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ORGANICKÉ MATERIÁLY PRO MOLEKULÁRNÍ ELEKTRONIKUA FOTONIKU

ORGANIC MATERIALS FOR MOLECULAR ELECTRONICS AND PHOTONICS

AUTOREFERÁT DIZERTAČNÍ PRÁCE
SUMMARY OF DOCTORAL THESIS

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CONTENT

1 INTRODUCTION

Semiconducting properties and wide range of different derivatives make organic materials to be very promising substitution of inorganic semiconductors for applications in optical and electronic devices. Low cost of the device production is the main reason, why modern technologies tend to prefer organic materials over silicon for use in the semiconducting devices such as solar cells. Even though they have not yet reached the efficiency and lifetime of silicon, in many cases their usage brings new advantages, which silicon solar cells cannot offer. Thin film organic solar cells can be made mechanically flexible, light transparent and can also work in the interiors thanks to their higher light absorbance efficiency. The solubility and printability enables to produce large area devices for a low price. Furthermore, compared to silicon, thin film organic devices are easier to dispose at the end of life.

This work is focused on the structure and properties relationship of diketopyrrolopyrrole (DPP) derivatives, considering their potential application in organic electronics. In the theoretical part, the current knowledge in the field is researched and briefly summarized. Aim of the experimental work was to introduce and characterize novel DPP based materials, to study them from the perspective of structure-properties relationship and suggest the most effective ways of their application.

Formally the thesis is, based on article 42 of paragraph 1b of The Study and Examination Rules of BUT, designed as thematically arranged set of published works and works accepted for publication.

Results of the experimental work were published within 7 scientific papers and 11 conference contributions. Experimental part consists of 6 selected papers, which focused on 2 groups of DPP derivatives and methods of their applications in organic photovoltaics. Brief introduction to each of the publication is accompanied with evaluation of author's personal contribution.

2 GOALS OF THE THESIS

The general aim of this work was to study the relationship between the molecular structure of selected DPP derivatives and their properties related to their possible application in organic electronic devices, especially solar cells. Therefore, several particular tasks were defined to reach the aim:

- Study novel DPP based materials, which could be used in organic photovoltaics
- Perform optical and electrical characterization of pure materials
- Discuss structure-properties relationship
- Study interactions with commonly used acceptor material
- Prepare and study OSC device prototypes
- Study performance of particular material in OSC system and discuss influence of molecular structure
- Optimize OSC prototypes
- Study alternative methods of OSC optimization
- Optimize alternative methods of thin film deposition

Diketopyrrolopyrrole based materials have a great potential for organic electronics exploitations, therefore one aim of this work was to search for novel DPP based materials, which could be used in organic photovoltaics. One of the challenges is to create the active layer, which would absorb maximum of incoming irradiation. For this is important to find the material with high molar extinction coefficient, and also covering the widest part of solar spectrum, in the ideal case complementary part of spectrum to the used acceptor. To fulfil this demand, pure materials, as well as mixtures with acceptors, were studied by optical measurements. Interactions between donor and acceptor can also be studied by optical methods, therefore fluorescence lifetime and its quenching by the acceptor materials was studied by time-resolved fluorescence.

Charge carrier mobility of pure material was studied by electrical characterization and gives important view into materials behaviour. Charge carrier mobility must be not only high enough, but also balanced between donor and acceptor, to reach efficient charge transfer across the bulk.

Detailed characterization of pure material, both optical and electrical, is the way to get a view into structure-properties relationship, which is crucial for the future possibility of tailoring novel derivatives.

Studied materials based on DPP mainly maintain function of the donor material within organic solar cell. Thus important is to study the interaction with commonly

used acceptors, which are still mainly $PC_{60}BM$ and $PC_{70}BM$. Interactions were studied by optical methods in both solutions and thin films. Main sign of interaction is the fluorescence quenching. Kinetics of the quenching also helped to get the complete picture. Those processes were studied by time resolved optical spectroscopy.

Mentioning interactions between donor and acceptor material and their ratio in the active layer of OSC is one crucial parameter to be optimized. However numerous other variables also influence the OSC performance. Challenging task was to optimize OSC performance regarding all possible variables: type of donor, type of acceptor, their ratio, thin film thickness, method and conditions of deposition, substrate treatment prior the deposition, thermal or solvent treatment of the active layer after deposition, evaporation of electrodes, presence, type and deposition conditions of additional layers in OSC structure.

Important is not only to bring the prototype structure with high “record breaking” efficiency, but also to bring a novel approach, which could simplify of reduce the price of the process of OSC production, together with possibility to produce within the large scale. As one of the alternative deposition methods, spray coating was described and optimized.

