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**OPTICAL AND ELECTRICAL
PROPERTIES
OF ORGANIC MATERIALS
FOR ORGANIC ELECTRONICS**

BRNO UNIVERSITY OF TECHNOLOGY
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**OPTICAL AND ELECTRICAL PROPERTIES OF ORGANIC
MATERIALS FOR ORGANIC ELECTRONICS**

OPTICKÉ A ELEKTRICKÉ VLASTNOSTI ORGANICKÝCH
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Organic electronics, organic photovoltaic, organic light emitting diodes, OLED, organic field effect transistors, fluorescence, absorption, chromophore

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CONTENT

1	INTRODUCTION.....	5
2	DEVELOPMENT OF NEW MATERIALS FOR ORGANIC ELECTRONICS.....	6
2.1	Modification of solubility od DPPs.....	7
2.2	Multicolour emission by substituent tuning.....	9
2.3	Soluble spectrally tuned DPP derivatives.....	10
	2.3.1 Soluble polar DPP derivatives – alkylated.....	11
	2.3.2 New soluble polar DPP derivatives – acetated.....	12
2.4	Model electronic devices made from DPPs.....	14
3	LIGHT DRIVEN CURRENT SWITCH.....	16
3.1	Concept of the switch.....	17
3.2	Optical properties.....	17
	3.2.1 Photochromism in the films.....	18
	3.2.2 Fluorescence quenching.....	19
3.3	Electrical properties.....	20
	3.3.1 Capacitance and photocurrent.....	21
	3.3.2 Impedance spectroscopy.....	21
	3.3.3 SCLC spectroscopy.....	22
3.4	Quantum chemical modeling.....	23
4	SUMMARY.....	24
5	PAPERS INCLUDED IN THE HABILITATION THESIS.....	25
6	REFERENCES.....	26
	ABSTRACT.....	30

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1 INTRODUCTION

Organic electronics (also called molecular electronics) might be defined as set of electronic behaviours in molecule-containing structures that depend upon the characteristic molecular (rather than atomic) organization of space. This behaviour is fixed at the scale of individual molecule, which is the pico to nanoscale. While the structures and devices may be macroscopic, the fundamental processes that govern the behaviour arise at the molecular level.

Advantages of organic semiconducting devices include simplicity in device structure, good scalability, low-power operation and the possibility for device design through chemical synthesis. In addition, organic materials including polymers possess unique properties, such as good mechanical strength, flexibility, and most important of all, ease of processing which should ensure low production costs.

Organic semiconductors have been the subjects of intense scientific investigation for the past 50 years. During most of that time, these materials, primarily consisting of carbon, hydrogen and oxygen, were considered to be merely a scientific curiosity. Organic materials weak intermolecular bonds in the solid state give them properties of both semiconductors and insulators; so their study has deepened our fundamental understanding of the electronic and optical properties of solids. But, organic semiconductors attracted the industrial interest when it was recognized that many of them are photoconductive under visible light. This discovery led to their use in electrophotography (or xerography) and as light valves in liquid crystal displays (LCDs).

In 1987 Ching Tang and Steven Van Slyke of Eastman Kodak Co., Rochester, N.Y., successfully produced the first efficient light emission from a two-layer organic structure resembling a p-n junction [1]. The Kodak group used a class of synthetic dyes that is closely related to xerographic materials to develop a device called a small-molecule OLED (Organic Light Emitting Diode) that produced light with about one percent efficiency. The materials used consist of often no more than 30 or 40 atoms covalently bonded into stable, individual molecular units.

While this first demonstration of reasonably efficient light emission at low voltage attracted interest from potential display manufacturers, particularly in Japan, the technology attracted public attention when, in 1990, researchers at Cambridge University in England under the direction of Sir Richard Friend reported a similar effect in a semiconducting organic polymer film consisting of poly(p-phenylenevinylene) (PPV) [2]. Unlike small molecule compounds, polymers are long chain molecules whose monomer segments are attached in a continuous covalently bonded high-molecular-weight chain. The discovery and development of the conductive polymers [3]-[6] earned the Nobel Prize in Chemistry to Alan Heeger, Alan McDiarmid and Hideki Shirakawa for the year 2000.

Gradually, there were several strategies developed for optimizing of the electroluminescence efficiencies targeting (i) charge carrier injection at the contacts, (ii) transport of both charge carriers and excitations, and (iii) recombination of charge carriers to yield the emissive state. This strategies involve for example multilayered designs using organic charge transport layers between contacts and the actual emissive material [1], [7], [8] doping of the active material into a charge-transporting matrix [9], matching of the Fermi energies of the electrode materials to the HOMO and LUMO energies of the organic semiconductor either by choosing appropriate electrode materials [10] or by tuning of the redox properties by introducing suitable substituents [8]. Further strategies involve utilization of triplet states that are produced with singlets in the ratio 3:1 (assuming that the electron-hole capture process is spin-independent) [11].

Besides the development in OLED technology, there has also been an intense research in other areas like organic solar cells, organic thin film transistors, and various sensors and switches. Anthracene was the first organic compound in which photoconductivity was observed by Pochettino in 1906 [12] and Volmer in 1913 [13]. In the late 1950s and 1960s the potential use of organic materials as photoreceptors in imaging systems was recognized [14]. The scientific interest

as well as the commercial potential led to increased research into photoconductivity and related subjects. In the early 1960s it was discovered that many common dyes, such as methylene blue, had semiconducting properties [15]. Later, these dyes were among the first organic materials to exhibit the PV effect [16].

Nowadays first commercial devices based on organic semiconductors are already entering the commercial world [17]. The solar cells are based on combination of two materials with different electron affinities and ionisation potentials. This favours exciton dissociation: the electron is accepted by the material with the larger electron affinity and the hole by the material with the lower ionisation potential, see e.g. review articles [18]-[20].

On the other hand, the OLED based displays are available on the market for about a decade. However, the stability, power consumption (efficiency) and colour purity remain still topical in the research. The same remains true also for the photovoltaic devices: the stability and efficiency are the main topics. On the other hand, the attention is paid not only to the increase of performance of existing devices but is also focused on designing new applications based on specific attributes of molecular solids. Present-day progress allows designing desired structure (using quantum-chemical methods), synthesizing required compounds and with the help of physical chemistry and physics allow characterizing the phenomenon occurring on molecular level.

The results discussed here also follow this approach. In our work referred in this thesis, we choose the relatively new class of mostly stable organic materials, the diketo-pyrrolo-pyrroles, and modified them to be used as the active materials in organic-based electronic devices. The author's and his co-workers' aim is to contribute to the understanding of the relations between the chemical structure and properties important for the respective applications. Contributions to this issue are addressed in the first part of the thesis (Chapter 2). In Chapter 2.1 we modified the basic non-soluble diketo-pyrrolo-pyrrole with the help of *N*-alkylation. This allows for introducing cheap wet solution deposition techniques. The Chapter 2.2 deals with introduction of electron-donating or withdrawing groups as the counterparts to the diketo-pyrrolo-pyrrole core. In the Chapter 2.3 and Chapter 2.4 we combined these two approaches to get soluble but in the same time spectrally tuned structures for utilization in organic electronic devices. Some of the devices studied are discussed in Chapter 2.5.

Second part (Chapter 3) deals with our contribution to the domain of conducting polymer based current switch. This fundamental electric device utilizes properties of organic materials, which do not have their counterparts in traditional inorganic semiconductors. The aim is to construct model devices and study the basic processes, which govern the switching. The theoretical expectations based on quantum chemical calculations are experimentally evidenced. We showed that the optical signal can be transformed into an electrical one in these systems. Since the switch uses light for switching between the two states (ON and OFF), the Chapter 3.2 deals with the optical studies of the model devices and the Chapter 3.3 is devoted to the electrical responses.

2 DEVELOPMENT OF NEW MATERIALS FOR ORGANIC ELECTRONICS

This part deals with studies directed to the fundamental properties of new materials designed for utilization in organic electronics. The author papers dealing with this issues are [V1]-[V4], [V7], [V16].

As the actual demands the materials have to fulfil are application dependent and often contradictory, the material basis in organic electronics is broad. In following chapters, one of the advantages related to the organic materials is shown: the nearly infinite possibilities for chemical modification in order to gain the desired physical, physicochemical and chemical properties.

Nowadays, the most efficient devices used in industrial production or as prototypes utilize a combination of various materials providing specific functionality: the hole or electron transport,

reduction of injection barrier for holes and electrons, high absorption coefficient and exciton formation, efficient radiative recombination, etc. The materials chosen to build the device have to fulfil not only those core requirements mentioned, but also their ionisation potential (IP) and electron affinity (EA) have to be aligned to be matching with the surrounding and allow effective charge migration and balance, the processing have to be compatible (production of one layer must not affect the other) etc. As can be seen, only one advantageous attribute is not enough to build an efficient device. It is therefore common to functionalise promising material in such way, which does not impair the intrinsic desired properties.

Among others, derivatives of 3,6-diphenyl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione, commonly referred to as DPP, are considered as a new promising material class for organic electronics (Figure). The next chapters describe our attempts to influence their solubility, polarity, electron spectra, position of HOMO and LUMO etc. while keeping their original advantages.

