimulovanou primární disociaci excitonů na vázaný pár elektron-díra, ve druhém případě je disociace vázaného páru elektron-díra podpořena energií opačného náboje, který je na polymeru v blízkosti vázaného páru elektron-díra. Závislost účinnosti fotogenerace na elektrickém poli a na teplotě byla modelována novou teorií Arkhipova a spol., která se liší od doposud používané Onsagerovy teorie.

Detailně jsem studovali rovněž transport nosičů náboje v dendrimerech s iridiovým jádrem, které vykazují velkou elektroluminiscenční účinnost. Zjistili jsme, že lze velice dobře modifikovat pohyblivost nosičů náboje pomocí struktury (generace) dendrimeru a že rovněž dynamika transportu nosičů náboje závisí na struktuře dendrimeru.

Podrobně jsme rovněž studovali transport nosičů náboje v konjugovaných polymerech, které obsahují vhodnou fotochromní látku. Naše výsledky ukázaly, že fotochromní reakce v těchto materiálech vede ke změně jejich elektrických vlastností jako například ke změně jejich vodivosti. V důsledku náboj-dipólové interakce fotochromího aditiva jsou v blízkosti polárních částic vytvářeny bipolární pasti, jenž jsou rozptýlené v nepolární matrici. Kromě vytváření pastí lze rovněž pozorovat rozšíření distribuce transportních stavů. Oba dva tyto jevy způsobují pokles pohyblivosti nosičů náboje. Tímto způsobem je tedy možno využít fotochromní jev pro reverzibilní vytváření pastí pro nosiče náboje a následně modulovat jejich pohyblivost. Tyto procesy tedy umožňují transformaci optického signálu na signál elektrický a v důsledku tak umožňují konstrukci polymerního optronu.

V mnoha typech organických polovodičů ještě stále nejsou mechanismy procesů spojených s fotogenerací a transportem nosičů náboje dobře prozkoumány a jsou stále předmětem odborných diskuzí. Lepší porozumění těmto jevům může urychlit pokrok na poli molekulárních elektroniky a organických elektronických součástek založených na materiálech s unikátními vlastnostmi, které jsou kombinací elektronických a optických vlastností kovů a polovodičů s mechanickými a technologickými výhodami polymerů.