3 RESULTS

3.1 RESULTS OVERVIEW

Thematically, work during PhD studies can be divided into following groups:

- Materials based research
    - Diphenylamino stilbene derivatives of diketopyrrolopyrrole
    - Thiobenzofuran derivatives of diketopyrrolopyrrole
- Application based research
    - Alternative methods for thin film deposition of BHJ layers
    - Methods of solar cell optimization

Results of the experimental work were published within 7 scientific papers and 11 conference contributions. Experimental part consists of 6 selected papers, which focused on 2 groups of DPP derivatives and methods of their applications in organic photovoltaics. Besides this work a variety of other materials were characterized, as well as processing and optimization methods. However, in order to keep concept of this thesis, only results which were published by the author, within the scientific journals are included in this thesis.

3.1.1 Material-based research

1.1.1.1. Diphenyl-amino-stilbene-diketo-pyrrolo-pyrrole derivatives

Study of DPP based molecules containing diphenylamino stilbene was set in cooperation with Centre for Organic Chemistry Ltd, Rybitví. Within this work, numerous DPP based molecules containing diphenylamino stilbene were characterized. Author performed extensive optical study of available molecules and consider the possibility of their further usage. As a result, 4 derivatives were chosen to have potential for application in organic photovoltaics.

All four materials (*Fig. 1*) show wide structureless absorbance band with maxima 490 nm, resp. 520 nm, which responds to the non-planar conformation of N-alkylated DPP. Red shift of 25 nm, respectively 27 nm could be observed between symmetrical and asymmetrical derivatives and can be assigned to conjugation length. Influence of different solubilizing side chain is negligible, because of the molecular distances, intermolecular interactions do not play significant role. In weakly polar toluene, all studied materials showed strong fluorescence in solution, with considerable stokes shift of about 90 nm.

In a thin film, absorbance of each derivative showed apparent bathochromic shift due to the intermolecular interactions in the solid state. Unlike the solutions, a slight red shift between the molecules with ethyl acetate and ethyl-hexyl acetate N-alkylation (DPP 1 vs DPP 3 and DPP 2 vs DPP 4) was observed, which indicates that the solid state planarity decreases within the branched solubilizing chain reducing thus the length of the conjugated system.

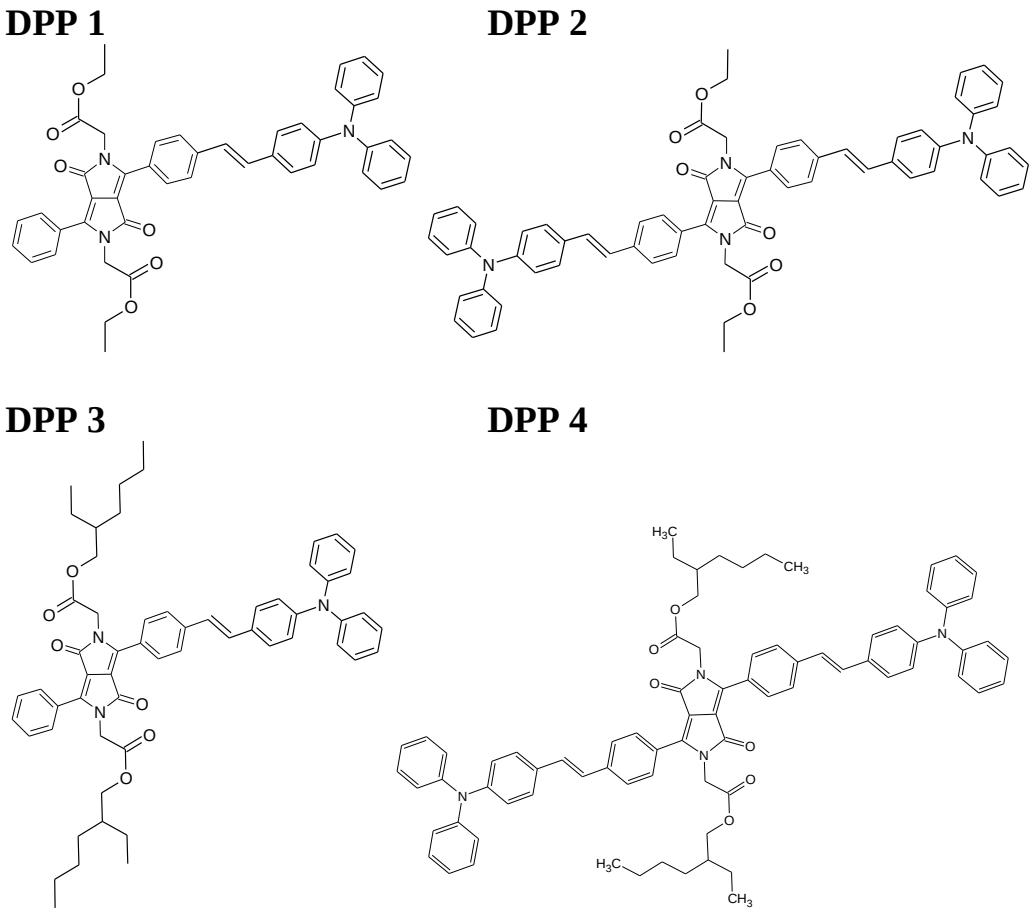

Fig. 1 Derivatives of diketopyrrolopyrrole containing diphenylamino stilbene group. Structures differes in solubilizing groups and also molecular symmetry. DPP1 and DPP3 are D-π-A type, while DPP2 and DPP4 are D-π-A-π-D pattern.