The DPPs constitute an important class of high-performance pigments [21]-[33]. The compounds are endowed with brilliant shades (ranging from yellow-orange to red-violet) and exhibit exceptional resistance to chemical, heat, light, and weather. It has been shown that DPP units introduced into various materials, such as polymers [34]-[43] dendrimers, [44] polymer-surfactant complexes [45], and oligomers [46] results in deeply coloured, highly photoluminescent [47]-[58] and electroluminescent [51], [52] materials. Owing to their interesting properties, there is wide range of possible applications which have been already investigated covering for example latent pigment [59], charge generating materials for laser printers and information storage systems [60]-[65], solid-state dye lasers [62] or gas detectors [66], [67].

2.1 MODIFICATION OF SOLUBILITY OF DPPS

Solubility of the materials is one of the key issues for cheap deposition of organic electronics devices. The DPPs are insoluble in majority of common solvents. Whilst this is favourable for many applications, the ability to solubilize the compounds would offer the possibility of using wet solution-based techniques (spin-coating, drop-casting, inkjet printing, etc.) to prepare organic electronic devices from DPPs. Therefore, we performed study targeting to obtain solubilised DPPs in [V7]. One reason for their insolubility is the existence of H-bonds between the -NH group and oxygen (see the parent structure in Figure 1). Since the basic DPP core is perfectly planar, π - π electron overlap occurs in the solid state and also contributes to their insolubility. These interactions can be so strong as to impart colour change between the solid and dissolve forms and influence other properties, such as fluorescence and Stokes shift [68]. It is therefore clear, that modified solubility can be achieved either through *N*-substitution and/or disruption of molecular planarity [V7].

In [V7] we designed and investigated group of several DPP derivatives in order to increase the solubility for utilization of these materials as the active media in organic light emitting diodes (OLEDs). The DPP itself has a high quantum yield of fluorescence (Φ_F) which is the key prerequisite for this application. To alter the solubility we used the *N*-substitution by different alkyls (R_1 and R_2 in Figure 1).

The quantum mechanical computations were used to obtain optimised conformations. The results shows, that the *N*-substitution influences the molecular geometry of the central DPP unit. The most important conformational parameters are the torsion angles α and β of the phenyls (see Figure 1). While the unsubstituted DPP molecule is planar $\alpha = \beta = 0^\circ$, derivatives with substitution on both nitrogens possess significantly rotated phenyl groups. For the unsymmetrically substituted ones, only the phenyl next to the substituted nitrogen atom is rotated. Phenyl group rotation significantly reduces the charge transfer integral between phenyls and the central DPP unit. Consequently the effective extent of conjugation is decreased due to the reduction of charge

transfer integral between phenyls and central pyrrolo-pyrrole part. Therefore, many electronic properties like absorption and luminescence are modified.

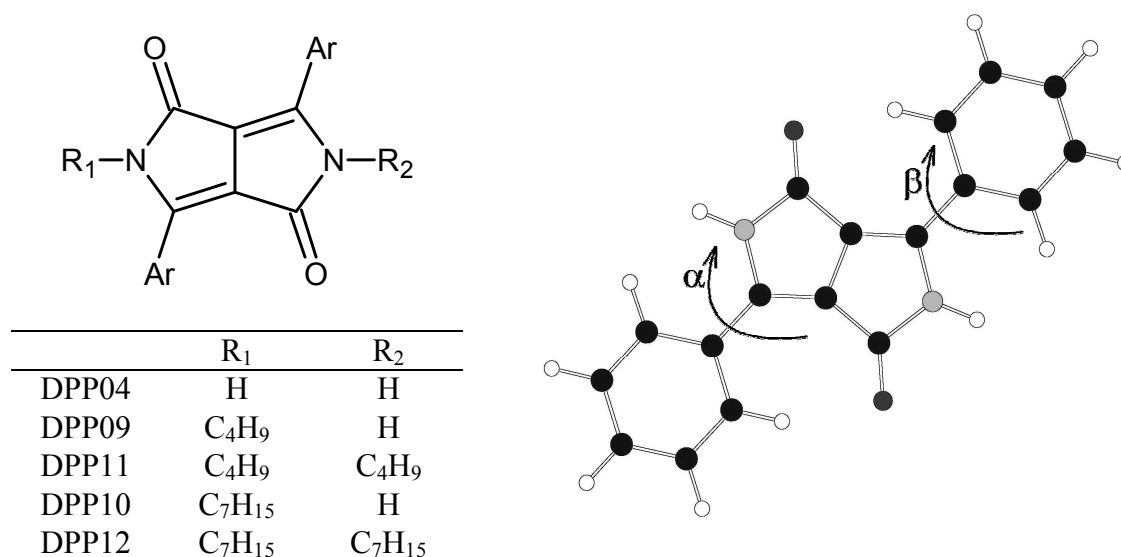


Figure 1 The basic structure of 3,6-diphenyl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4 dione, also known as DPP ($R_1=R_2=R_3=R_4=H$) and the definition of the phenyl torsion angles α and β [V7].

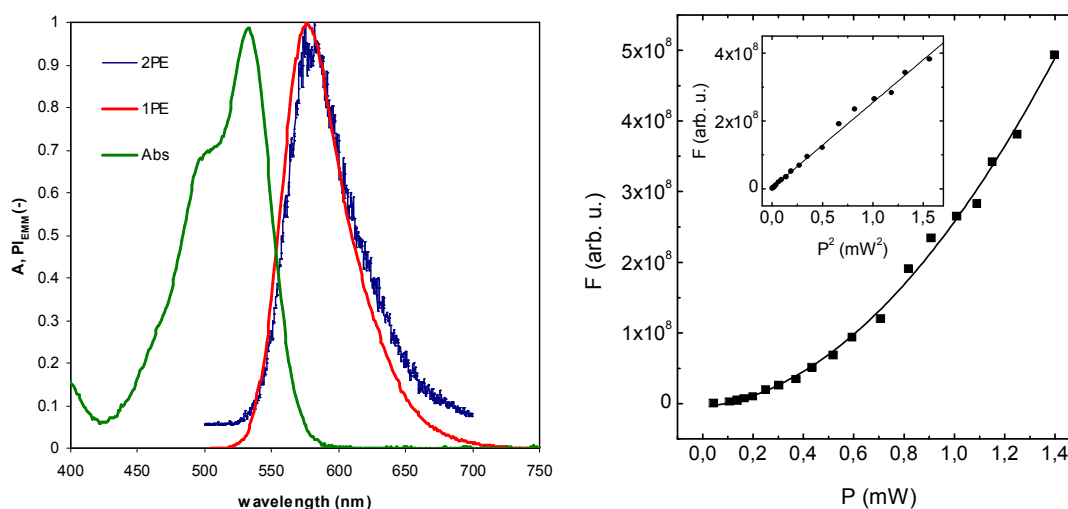


Figure 2 The left plot shows normalized fluorescence after one (1PE, red) and two-photon (2PE, blue) absorption of X derivative, see Figure 3. The right plot shows typical response of the integrated fluorescence F on the incident light power P . The inset shows linear fit to the F versus P^2 used for the two-photon absorption cross-section calculations.

We found that the excitation energies $E_{S_0-S_1}$ of the derivatives with the rotated phenyl groups exhibit a hypsochromic shift strongly correlated with the values of the torsion angles α and β . Similarly also ΔE_{Stokes} and E_{def} (deformation energy of the relaxed excited state) are significantly influenced by the phenyl rotation. The calculated first luminescence peak changes only slightly [V7].

The substitution of central DPP unit by alkyl side chains resulted in hypsochromic shift of the absorption. This shift increases with the number of alkyl groups but is not influenced by the length of the alkyls used. The spectral shift is accompanied with decrease of molar absorption coefficient. The fluorescence spectra of the *N*-substituted derivatives shows bathochromic shift with respect to the primary DPP.

The behaviour correlates with the quantum chemical calculations described above. Therefore, we assigned the observed to the rotation of the adjacent phenyl group and therefore to the loss of planarity and effective conjugation due to the substitution of alkyl group. This is exemplified as the decrease of molar absorption coefficient and hypsochromic shift of the absorption [69]. Introduction of the second alkyl rotates also the second phenyl and the effective conjugation is even more decreased.

However, the experimental outcomes showed that the original high fluorescence quantum yield remains nearly the same. Therefore, we showed that there is a possibility to prepare derivatives soluble in solvents suitable for cheap large-scale production without loss of fluorescence quantum yields and to use these materials for construction of electroluminescent devices. We prepared and tested the devices in [V2, V7].

2.2 MULTICOLOUR EMISSION BY SUBSTITUENT TUNING

Various electronic applications require materials with different energy of electronic states and transitions. For example, to tune the colour of emitted light one has to utilise materials with wide band-gap (blue), small-band gap (red) and also in between (e.g. green). The possibility to have all of the emitters from one family (having not too much different structure) is particularly favourable for white light emitting diodes due to the reduction of possible structural defects. Another example might be the organic solar cells where the band-gap should be matched to the solar radiation in order to maximize the performance. And finally the charge conducting layers have to have matched the positions of the bands with the electrodes to allow for efficient charge injection. In paper [V3] we modified the DPP to obtain such multicolour emission by substituent tuning.

In case of organic semiconductors, the spectral engineering can be done by introduction of polar substituents into organic chromophores which causes a redistribution of electronic density in both the ground state and the excited state. This can strongly modify their absorption and fluorescence properties [70]. The important parameters such as positions of the electron and/or hole transport levels, the absorption coefficients and fluorescence quantum yields, etc. are modified. Furthermore, the push-pull substituted organic π conjugated compounds are at the centre of interest of physicists, because they can produce strong second-order nonlinear optical effects [71]. On the other hand, quadrupolar chromophores are suitable for producing NLO behaviour, which we also demonstrated, see Figure 2. As organic pigments generally represent photostable systems, their modification by introduction of polar substituents to get dipolar or quadrupolar molecules is very promising in this respect.

We investigated the effect of electron-donor (piperidino) and electron-acceptor (cyano) groups (Figure 3 left) on the electronic spectra both, experimentally and theoretically in [V3].

It was found, that in general, cyano group stabilizes both phenyl molecular orbitals, while piperidino group destabilizes them (and even to a greater extent). An electron-donor substituent increases the electron density on the phenyl group to which it is attached, and on acceptor C=O group of the second pyrrolinone ring in HOMO, while in LUMO further CT is observed to the opposite phenyl group. This indicates the electron-acceptor character of the whole central dipyrrolinone is mainly localized on keto groups.

The absorption spectra show poor resolution of vibronic structure in the case of asymmetrically piperidino substituted and push-pull piperidino-cyano substituted compounds. We ascribed this to

the significantly higher dipole moment interacting with the polar solvent by dipole–dipole interaction.

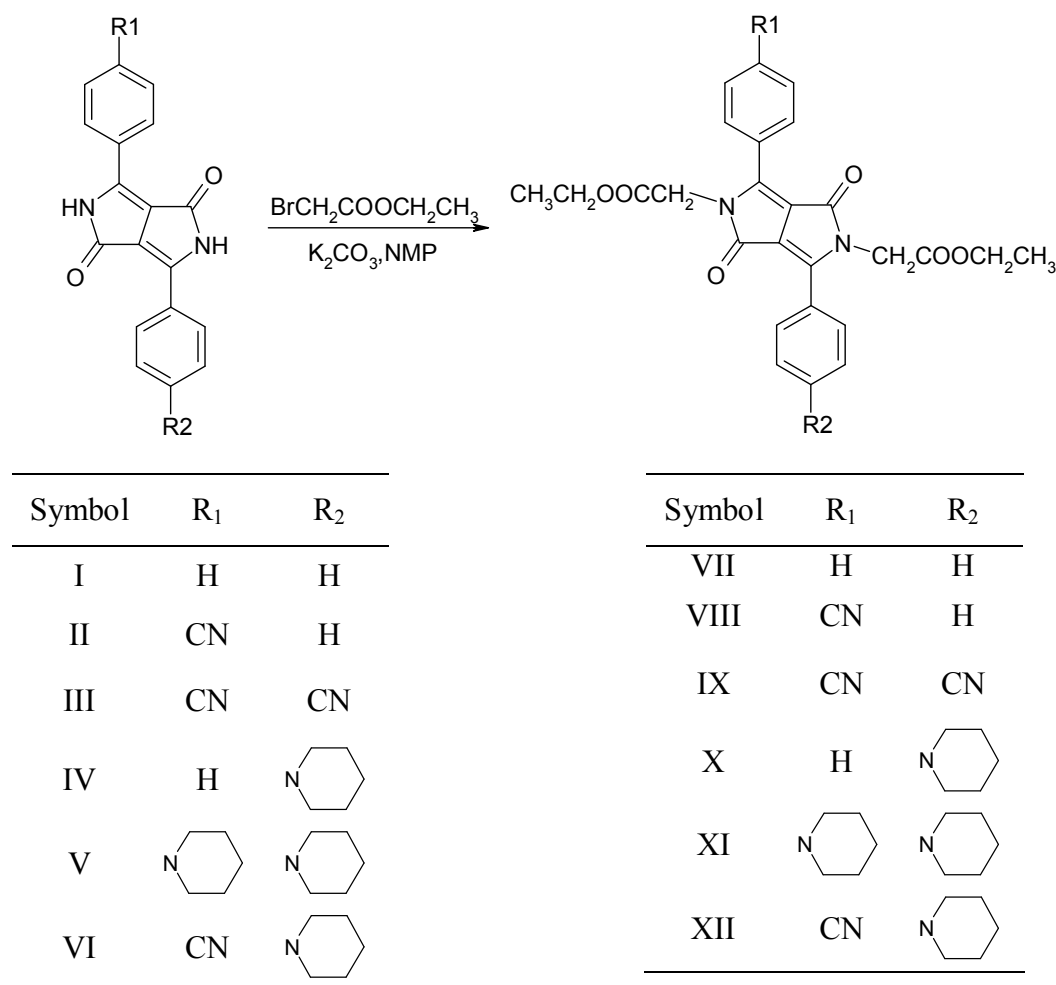


Figure 3 The structures studied in [V3] (left table) and [V16] (right table).

The fluorescence spectra of DPPs usually show small Stokes shifts, which are significantly increased by *N*-substitution (e.g. alkylation) inducing higher degree of nonplanarity [V7]. Thus the *N*-substituted derivatives are promising with respect to applications like OLED, laser, etc. The Stokes shift between 0-0 vibronic bands in absorption and fluorescence spectra is higher for all five derivatives (II, III, IV, V, VI) than that for parent compound (12 nm) studied in [V3]. It is quantitatively similar for symmetrical derivatives and unsymmetrical compound (26–28 nm). Its significant increase is observed for the asymmetrically piperidino substituted IV (47 nm) and push-pull piperidino–cyano substituted VI (78 nm), as a result of much stronger excited state solvent (dimethylsulfoxide) relaxation of these polar compounds. It is the dipolar character of these compounds that gives them some chance to produce nonlinear optical phenomena. We have already confirmed this behaviour using two photon excited fluorescence and the publication process is in manuscript preparation stage, see Figure 2.

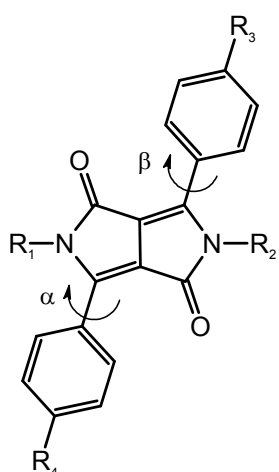
2.3 SOLUBLE SPECTRALLY TUNED DPP DERIVATIVES

For practical applications also other properties than the main functionality are important. Therefore, we combined the spectral tuning with improved solubility to obtain materials for cheap wet solution based production with precisely tuned energetic states (Figure 3 right and Figure 4).

This we investigated in papers [V1] and [V16] where we also discuss further effects like solvatochromism and solid state fluorescence.

2.3.1 Soluble polar DPP derivatives – alkylated

In [V1] we showed also for other electron-donating group (dimethylamin), see Figure 4), that the molar absorption coefficient ϵ increased and was accompanied with strong bathochromic shift. This behaviour implies that charge separation occurs via electron delocalization leading to creation of permanent dipole moment. Blurring of vibration structure in absorption spectra of mono substituted derivatives imply interaction with polar dimethylsulfoxide (DMSO) and shows polar character of the mono substituted DPP [V1].









	R ₁	R ₂	R ₃	R ₄
DPP04	H	H	H	H
DPP09	C ₄ H ₉	H	H	H
DPP10	C ₄ H ₉	C ₄ H ₉	H	H
DPP26	H	H	N(CH ₃) ₂	H
DPP22	H	H	N(CH ₃) ₂	N(CH ₃) ₂
DPP14	H	H		
DPP30	C ₄ H ₉	H		
DPP29	C ₄ H ₉	C ₄ H ₉		
DPP18	C ₄ H ₉	H	Cl	Cl
DPP17	C ₄ H ₉	C ₄ H ₉	Cl	Cl

Figure 4 The structures designed for simultaneous study of spectral and solubility tuning in [V1].

Introduction of the *N*-alkylation led to the decrease of the ϵ and hypsochromic shift. First *N*-alkylation causes only small change, whereas second alkylation lead to the value of ϵ almost similar to the parent, non *N*-substituted, DPP. This decrease is accompanied by the hypsochromic shift and loss of vibrational structure. We proposed the same mechanism as for the *N*-alkylated only derivatives discussed in Chapter 2.1: the *N*-alkylation causes rotation of the phenyls and consequently breaks the molecule symmetry, and hence, the effective conjugation and increases the polarity, see Figure 5.

The introduction of one electron-donating group to the DPP led to a smaller fluorescence quantum yield (PLQY) compared to the *N,N*-disubstituted molecules. This is in accordance with the obtained values of the absorption coefficient: the polarity of the mono-substituted molecule is higher compared to the symmetric ones. The observed higher Stokes shifts for mono substituted than to the di-substituted DPP also confirmed this hypothesis. The *N*-alkylation of the functionalised DPPs by electron-donating or withdrawing groups caused further decrease of PLQY accompanied with increasing Stokes shift similarly to the *N*-alkylated only derivatives.

The calculated molecular parameters of the studied derivatives showed that the substitution of phenyls by donor or acceptor groups has almost no influence on the phenyl torsion angles and the

molecular conformation of the central DPP unit. However, it leads to the bathochromic shift of the absorption and luminescence peaks due to the increased effective extent of the conjugation and support the conclusions drawn above.