This difference also projects into solid state absorbance edge, and shows, that shorter solubilizing chain has ability to lower the optical bandgap.

For the thin film of symmetrical derivatives (DPP 2 and DPP 4) there is only 4 nm difference in the solid state absorbance maxima and 0,01 eV difference in the optical band gap, whereas for asymmetrical derivatives (DPP 1 and DPP3), those differences are higher, 11 nm within solid state absorbance maxima and 0,17 eV in optical bandgap. Results show that longer and branched ethyl-hexyl acetate N-alkylation has more significant effect on asymmetrical derivatives, because the phenyl on one side of DPP core is more susceptible to the rotation, so that the loss of planarity destabilizes the molecule and shorten conjugated system.

Measured hole mobility was by 2 orders lower than optimal for donor OSC, because the absence of thiophene in the structure enables rotation of the individual molecular building blocks (intermolecular π–π interaction is weaker) and thus high charge carrier mobility is barely reachable.

In general, higher charge carrier mobility can be observed for symmetrical derivatives than for the asymmetrical ones. This effect can be ascribed to the longer

conjugated chain and corresponds well with the results of optical measurements. The short solubilizing chain undoubtedly has a positive effect and improves the hole mobility; for a symmetrical derivative, the improvement is of only about 40 %, but for the asymmetrical one, an increase of almost three orders of magnitude was found. The main reason is probably the morphology as the branched ethyl-hexyl acetate chain causes rotation and thus shortening of the conjugated system. Phenyl compared to the DPA stilbene group is more susceptible to rotations, so this effect is more emphasized in asymmetrical derivatives.

The trend shown in the field effect measurements was confirmed within the current voltage measurements. DPP 2 with the highest carrier mobility exhibited the highest photocurrent, as the J_{sc} corresponds with the charge carrier mobility. Also, the external quantum efficiency was higher throughout the whole spectrum.

Symmetrical D-π-A-π-D type molecules always exhibited better photovoltaic and mobility parameters. Comparison of 2-ethyl-hexyl acetate and ethyl-acetate N−alkylation showed an interesting effect: shorter solubilizing chain has been proved to provide better molecular planarity, and therefore higher mobility. For bulk-heterojunction devices, the domains formed on their surface are smaller and the surface is smoother. Combination of the above mentioned parameters results in a better fill factor, current and efficiency within the prepared solar cell prototypes. The effect of the solubilizing chain was more significant for asymmetrical molecules, where a 2-ethyl-hexyl acetate chain led to destabilization so crucial that domains created in the thin film were about 20 times larger than in other materials. Large domains lead to low charge carrier mobility, which affected the total photovoltaic performance. On the other hand, higher V_{oc} was observed if DPP 4 was used as a donor. DPP 4 compared to DPP 2 has a lower HOMO level and bigger bandgap, which increase the V_{oc} level in general. Also, the longer and branched side chain leads to a surface with slightly higher RMS and improves the phase separation. However same effect could not be observed for DPP 3, where combination of asymmetrical molecule and long solubilizing chain led to loss of planarity and drop in all parameters.

Using of $PC_{70}BM$ instead of $PC_{60}BM$, as an acceptor material, lead to an improvement of all parameters, except from the fill factor. Therefore the mobility of the donor material is probably the most limiting factor for all four thiophene-free materials.

Results summarized within this chapter were published within the scientific papers P2 and P5, which are listed and commented below.

2.1.1.1. Thiobenzofuran derivatives of diketopyrrolopyrrole

Study of DPP based molecules containing thiobenzofuran group was set in cooperation with Centre for Organic Chemistry Ltd, Rybitví. Author performed extensive optical study of available molecules (*Fig. 2*) and discuss the possibility of their further usage.

Optical properties were studied in form of solutions in different solvents (chloroform, toluene, DMSO) and in the thin film, including absorbance spectra, emission spectra, time resolved fluorescence and fluorescence quantum yield. Behaviour of material as a donor, while mixed with accepting material, was also studied. Solar cell prototypes were prepared and optimized for each material.