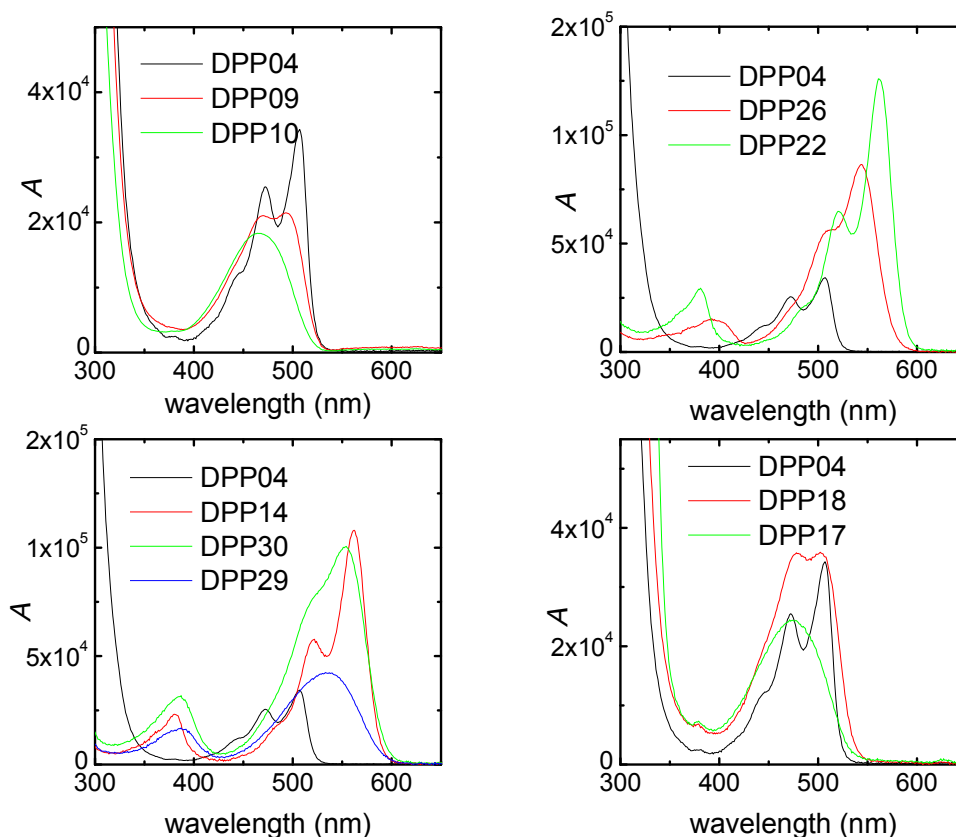


Figure 5 The influence of *N*-alkyl substitution (a), donor substitution (b), combination of donor with *N*-alkylation (c) and acceptor with *N*-alkylation (d) on the DPP on molar absorption coefficient in dimethylsulfoxide [V1].

2.3.2 New soluble polar DPP derivatives – acetated

The derivatives which we introduced in [V3] showed bathochromic and hyperchromic shift of absorption and bathofluoric shift of fluorescence with respect to parent DPP compound invoked above all by piperidino electron donating substituent. Dimethylsulfoxide (DMSO) was found to be the only common solvent able to dissolve all these pigments. In order to make these compounds better treatable we have decided to substitute them on pyrrolinone nitrogens and so eliminate the already mentioned intermolecular hydrogen bonding. On the contrary to more usual *N*-alkylation by alkylhalogen, used in our previous studies [V1, V7], we applied ethyl bromoacetate in this case [V16] (Figure 3). Such substitution was reported only once [69].

As expected, DFT optimized geometries of these new derivatives [V16] predict non-zero dihedral angles, describing phenyl-pyrrolinone rotation, on the contrary to strictly planar precursors studied in [V3]. The computed values of dihedral angles are the result of a compromise between steric effect of methylene and *ortho* phenyl hydrogens (more or less the same for all six derivatives), invoking nonplanarity, and conjugation effect (dependent primarily on *para* phenyl substituent of each derivative), maximal for planar arrangement. Average values are 26°, 36° and 38° for piperidino, cyano and unsubstituted phenyls, respectively.

The absorption maxima of derivatives in [V16] in DMSO show hypsochromic and hypochromic shifts with respect to corresponding precursors in [V3]. Hypsochromic shift is in fact a net effect of three contributions: 1) An increase of excitation energy due the less efficient conjugation because of the loss of molecular planarity, 2) the redistribution of the intensities of vibronic sub-bands from 0-0 maximum of non *N*-substituted DPPs in favour of 0-1 in *N*-substituted, as shown by a successive *N*-alkylation of parent DPP [V1], [V7] and 3) the opposite effect – the decrease of excitation energy due to the increase of electron-donating strength of a pyrrolinone nitrogens in central DPP core composed of two coupled merocyanines (H-chromophore). We consider that the second and third contributions are almost constant over the whole series and the differences in hypsochromic shifts caused by *N*-alkylation go almost exclusively on account of the first one, i.e. the substituent dependent changes in the ground state planarity.

From the shifts of the absorption, it was shown, that the piperidino substitution dramatically decreases the phenyl-pyrrolinone dihedral angles compared to the parent *N*-acetated DPP in accordance with DFT predictions, while cyano substitution increases these angles considerably.

The electron-acceptor (cyano) phenyl substituted *N,N*-dialkylated DPPs show small hypsofluoric shift compared to their non-alkylated precursors, whereas the electron-donor (piperidino) phenyl substituted derivatives show moderate bathofluoric shift.

In combination with the hypsochromic shift of absorption, the Stokes shift is generally increased compared to the precursors we introduced in [V3]. An increment of a Stokes shift increase connected with *N,N*-disubstitution is relatively similar (35 – 39 nm) for all three pairs of piperidino substituted compounds and rather higher (48 – 53 nm) for unsubstituted or cyano substituted pairs.

The main reason for the general increase of the Stokes shift due to *N*-alkylation is caused by the fact, that it is considered as a difference between absorption and fluorescence maxima. The maxima correspond to 0-0 vibronic transition in fluorescence spectra for all twelve compounds we discuss in [V3] and [V16], to 0-0 vibronic transition in absorption for precursors [V1] and to 0-1 transition for derivatives in [V16]. An increase of Stokes shift goes on account of the differences in internal (geometrical) and external (solvent) relaxation, when going from vertical Franck-Condon (FC) state to relaxed excited state. Internal relaxation is probably mainly connected with the changes of above discussed dihedral angles. In order to have a better view on external contribution, we carry out the spectral measurements in other solvents with different (lower) polarity.

The shape of the absorption spectra is the same in all three solvents, i.e. the vibronic structure is completely unresolved even in toluene, while the vibronic structure of fluorescence spectra is best resolved for all compounds in toluene, in which clearly 0-0 vibronic transition is the absolute maximum, and its resolution decreases in acetonitrile and is almost lost in DMSO.

It was shown, that the introduction of piperidino group brings two general trends with respect to excited state relaxation in piperidino substituted compounds: The contribution of internal relaxation is decreased, which well relates with lower rotation of *p*-piperidino-phenyl in FC state, while the external contribution is increased, as the electron-donating substitution changes the intramolecular charge distribution.

All six *N,N*-alkylated compounds also show a relatively high fluorescence quantum yields (ϕ_F) in toluene and the fluorescence decay is strictly monoexponential with lifetimes similar to corresponding non alkylated precursors in DMSO. However, there is a dramatic change for mono-piperidino phenyl substituted compounds when going to polar solvents. The quantum yield of fluorescence is significantly decreased, especially for the push-pull derivative, and the decay is biexponential. It implies that some specific process connected with the excited state intramolecular charge transfer (ICT) must be present.



Figure 6 Polycrystalline samples of I - XII under daylight (top) and fluorescence of the samples of VII – XII under UV irradiation (365 nm) with the same settings of Panasonic DMC-FZ7 camera (bottom) [V16].

Although it is generally difficult to prove, it was argued that such behaviour may be connected with a conformational change in excited state known as twisted intramolecular charge transfer (TICT). According to our opinion, the observable fluorescence in polar solvents comes from the minor portion of excited molecules, for which the charge separating twist did not pass.

All six studied DPP derivatives show pronounced solid state fluorescence (Figure 6), on the contrary to any of their non-alkylated precursors. The fluorescence of symmetrically phenyl substituted derivatives is strong, easily observable by naked eye under UV irradiation. The fluorescence of unsymmetrical cyano and piperidino substituted DPPs is less intense, but observable. Solid-state fluorescence of push-pull derivative is almost not observable partly because of its significantly lower intensity and also as it falls almost fully into the infrared region, where the solid-state fluorescence is quite rare [72].

2.4 MODEL ELECTRONIC DEVICES MADE FROM DPPS

Organic electronic devices based on different types of organic semiconductors (among them also based on the small organic molecules, e.g. DPPs) are the subject of intense research activity. As already mentioned, the only one advantageous attribute of the material used is not enough to build an efficient device and therefore we introduced soluble functionalised derivatives discussed above. The performance of small molecular organic devices has been shown to be highly sensitive to film morphology and processing conditions. Therefore, in our paper [V2] we focused on the role of different preparation techniques on the consequent thin film morphology and corollary the device performance.

Thin films of small molecular semiconductors are usually prepared by means of a variety of complex techniques including physical or chemical vapour deposition, organic molecular beam

epitaxy or solution-based deposition techniques. Often, the solution deposited active layers of devices (e.g. spin cast films) exhibit a high portion of microcrystallites and aggregates whereas the vapour deposition techniques provide high quality crystalline films, characterized by improved charge transport properties compared with those of solution deposited films.

In [V2] we investigated the morphology and properties of thin films made from a group of five DPP derivatives prepared and characterized in [V1, V7]. These derivatives were modified in order to increase solubility required for low cost wet solution-based casting.

We have shown that the thin layers prepared by both spin casting and vacuum depositions were polycrystalline but the shapes and dimensions of crystallites were found to be dependent on the structure of the materials and temperature of the substrate during deposition (T_S). The formation of larger clusters with increasing T_S was described as a thermally activated process where a particle impinging onto the substrate surface can move laterally unless it loses its kinetic energy and finds the energy potential well.

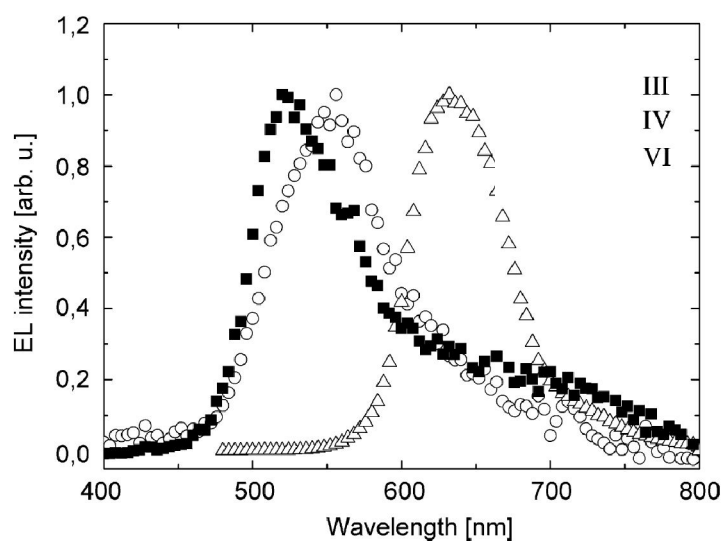


Figure 7 The normalized electroluminescence spectra of symmetrically *N*-substituted DPP derivatives (square: DPP10, circle: DPP12, triangle: DPP29, see Figure 1 and Figure 4) [V2].

The studies we made with different substrates show that the morphology is practically independent on the nature of the substrate. The key impact on the morphology of thin layers was found to be based on the *N*-substitution of central DPP unit by alkyl side chains. The crucial factor is the type of substitution: the unsymmetrical (one substituted alkyl chain) or symmetrical (two substituted alkyl chains). The symmetrically substituted derivatives form planar large crystallites with sizes increasing up to 1 μm , whereas the asymmetrically substituted derivatives form highly rough fiber crystallites, their lengths being up to 1 μm .

On the basis of the findings described above, the symmetrically substituted derivatives resulted as suitable for construction of electroluminescence devices (organic light emitting diodes – OLEDs). The prepared organic diode from the phenyl di-piperidino substituted *N,N*-alkylated DPP (DPP29, see Figure 4) showed that the turn-on voltage for this diode is $\sim 3\text{V}$. At this voltage the previously ohmic nature of the I - V characteristic changes to the space-charge-limited, where the current flow is bulk-limited. The low value of the turn-on voltage implies that reasonable charge balancing was achieved due to the barrier reducing pre-contact layers (PEDOT:PSS and Alq3). This allowed us to measure also the spectrally resolved electroluminescence of several selected derivatives.

The electroluminescence spectra (Figure 7) show that the EL depends on the substitution used rather than on the length of the alkyl chains used, which is in accordance with the quantum chemical calculations and optical spectroscopy measurement [V7, V8].

We also performed comparative study of acid protonation of pyridyl functionalised diketopyrrolopyrrole derivatives. Such derivatives (also with piperidyl or a morpholinyl ring) change their colour after protonation [73]. Since these materials are also semiconductive the protonation can influence their conductivity. The mechanism of the material conductivity change is based on the donor function of protonated quaternary nitrogen in a pyridyl ring. The electron contributes to the conductivity after hydrogen capture.

In [V4] we described influence of acid vapour treatment on DPP thin films by means of changes of UV-VIS spectra, IR spectra and electrical conductivity. UV-VIS absorption exhibits hypsochromic shift and significant growth of the absorption at 580 nm and decrease at 470 nm that results in a colour shift from red to violet. The protonation releases conductive electrons enhancing conductivity in orders of magnitude 10^{-10} to $10^{-6} \Omega^{-1} \cdot \text{cm}^{-1}$. All processes described are reversible and the material can be recovered by annealing at 170 °C. These results were further used to construct hydrogen sensor (not discussed here).

3 LIGHT DRIVEN CURRENT SWITCH

Among other applications which have been already discussed, the organic materials are promising candidates also for future organic electronic devices for new information technologies and nanoelectronics [74], [75]. As an emerging area in organic electronics, polymer memories and switches have become an active research topic in recent years [76], [77]. A molecular switch is a molecule that can be switched between different states upon exposure of an external stimulus, such as temperature, electrical stress, or light. The transformation of molecular switch from one state to another is often accompanied by a change in its conformation or molecular structure, which is accompanied by a rearrangement of the electronic structure. Moreover, the reversible changes in physical or chemical properties of the active switching units can also be transferred to the microenvironment and supramolecular structure, and thus, can induce modifications in their surroundings.

For practical applications the main attention is paid to photo- or electro-induced switching. Optical switching processes are usually based on reversible photochemical reaction. Electrical switching phenomena are usually accompanied by trapping-detrapping, charge transfer, conformational change and redox effects [78], [79]. A wide variety of organic materials, including organic dyes [80]-[83], charge transfer (CT) complexes [84]-[86], conjugated oligomers [87]-[89], redox metal complexes [90]-[92] and other molecules [93]-[96], have been explored for switching and memory applications. The representative class of organic molecules is photochromes. Photochromic molecules have been scrutinized for their potential applications in optical storage [97], [98], electrical switch devices [99], [100], and as molecular wire switches [101], [102]. Despite recent advances in device fabrication and chemical synthesis, organic switching materials are not commercially used in optical storage or electronic switches because of their limitation with respect to the material and technical requirements of such devices e.g. high storage capability and rapid response, high sensitivity in a specific wavelength range, high fatigue resistance, and high optical and thermal stability.

One of the reasons for which the controlled switching of the properties of optoelectronic devices with organic solids is not exploited nowadays is the lack of the understanding of the underlying science that controls the properties of the devices at nano-scale level. In the papers included in this part we aimed to address this fundamental problem.

3.1 CONCEPT OF THE SWITCH

This work deals with design and characterization of light driven electric current switch build from organic materials. The switch is based on a molecular solid build of non-polar polarizable units, e.g. polymer segments, containing a small amount of polar guest species. It is based on the assumption that the dopant dipole moment contributes to the field acting on surrounding molecules and modifies the local values of the polarization energy [100], [102]-[104], [V12]. In the papers included in this part we showed that the presence of polar species results in production of local states in their vicinity; even thus they are not necessarily trapping sites themselves.

The switch consists of a molecular wire with suitable bistable species in their vicinity. The molecular wire can be realised by π - or σ - conjugated polymer chains (A and B parts on the Figure 8) where delocalisation of electrons allows conducting of the electric charge. The active switching molecules should be selected in order to produce large dipole change in its two states as described above (D part on the Figure 8). Optical control of the charge transport can be realised by photochromic molecules such as spiropyrans.

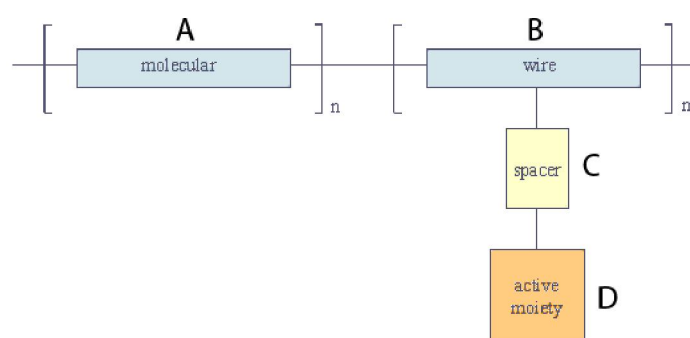


Figure 8 Schematic representation of a molecular current modulator.

Photochromism, which is defined as a light-induced reversible reaction of a molecule [105], gives rise to the formation of photoisomers whose electronic absorption spectra are markedly different from that of the reactant molecule which results into a dramatic colour change. The characteristic that identifies photochromism from other photophysical processes is thermal or light induced reversibility. Photochromic transformations causes not only colour changes but are also accompanied by differences in emission spectra, refractive index, dielectric constant, enthalpy etc. These modifications other than colour changes are intrinsic in photochromic phenomena and thus offer wider possibilities for practical applications of photochromic compounds. These differences in physical or chemical properties can be transferred to the microenvironment or supramolecular structure.