Author studied effect of different solubilizing chain, comparing previously published derivative substituted with ethyl-hexyl, and two novel derivatives substituted by ethyl-hexyl acetate, and diethyl acetal solubilization groups. Other studied derivatives, based on the ethyl-hexylated TBFu DPP, were synthetised with longer conjugated chain, bithiophene benzofuran and hexylbithiophene benzofuran (DPP D and DPP E). Since solubility of DPP D was very low and derivative could not be used for solution-based process, DPP E was synthetised with additional hexyl solubilizing chain. Assymetrical derivative (DPP F) was also studied, with phnely instead of one thiobenzofuran group.

Out of three $(TBFu)_2DPP$ derivatives with different solubilizing chains, ethyl-hexylated derivative exhibit absorbance maxima of 629 nm in the chloroform solution and 670 nm in the thin film. Both alternative polar solubilizing chains caused red shift of a few nanometers, which was slightly more remarkable for diethylacetal chain (622 nm and 615 nm respectively). Same effect was observed in emission spectra. In general, this effect was almost negligible and neither in the thin film, nor the lifetime of the excited state, difference was observed.

Within DPP A, the change of absorbance of the thin film after thermal annealing was the most pronounced, the intensity of absorbance in the area of main peak increased dramatically. On the other hand for DPP B there was not change observed between the absorbance of annealed and not annealed thin film. Therefore during the thermal annealing, important change in molecular organization occurred for DPP A, while DPP B stays unchanged. It can be concluded, that an optimal donor phase arrangement for DPP B is formed immediately during casting, improving thus a phase separation.

Remarkable red shift was observed for asymmetrical molecule (derivative DPP F), which has the shortest conjugated system. In the thin film then, presence of phenyl led to rotation and loss of molecular planarity.

On the other hand, both derivatives DPP D and DPP E with longer conjugated chain exhibit blue shift and wide absorbance peak with maxima of 647 nm and absorbance edge of 730 for solution and 790 in a thin film. Also molar absorbance coefficient is the highest for molecules with the longest conjugated chain.

Regarding electrical characterization, the highest efficiency was reached using derivative DPP A. Although PCE of the reference ethyl-hexyl alkylated DPP(TBFu)2 was not exceeded by the materials with electrophilic side chains, obtained efficiencies were reasonable, concerning the higher reaction yields in the case of alkyl esters, which makes considered materials promising for potential use.

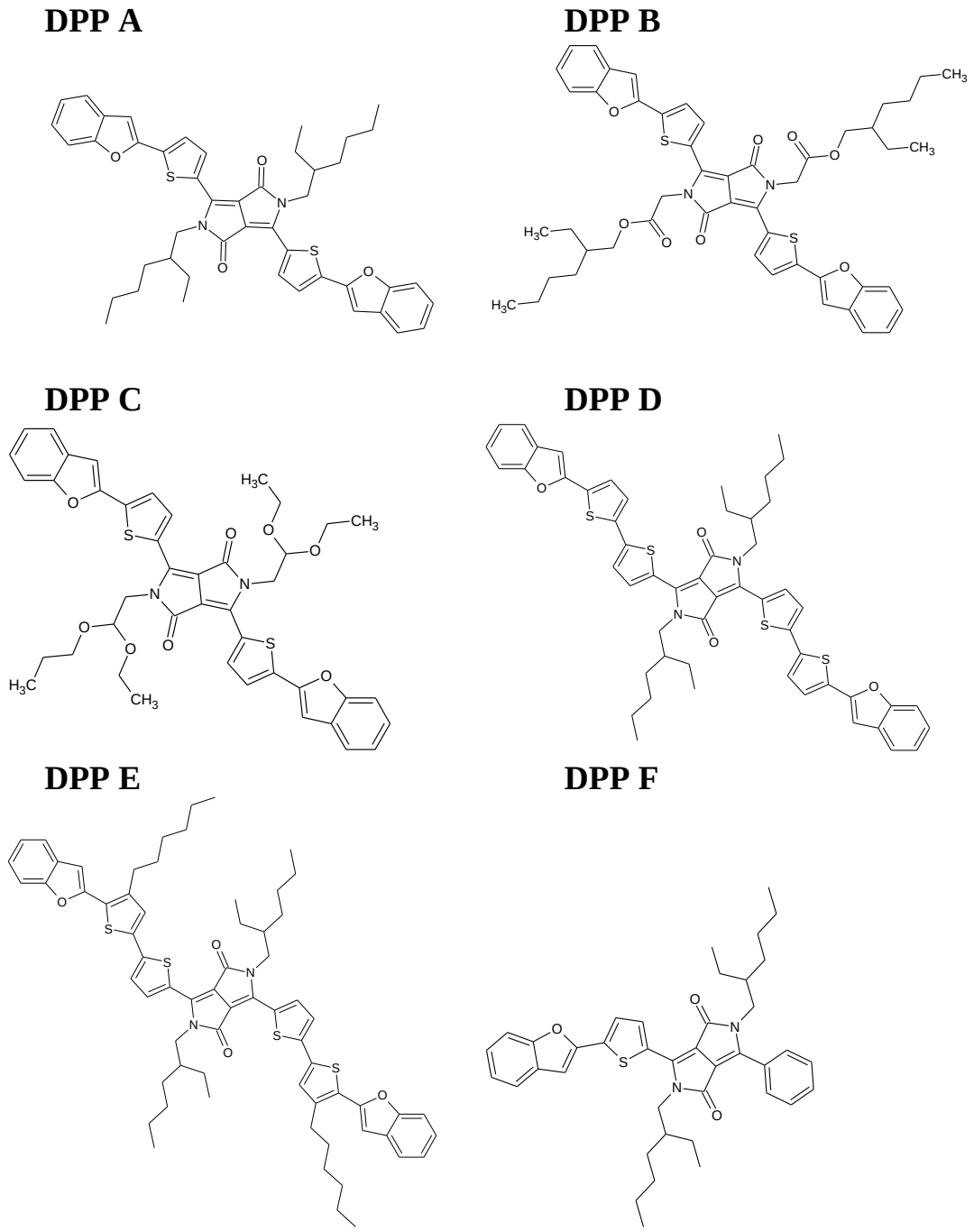

Fig. 2 Structures of thiobenzofuran based DPP derivatives. Derivatives A, B and C differ from each other in solubilizing chain, derivative E contain additional thiophene ring, while DPP F is soluble (hexylated) alternative. DPP F is asymmetrical derivative containing phenyl instead of thiobenzofuran unit.

The substitution of widely used ethylhexyl with ethyl-hexyl acetate solubilizing groups thus enables a formation of an appropriate bulk-heterojunction without the thermal annealing. Corresponding to no change in absorbance spectra of the annealed and not annealed thin film, OSCs using DPP B as the donor exhibit good power-conversion efficiency even without any thermal treatment. This effect poses a

potential for cheap and easy processing of BHJ solar cell and can be advantageous if thermally unstable materials are used in a fabrication of OSC. This fact, together with above mentioned better reaction yields, makes the ethylhexyl acetate side-chain promising for further studies.

Derivative DPP D was not used because of its extremely low solubility, but with soluble alternative DPP E was reached efficiency of 3,73% and fill factor of 55.6%. This material, similar to DPP B, was showing interesting performance already without any thermal treatment, but with gradual annealing, the reorganization within the structure led to very high fill factor.

Asymmetrical molecule (DPP F) was not further studied, because domains created in the thin film (studied by AFM) were too big, resulting from the molecular rotation. Also the band gap of this material was very high, thus no promising results were expected.

Results summarized within this chapter were published within the scientific papers P4 and P6, which are listed and commented below.

3.1.2 Application based research

One important part of research connected to diketopyrrolopyrrolo based materials is the effort to find the optimal way of their application. Efficiency of final application depends not only on the molecular structure of used donor, but also on the way of deposition, thermal treatment, additional layers within the solar cell structure, kind of used acceptor molecule and ratio of donor:acceptor within the bulk heterojunction.

3.1.1.1. Methods of solar cell optimization

3.1.2.1.1 Gradual annealing

New method of gradual annealing was introduced. Author had studied this method on OSCs using thiobenzofuran based DPP donors. It was discovered, that while using gradual increase of temperature, above mentioned solar cells can not only sustain higher temperatures but also reach higher PCE values when temperatures up to 140 °C were applied. Studied devices exhibit highest PCE within direct annealing of 110°C, applying of higher temperature directly lead to lower PCE. On the other hand, applying gradual increase of temperature resulted in PCE increasing up to 140°C and reaching higher absolute value. Increase of the PCE during the annealing is observed due to the fill factor increase, which is influenced by the series resistance decrease. This observation can be related to the changes in contact/BHJ interface population during the annealing process.

Results summarized within this chapter were published within the scientific paper P4, which is listed and commented below.

3.1.2.1.2 MoO_3 as a hole transporting layer

Evaporated 10 nm thin layer of MoO_3 was used as an alternative material for hole transporting layer. It is known, that in some cases, using MoO_3 instead of PEDOT:PSS can improve OSC performance [1].

During the experiment studying gradual annealing, thermal degradation of devices using PEDOT:PSS as a hole transporting layer was observed. Since PEDOT:PSS is known to sustain even higher temperatures, this phenomenon can be associated with the donor-acceptor morphology and PEDOT:PSS/ DPP(TBFu)2 interface degradation. It was demonstrated that MoO3 anode contact advantages in case of the OSCs based on DPP(TBFU)2, where more thermally stable interface of active layer and anode contact allows using higher annealing temperatures resulting in higher efficiencies in comparison with PEDOT:PSS.

Results summarized within this chapter were published within the scientific paper P4, which is listed and commented below.