Spiropyrans (SP) consist of two heterocyclic moieties linked together by a common spiro carbon atom. The two parts of the molecule are oriented in two orthogonal planes. The absorption of UV light results in a cleavage of the oxygen–spiro carbon atom bond leading to the formation of a coloured open isomer possessing high dipole moment (depending on substituents) as opposed to the closed form, which is colourless, see Figure). The open form is often called photomerocyanine (MC) because it is similar to merocyanine dye. The MR form reverts thermally to the closed form which manifests itself in bleaching of the samples. Depending on substituents attached to their backbones, these molecules can change their dipole moment from ca 6 D to 12 D [V13].

3.2 OPTICAL PROPERTIES

To understand the behaviour of the spiropyran dopant in the polymeric matrix and their eventual interactions, the non-invasive optical detection of the photochromic reaction is

advantageous. In this chapter we will describe the main outcomes we revealed by optical spectroscopy which are related to the proposed light driven current switch.

3.2.1 Photochromism in thin films

In the paper [V10] we report the results of studies of the photochromic reaction of 6-nitro-1,3,3-trimethylspiro[2H-1-benzopyran-2,2-indoline] (SP) in poly(methylmethacrylate) and in various matrices including π -conjugated photoconductive polymers based on poly(p-phenylenevinylene).

As mentioned earlier, the photochromic reaction of SP causes reversible change between non-coloured and coloured state. The transition can be thus easily studied by optical spectroscopy. The absorption spectra of the PMMA/SP sample prior to and after illumination with UV light are shown in Figure 9. Upon illumination, a new absorption band appears in the 500 – 650 nm region, and the spectrum also changes in 350 – 450 nm region. By thermal relaxation the coloured form reverts to the original state.

In [V10] we used two models for the analysis of the back photochromic reaction. The first model assumes that the photochromic molecules are surrounded by microheterogenous matrix and therefore experience statistically different environment. This results in a distribution of activation energies E_a (assumed to be Gaussian), which control the reaction rates. Such processes can be described by so-called stretched exponential function. This approach assumes that the photochromic molecules are placed in a completely ‘frozen’ medium during the decay.

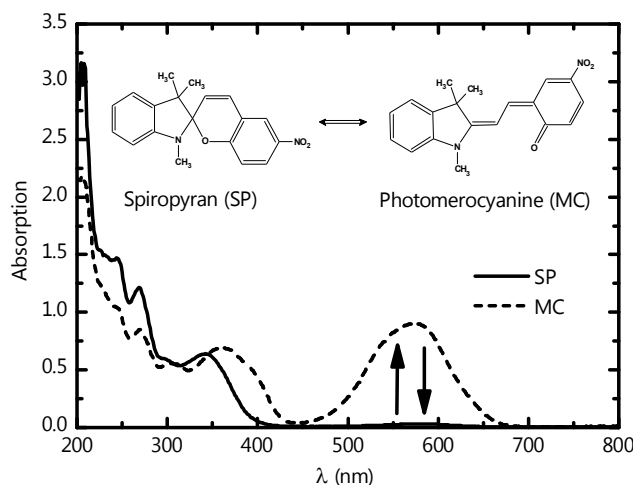


Figure 9 The change in absorption of spiropyrane (SP) after the photochromic conversion in polymethylmetacrylate. The inset depicts the structure of spiropyrane and (photo)merocyanine (MC) forms.

The second theory is based on the assumption that the modification of the first-order rate constant is caused by the relaxation of the surrounding matrix from a nonequilibrium state immediately after the probe reorientation into relaxed state (therefore referred to as the relaxation model) in a comparable time scale as the probe decay kinetics. The initial value of the first order rate constant is thus modified by the matrix relaxation into its final (relaxed) value and the rate of the change is governed by a matrix mean relaxation time.

Assuming a statistical distribution of microenvironments in a frozen matrix (resulting in a Gaussian distribution of activation energies), we obtained the following result: longer times of exposition of UV radiation resulted in higher values of the activation energy and in broader dispersion of the activation energies. Similar conclusions were drawn if the relaxation model is

employed to interpret our data. Exposure to higher irradiation (longer conversion times) led to lower values of the rate constants and consequently to higher activation energy.

It was therefore shown, that the polymer matrix strongly influences the reaction rate, lifetime of coloured species and the value and distribution of activation energies of the bleaching process. Using these outcomes, we were able to correlate the obtained activation energy with parameters revealed from the electrical characterization of the studied switching system [V14].

3.2.2 Fluorescence quenching

Another feature which is useful in order to probe the interactions between two components is fluorescence. If we prepare mixture of the photochromic spiropyran with polymer which is natively fluorescent, we can compass these data either, from the change of the polymer fluorescence, or from the spiropyran fluorescence. The SP form is not fluorescent compared to the MR form which gives us additional sensitivity compared to the absorption.

In the [V9] we observed a decrease of polymer fluorescence after photochromic conversion of spiropyran. Based on these findings, we performed deeper analysis to understand what are the mechanisms which cause such behaviour.

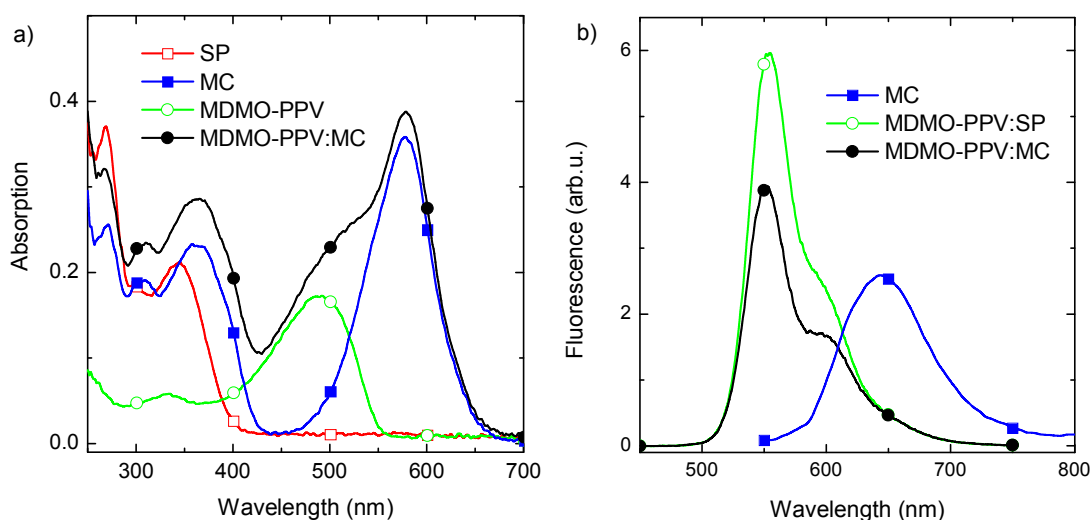


Figure 10 Absorption (a) and fluorescence (b) spectra of $2 \cdot 10^{-5}$ mol/l spiropyran (SP), its metastable photoproduct merocyanine (MC), $5 \cdot 10^{-6}$ mol/l polymer (MDMO-PPV) and mixture of the polymer and merocyanine at the same concentrations ($2 \cdot 10^{-5}$ mol/l SP plus $5 \cdot 10^{-6}$ mol/l MDMO-PPV) before the photochromic conversion (MDMO-PPV:SP) and after (MDMO-PPV:MC) the photochromic conversion in chloroform. Note: The fluorescence of pure MC was 10 times increased for the sake of clarity [V15].

In studies of this phenomenon elaborated in [V15] we chose poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) as the polymer matrix. Absorption and fluorescence spectra in chloroform of the MDMO-PPV, SP and their mixture are shown in Figure 10. Pure SP has no absorption and fluorescence in the visible range and its first absorption band is centred at 330 nm. Light absorption in this range causes a reversible photochromic reaction, producing a metastable photoproduct called (photo)merocyanine (MC). The presence of MC is revealed by a strong absorption peak at ~ 580 nm and fluorescence peaking at 650 nm. The absorption spectrum of pure MDMO-PPV shows a major broad peak of lowest-energy at ~ 490 nm, and a weaker absorption band at about 330 nm assigned to the $\pi \rightarrow \pi^*$ transitions along

the polymer main chain. The further band coincides with the absorption of SP. The polymer is strongly fluorescent with maximum around 550 nm.

Addition of SP into the MDMO-PPV does not influence the polymer fluorescence. However, the formation of MC form causes considerable PPV fluorescence decrease. The observed PL emission of the MDMO-PPV:MC mixtures decreases linearly as the molar concentration of MC increases. It was not possible to explain the drop only by means of simple re-absorption. Using the Stern-Volmer relation we obtained quenching constant $K_{SV} = 1.2 \times 10^4$ l/mol.

This value is rather high showing that there is significant MC induced exciton quenching. Since the measured $\tau_0 = 0.45$ ns, the quenching rate constant k_q equals roughly $27 \times 10^{12} \text{ s}^{-1}$ yielding 40 fs as the speed of quenching. This process occurs so fast, that other processes cannot effectively compete.

To explain this observations we tested several possible mechanisms, e.g. resonance energy transfer, fluorescence quenching and photoinduced charge transfer. The large spectral overlap of the MDMO-PPV emission and the MC absorption suggests that the resonance energy transfer can be responsible for the observed fluorescence decrease. It was shown, that the Förster radius R_0 [106]-[108] obtained from the measured and corrected fluorescence gives value nearly five times higher than the expected one from the electronic spectra. Due to this discrepancy and disagreement in expected and observed behaviour in solvents with different polarity (and also using different derivative of the PPV polymer), this mechanism was refused. The time resolved fluorescence also supported these conclusions.