3.1.2.1.3 Inserted fullerene cathod

Due to the better stability over the lifetime, OSC devices with inverted architecture are in the centre of interest. However, due to the lower efficiency, solar cells based on small molecules donor materials are still underrated. Lower efficiency is mainly caused by low fill factor, which is connected with low fullerene population on the cathode.

Inserted 10 nm thin layer of C60 leads to rapid increase of fill factor factor together with slight increase of short circuit current and therefore increase of the efficiency to contemporary record value with DPP(TBFU)2 donor material. Slight decrease of V_{oc} was observed, due to the difference of LUMO levels of $PC_{60}BM$ and C_{60}.

Results summarized within this chapter were published within the scientific paper P6, which is listed and commented below.

4.1.1.1. Alternative methods for thin film deposition

For the fabrication of OSC prototypes spin coating is usually succesfully used to get the best morphology of bulk heterojnction. However, spin coating cannot be used for unsoluble materials and it is not suitable for large scale production. Therefore vacuum deposition and spray deposition were studied.

3.1.2.1.4 Vacuum deposition

Vacuum deposition is method widely used in OSC preparation, but it is mostly used only for deposition of anorganic layers. It is advantageous to use vacuum deposition also for organic layer,so that complete multilayer device can be prepared within one vacuum cycle. Vacuum deposition brings the main advantage in possibility to deposit insoluble materials. Even bulk heterojunction can be created by co-deposition and deposition rate regulates the donor:acceptor ratio within the heterojunction. Vacuum deposition enables to precisely control requirements placed

to the properties of thin film, e.g. film homogeneity, thickness uniformity and roughness. Since modern organic semiconductor devices are designed as stacked organic/inorganic thin film, very important is also the capability to create whole multilayer structure in the same vaccum cycle. Vacuum deposition also enables easy preparation of multijunction cells [2].

Author optimized the process of vacuum deposition of DPP(TBFu)2 as a donor, as well as mixture with acceptor C60 to create the bulk heterojunction via co-deposition method and deposition of anorganic layers used in OSC structures, aluminium, calcium and MoO_x.

Results summarized within this chapter were published within the scientific papers P1, P2, P4, P5 and P6, which are listed and commented below.

3.1.2.1.5 Spray coating

Spray coating as solution-based deposition method is suitable for large scale production. Unlike the widely used spin-coating, sample does not have to rotate. Furthermore, it is possible to move the substrate and to cover large area or more substrates in a short time, from one store tank.

Within this work, homogenized spray deposition was introduced. During the homogenization, deposited mixture was mixed with the hot air with temperature of 30-70 °C.

Since this method is very variable and many parameters can be changed, also numerous parameters had to be optimized to reach homogenous layer. Huge amount of material had to be used, therefore optimization was started with PPV polymer to adjust the most volatile parameters of deposition. Among adjusted parameters was: movement of the substrate and its speed, temperature of the substrate, substrate treatment prior spraying, concentration of material in base solution, number of sprayed layers and annealing, both thermal and solvent. Reaching homogenous thin film of PPV, applicable in OSC, using of $DPP(TBFu)_2$ started to be reasonable and optimization continue with this donor material, later on also as a mixture with acceptor. However, this research is still in very beginning and it would take longer time to prepare device with efficiency comparable to spin coated device.

Results summarized within this chapter were published within the scientific paper P3, which is listed and commented below.

3.2 LIST OF MANUSCRIPTS COMPRISING THE THESIS

[P1] GEORGIEV, Y, I ZHIVKOV, T TAKOV, G ANGELOV, R PRIKRYL, S STRITESKY, **J HONOVA** a M WEITER. Vacuum-deposited diphenyl-diketo-pyrrolopyrroles structures with photoelectrical applications. *Journal of Physics: Conference Series* [online]. 2014, 514, 012005-. DOI: 10.1088/1742-6596/514/1/012005. ISSN 1742-6596.

[P2] FREBORT, Štěpán, Martin VALA, Stanislav LUŇÁK, **Jana HONOVÁ**, Tomáš MIKYSEK, Zdeněk ELIÁŠ a Antonín LYČKA. Diphenylamine end-capped diketopyrrolopyrroles with phenylene–vinylene conjugation extension. *Tetrahedron Letters* [online]. 2014, 55(17), 2829-2834. DOI: 10.1016/j.tetlet.2014.03.080. ISSN 00404039.

[P3] MILENKOV, V, **J HONOVA**, I ZHIVKOV, R YORDANOV, M VALA, D MLADENOVA a M WEITER. Aerosol flow homogenization in the spray polyphenylene vinylene thin film deposition. *Journal of Physics: Conference Series* [online]. 2014, 514, 012006-. DOI: 10.1088/1742-6596/514/1/012006. ISSN 1742-6596.

[P4] KOVALENKO, Alexander, **Jana HONOVÁ**, Martin VALA, et al. Effect of the Side Chains and Anode Material on Thermal Stability and Performance of Bulk-Heterojunction Solar Cells Using DPP(TBFu) 2 Derivatives as Donor Materials. *International Journal of Photoenergy*[online]. 2015, 2015, 1-9. DOI: 10.1155/2015/734917. ISSN 1110-662X.

[P5] **HONOVÁ, Jana**, Stanislav LUŇÁK, Martin VALA, Stanislav STŘÍTESKÝ, Ladislav FEKETE, Martin WEITER a Alexander KOVALENKO. Thiophene-free diphenyl-amino-stilbene-diketo-pyrrolo-pyrrole derivatives as donors for organic bulk heterojunction solar cells. *Chemical Papers*[online]. 2016, 70(10), -. DOI: 10.1515/chempap-2016-0068. ISSN 1336-9075.

[P6] KOVALENKO, Alexander, Ivaylo ZHIVKOV, Patricie HEINRICHOVA, Jan POSPISIL, **Jana HONOVA**, Martin VALA a Martin WEITER. Reducing Recombination Processes in the Inverted-Solution-Processed Small-Molecule Solar Cells by the Inserted Fullerene Cathode. *IEEE Journal of Photovoltaics* [online]. 2016, 6(4), 1051-1054. DOI: 10.1109/JPHOTOV.2016.2557062. ISSN 2156-3381.

3.3 COMMENTS TO THE ENCLOSED MANUSCRIPTS

3.3.1 P1: Vacuum-deposited diphenyl-diketo-pyrrolopyrroles structures with photoelectrical applications

Aim of this work was to prepare and study functional multilayer OSC device, which would be fully prepared by vacuum deposition, using only one vacuum cycle. Devices with DPP(TBFu)$_2$:C60 bulk heterojunction layer of about 100 nm thickness were prepared by vacuum deposition within 1 cycle and encapsulated in an inert atmosphere. Devices were studied by photoelectrical measurements and SEM.

Evaluation of personal contribution

Author prepared samples for deposition. Sample preparation took place in the clean room class C, to prevent the dust and particles from disrupting the thin layer. Samples before the encapsulation of the structures were manipulated within the MB-200B MBRAUN glovebox. Author performed encapsulation of the samples. Author assisted with the electrical measurement setup. Keithley 6517A electrometer voltage source; monochromatic light was produced by an LSH502 LOT-Oriel halogen lamp and an MSH101 LOT-Oriel monochromator. Author wrote the introduction, and contributed with part of results and discussion chapters of the paper.

3.3.2 P2: Diphenylamine end-capped diketopyrrolopyrroles with phenylene–vinylene conjugation extension

Aims of this work were to synthesise and characterize diketo-pyrrolo-pyrrole derivatives containing diphenyl-amino group, connected by the stilbene bridge to the diketo-pyrrolo-pyrrole core, and to consider the potential of their application in OSC. Two extended DPP pigments have been synthesized by a direct base-catalysed reaction of an aromatic nitrile and succinic, and pyrrolinone esters. Their highly soluble derivatives were prepared by alkylation using a branched ester of bromoacetic acid. Prepared structures were confirmed by NMR spectroscopy and their electrochemical properties were studied by cyclic voltammetry. Based on electrochemical and spectral properties authors concluded, that materials can be used as electron donor materials for photovoltaics. Therefore basic prototypes of solar cells were prepared and reached moderate efficiencies. To study deeply their optical and electrical properties, as well as structure-property relationship, and to optimize usage in OSC, was aim for the extended study [P6].

Evaluation of personal contribution

Author participated on designing of the experiments. Author prepared solutions of studied materials in different solvents and perform characterization of studied materials by optical spectroscopy. Absorbance spectra were measured employing the

Varian Cary Probe 50 UV-VIS spectrometer and fluorescence spectra were measured utilizing both Thermo Spectronic Aminco Bowman AB-2 fluorescence spectrometer (both previously described in 3.2.1).

Author optimized the method of thin film preparation to create the film with optimal thickness and morphology for optical measurement. Author performed optical characterization of materials in solid state – thin film engaging previously described methods for absorbance and fluorescence measurements.

Author prepared substrates for organic solar cell prototypes. Author studied behaviour of studied materials in interaction with commonly used acceptors $PC_{60}BM$ and $PC_{70}BM$ and perform the optimization of donor:acceptor ratio.

Author evaporated aluminium cathode layers using MBraun vacuum system located in the inert atmosphere of nitrogene glovebox MB-200B MBRAUN.

Author optimized the method of the thin film deposition suitable for particular materials, structure of OSC prototype and thermal/solvent treatment of the active layer. Samples preparation took place in the clean room class C, to prevent the dust and particles from disrupting the thin layer. Samples before the encapsulation of the structures were manipulated within the nitrogen atmosphere of the glovebox. Author performed the encapsulation of the samples inside the glovebox.