From the dependence of the Stern-Volmer constant on the temperature, and from the fluorescence lifetime, we have concluded that the main mechanism is the static fluorescence quenching. From the possible mechanism, it was concluded, that the physical origin of the quenching could be the photoinduced charge transfer.

The extent of the photoinduced electron transfer is usually criticised by overall energy change. The reaction has to be energetically favourable, i.e. the energy due to the photoinduced electron transfer has to be released. The energy change is given by the Rehm-Weller equation. Following values were obtained, -0.24 eV for MDMO-PPV:SP and -0.54 eV for MDMO-PPV:MC. If the ΔG is more negative than -0.5 eV, the quenching due to the photoinduced electron transfer is 100% efficient and small change in ΔG does not affect the overall efficiency. Because the ΔG is negative, one would expect that the photoinduced electron transfer occurs in both cases. However, Friend et al previously showed that for PPV based polymers extra “penalty” energy about 0.35eV is needed to separate the exciton into two charges [109]. Only the MC based mixtures thus can undergo the photoinduced electron transfer.

These findings led us to the creation of electronic devices (organic diodes) and for the MDMO-PPV:MC samples, the photocurrent increase was observed. Therefore, because of the fact, that only one form of the spiropyran causes the quenching and that the conversion is light driven, we showed, that the photochromic spiropyran can be utilised for production of switching devices, e.g. fluorescence labels, memories, etc. based of fluorescence quenching. Switching in photocurrent can be further used for construction of electro-optical bistable devices or sensors.

3.3 ELECTRICAL PROPERTIES

In this part we focused on the impact of the photochromic conversion on the electrical and optoelectrical properties of the proposed current switch. The modelled influence of the polar species on the charge transport (Chapter 3.4.) is experimentally characterised.

3.3.1 Capacitance and photocurrent

The results of experimental studies on the modulation of charge carrier (hole) transport in poly[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylene vinylene] (MEH-PPV) doped with the photochromic additive 6-nitro-1',3',3'-trimethylspiro[2*H*-1-benzopyran-2,2'-indoline] published in [V13, V14] are presented in Figure 11.

Because the MEH-PPV is photoconductive, the conductance strongly increases under UV illumination due to the increase of the free charge carrier concentration. However, the UV light simultaneously triggers the SP→MC reaction, with high dipole moment of MR species as discussed previously. According to the theoretical model described in previous chapters, the dipolar species create new charge carrier traps and make the distribution of transport hopping states broaden. These effects lead to a decrease of the charge carrier mobility and free charge carrier concentration. The slow decay of the conductance with time can be ascribed to the formation of local states due to the SP→MC transformation. After the “switch off” of light (see time t_2 in Figure 11) the conductance strongly decreases due to the termination of the number of free charge carriers.

The formation of highly polar species during the UV illumination was simultaneously checked by the capacitance measurements (see Figure 11). After the fast increase at the beginning of the UV illumination, which can be ascribed to the photodielectric effect due to light generation of free and trapped charge carriers, a slower increase was observed. This part of the capacitance kinetics was explained by the formation of polar MC species and the increase of the orientational polarizability. After the “switch off” of light, a fast decay of the capacitance was observed followed again by a slow component. The rates and characteristic parameters of the photochromic processes detected from changes in the capacitance by impedance spectroscopy qualitatively follow the parameters of photochromic changes detected optically.

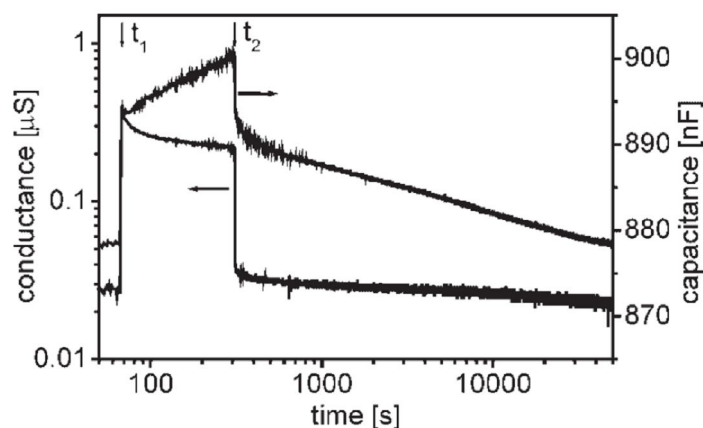


Figure 11 Temporal evolution of the conductance and capacitance of an MEH-PPV sample containing the photochromic SP. The vertical arrows at times t_1 and t_2 indicate “switching on” and “switching off” of the UV illumination, respectively [V13].

3.3.2 Impedance spectroscopy

As a next step we used an impedance spectroscopy to obtain further insight into the studied system [V6]. The real and complex part of the impedance Z_{Re} and Z_{Im} were recorded and analyzed in the form of Cole-Cole diagrams. It was shown, that all the Z_{Im} versus Z_{Re} dependencies formed a single semicircle which increase in size with increasing photon dose, see Figure 12. These single

semicircles were fitted very well to a parallel combination of bulk resistance R_p and capacitance C_p in series with a resistance R_s , which is probably caused by the contact at the hole injecting ITO/MEH-PPV interface. Following this evaluation, Figure 12 clearly demonstrated the increasing parallel resistance of the sample with increasing photon dose, i.e. with increasing concentration of the highly polar MC form.

3.3.3 SCLC spectroscopy

To evaluate the actual change of the charge carrier trapping states and their influence on charge transport we used a Space Charge Limited Current (SCLC) method in [V9]. The SCLC method is differential method which extracts information concerning energy distribution of traps inside the bandgap of semiconducting material from the shape of current (I) vs. voltage (V) characteristic. As the voltage applied to the sample is changed, the charge carrier concentration change in the bulk causes a shift of the Fermi level and the corresponding current. This causes the occupancy of states to change and enables to scan the distribution of energy from the current changes.

Figure 13 shows the influence of the spiropyran photochromic conversion on the current flowing. It shows the experimental I - V characteristic in the bilogarithmic scale. It can be seen that the current is decreased and also that the shape of the dependence has changed. In the first region (0–4 V) the slope of the two characteristics approaches identically to $m \sim 2$, suggesting that the currents are governed by the presence of one shallow trapping level. Above this region the slope increases differently according to their respective density of energy states.

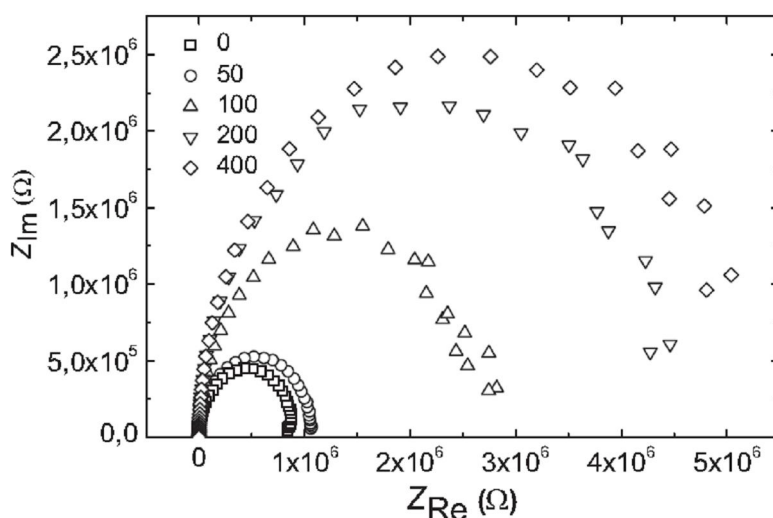


Figure 12 Cole-Cole plot of the 20% mixture of the MEH-PPV:SP before (0 pulses) and after the photochromic conversion for four light doses (initiating the photochromic conversion) expressed as a number of pulses ($1 \mu\text{J}/\text{pulse}$) [V6].

The revealed distributions of the energetic levels from these curves showed a change of the density of states in the bandgap of the polymer. Reversible creation of new trapping level during the photochromic conversion was observed. According to the trap controlled hopping model for the description of charge transport, the presence of new trapping level results in the decrease of the charge carrier mobility as predicted by the theoretical calculations [V9].

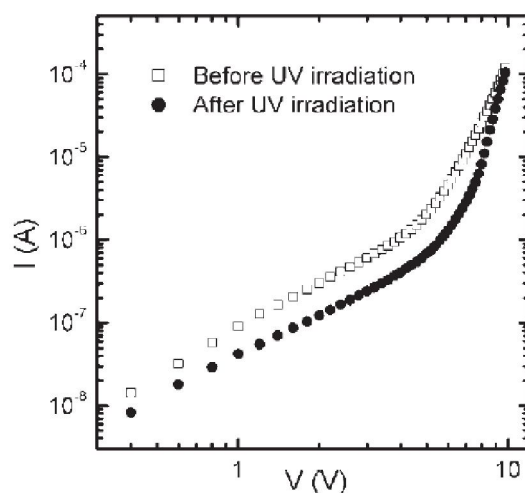


Figure 13 The current-voltage characteristics of the ITO/ PEDOT/MEH-PPV:SP/Al (30% by wt.) sample before (square) and after (circles) the photochromic conversion of spiropyran molecules by irradiation of UV light [V9].

We can conclude that photochromic transformation of spiropyran produced charge carrier traps affecting the electrical properties of the polymer matrix. Thus, an optical signal can be transformed into an electrical one and a polymeric optron can be, in principle, constructed

3.4 QUANTUM CHEMICAL MODELLING

The aim of this part was to predict the influence of the presence of the polar species on the on-chain and inter-chain charge transport in conjugated polymers. The calculations were performed by Dr. Toman from AVČR and are reported in papers [V5], [V9], [V11], [V13].

Polar species in the polymer chain vicinity modify the electrostatic potential due to the charge-dipole interactions. The change of the electrostatic potential shifts the site energies of individual polymer repeating units, and consequently the polymer transport levels are modified. Since the positions and orientations of the polar additive with respect to the polymer chain are essentially random, the effect results in a broadening of the distribution of transport states. The most important parameter of this distribution is its half-width, proportional to the standard deviation $\sigma(\epsilon)$ of the site energies from its average value [V13].

Figure 14 shows a typical diagram of the valence band of the as prepared and doped polymer. An increasing energetic disorder leads to the broadening of the originally sharp valence band edge and formation of the tail states in the gap. These states, owing to their relatively low density and consequently a weak connectivity, behave as hole traps.

From the modified model of Grozema et al [110] follows that the change of the additive dipole moment from ca. 6 D to 12 D (corresponding to the calculated change of the dipole moment during the photochromic reaction $SP \rightarrow MC$) should result in an almost five-fold decrease of the on-chain mobility [V13].

Charge carrier transport in 3D polymeric materials consists of charge moving through the chain (molecular wire) and of inter-chain hopping [111]. The transport states of the both features are usually characterized by geometrical and energetic disorder; thus, the charge moving is influenced by hopping mechanism through the intra-chain states (tail states) and by inter-molecular hops. The energy distribution of the transport states is strongly influenced by the dispersion of polarization energy. It was found that the mobility value can be influenced by doping [112]. Some highly polar additives decrease the value of charge carrier mobility in the doped polymer. The occurrence of

polar species in the polymer material results in the broadening of both types of the energy distribution.

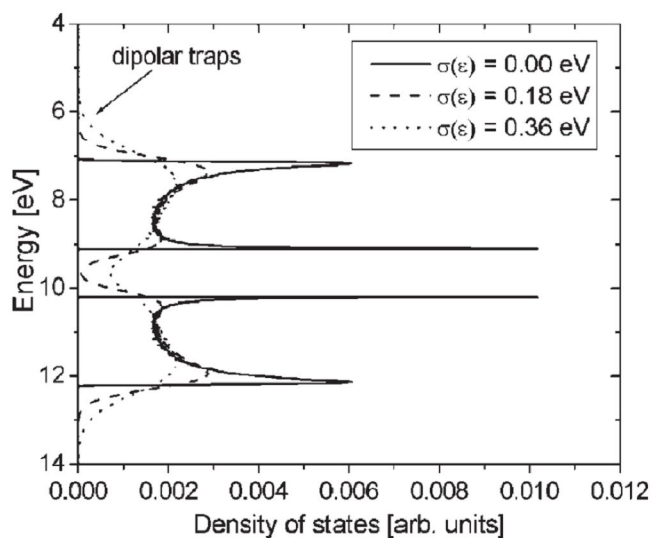


Figure 14 Diagram of the polymer valence band. The value of the energetic disorder is indicated by the standard deviation $\sigma(\epsilon)$. Curve $\sigma(\epsilon)=0$ corresponds to the as prepared polymer and curves $\sigma(\epsilon)=0.18$ and 0.36 eV to the polymer doped with the additives with different dipole moments. If the additive concentration is 0.4nm^{-1} , these values correspond to the additive dipole moments 6 and 12 D, respectively.

In [V5], we introduced a model which assumes the following steps of the inter-chain charge carrier transport: (i) charge carrier moving to any possible state on the initial chain A, (ii) charge carrier thermalization over all its possible states on the chain A, (iii) charge carrier hops to any possible state on one of the four nearest neighbouring chains; the transfer rate is given by the Marcus eq. [V5]. The outcomes shows, that there is a very strong dependence of the mobility on $\sigma(\epsilon_n)$. At lower frequencies, the mobility decreases by two or three orders of magnitude, if the width of the energetic distribution is doubled from 0.09 to 0.18 eV. Such a change of $\sigma(\epsilon_n)$ can be achieved by the change of the additive dipole moment.

The conclusions thus support the experimentally obtained findings. The SP \rightarrow MC conversion should be therefore capable of significant change of charge carriers mobilities.

4 SUMMARY

The habilitation thesis deals with design and characterization of new materials and devices for various applications in organic electronics. To understand the fundamental principles important for advanced applications the materials were studied by wide range of optical, optoelectrical and electrical experimental methods. These studies brought significant knowledge about the relation between the structure and related properties.

In the papers included in this thesis we have shown that by suitable modification of the diketopyrrolo-pyrrole it is possible to prepare advanced materials for organic electronics. The first studied relation was the influence of the chemical structure on the solubility. By theoretical modelling and experimental characterization we described that the *N*-alkylation cause molecule rotation and subsequently perturbation of intermolecular π - π interactions and *H*-bonds. Interestingly, the high fluorescence quantum yields were conserved while the solubility was improved dramatically. We have successfully tested these derivatives for utilization in organic light emitting diodes.

The second relation was the influence of the introduction of the electron donating and withdrawing groups on the diketo-pyrrolo-pyrrole molecule. We showed that the addition only of these groups in the para position on phenyls does not substantially influence the molecule planarity and thus the effective conjugation. By this approach, we prepared and tested new derivatives with seriously high absorption coefficients for organic photovoltaics. As this procedure influences also the fluorescence spectra, we showed that it allows for preparation of derivatives with desired colour of emission, so called multicolour emission by substituent tuning.

Studies of interaction between organic semiconductor and photochromic dopant provided results demonstrating the possibility of reversible formation and annihilation of charge carrier traps in molecular materials. Optical and electrical studies of the photochromic reaction of spiropyran revealed that the photochromic transformation of spiropyran produced charge carrier traps affecting the electrical properties of the polymer matrix, capacitance and photoconductivity in particular. Using further optical characterization we showed that photochromic reaction is strongly influenced by energy transfer processes between the conjugated chain and photochromic additive. These observations of the switching activity were supported by quantum chemical calculations. We showed that the increasing disorder destroys the resonance between energies on adjacent sites, and therefore limits the charge carrier motion. By this approach we constructed light driven electric current switch.

The author's work received so far more than 50 citations (without self-citations) during the 6 years of research. The work has been therefore recognized and the number of citations increases each year.

5 PAPERS INCLUDED IN THE HABILITATION THESIS

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ABSTRACT

This thesis gathers together the main results published in 16 papers by the applicant from 2005 to 2011. Following short introduction, the first part is devoted to the study of new materials exclusively designed and synthesised for their utilisation in organic electronics, covering organic photovoltaics, organic light emitting diodes (OLEDs), organic field effect transistors (OFETs), gas sensors etc. These materials were studied mainly by optical spectroscopy as exemplified by absorption and fluorescence spectroscopy and time resolved spectroscopy. The main aim was to describe the dependency between the chemical and physical structure of the materials and the important properties for the respective applications.

The next part deals with the issue of construction and characterization of systems capable of light-driven switching of electric current. The discussed electro technical element uses properties peculiar to the organic materials which do not have counterpart in the traditional inorganic semiconductors. The devices were studied by optical, optoelectrical and electrical methods. The published work proved that the presence of the photochromic additive significantly influences the charge carrier transport, as predicted by quantum chemical calculations, and that it is possible to construct such device.

ABSTRAKT

Tato práce shrnuje podstatné výsledky vědecké činnosti předkladatele publikované v 16 člancích v odborných periodikách od roku 2005 do roku 2011. Po krátkém úvodu se práce v první části zaměřuje na studium nových materiálů cíleně navržených a připravených pro použití v aplikacích organické elektroniky jako jsou organické solární články, organické světloemitující diody, tzv. OLED, organické transistory řízené elektrickým polem (OFET), detektory plynů apod. Tyto materiály jsou studovány převážně optickými spektroskopickými metodami jako je absorpční a fluorescenční spektroskopie, časově rozlišená spektroskopie a další. Cílem je popsat vliv chemické a fyzikální struktury těchto nových materiálů na jejich sledované vlastnosti s ohledem na příslušnou aplikaci.

V další části autor rozpracovává problematiku konstrukce a charakterizace modelového systému světlem řízeného proudového spínače. Tento systém využívá unikátních vlastností organických materiálů pro konstrukci elektrotechnického zařízení, které nemají analogii v tradičních anorganických polovodičích. Zkoumané modelové struktury jsou zkoumány jak optickými, tak optoelektrickými a elektrickými metodami. V autorem publikovaných člancích zahrnutých v této práci bylo prokázáno, že přítomnost fotochromního aditiva ovlivňuje transport náboje a že tedy lze takovouto součástku, popsanou nejprve teoreticky, skutečně zkonstruovat.