Author performed electrical characterization of prepared samples, measurement of current voltage characteristics with a a Keithley 2601B electrometer in the dark and under irradiance of 1 sun (100 mW/cm2) and a standard AM 1.5 spectrum, simulating sunlight after passing through the atmosphere, provided by AAA solar simulator (LOT Oriel). Author calculated performance parameters from measured data and evaluated influence of molecular structure on the parameters of power conversion.

Author formulated part of the paper describing used methods and evaluation of their results.

3.3.3 P3: Aerosol flow homogenization in the spray polyphenylene vinylene thin film deposition

Aim of this work was to introduce the method for spray coating of PPV material. Two different spray deposition techniques, SD and homogenized SD (h-SD), were compared within the study. Samples were studied by the microscopy and SEM. Functional photovoltaic device was prepared by homogenized spray deposition and characterized by photoelectrical measurements.

Evaluation of personal contribution

Author participated on designing of the experimental part. Author prepared substrates and solutions for the deposition. Author performed the deposition by spraying device and thermal treatment, cooperated on the optimization of the deposition parameters. Author performed microscopic analysis of the thin film homogeneity. Author performed electrical characterization of prepared samples,

measurement of current voltage characteristics with a a Keithley 2601B electrometer in the dark and under irradiance of 1 sun (100 mW/cm2) and a standard AM 1.5 spectrum, simulating sunlight after passing through the atmosphere provided by AAA solar simulator (LOT Oriel). Author calculated performance parameters from measured data.

Author measured and evaluated spectral resolved photocurrent. Spectral resolved electrical response was studied using a combined apparatus consisting of: picoampermeter Keithley 6478, xenon lamp LSH502 LOT Oriel, monochromator MSH101 LOT ORIEL, photometric head SiQE120 RaRe Solutions connected to the picoampermeter Keithley 485.

3.3.4 P4: Effect of the Side Chains and Anode Material on Thermal Stability and Performance of Bulk-Heterojunction Solar Cells Using DPP(TBFu) 2 Derivatives as Donor Materials

Aim of this work was to study the influence of the modification of solubilizing chain of DPP(TBFu)$_2$ molecule on the molecular properties and further on the properties of OSC, where DPP(TBFu)$_2$is used as a donor material. Paper also discussed effect of MoO_3 as an alternative hole transporting layer and effect on the thermal stability of the OSC.

Although PCE of the reference ethyl-hexyl alkylated DPP(TBFu)2 was not exceeded by the materials with electrophilic side chains, obtained efficiencies were reasonable, concerning the higher reaction yields in the case of alkyl esters, which makes considered materials promising for further use. Derivative substituted with ethyl-hexyl acetate exhibit good power-conversion efficiency even without any thermal treatment, which poses a potential for cheap and easy processing of BHJ solar cell.

MoO3 anode contact together with DPP(TBFu)2, exhibit creation of more thermally stable interface of the active layer and anode contact, allows using higher annealing temperatures, which leads to higher power conversion efficiencies in comparison with commonly most used PEDOT:PSS.

Least but not last, gradual annealing was introduced as a method to improve performance of OSC. Slow increase of temperature during annealing process caused the effective donor acceptor reorganization, resulting in higher power conversion efficiency.

Evaluation of personal contribution

Author cooperated on the research of actual situation and designing the experimental part.

Author prepared substrates for organic solar cell prototypes. Author studied behaviour of studied materials in interaction with commonly used acceptors

$PC_{60}BM$ and $PC_{70}BM$ and perform the optimization of donor:acceptor ratio. Author evaporated aluminium and MoO_3 layers using MBraun vacuum system

Author optimized the method of thin film deposition suitable for particular material. Sample preparation took place in the clean room class C, to prevent the dust and particles from disrupting the thin layer. Samples before the encapsulation of the structures were manipulated within the MB-200B MBRAUN glovebox. Author performed encapsulation of the samples inside the glovebox.

Author performed electrical characterization of prepared samples, measurements of current voltage characteristics with a a Keithley 2601B electrometer in the dark and under irradiance of 1 sun (100 mW/cm2) and a standard AM 1.5 spectrum, simulating sunlight after passing through the atmosphere provided by AAA solar simulator (LOT Oriel). Author calculated performance parameters from measured data and evaluated influence of molecular structure on the parameters of power conversion.

Author participated on formulation of the results.

3.3.5 P5: Thiophene-free diphenyl-amino-stilbene-diketo-pyrrolo-pyrrole derivatives as donors for organic bulk heterojunction solar cells

Aim of this extended study, based on previously synthesised materials [P2], was to describe more detailed characterization of diphenylamino stilbene based DPP materials and their application as donors in organic solar cells. Study focused on the relationship between structure and properties of 4 soluble derivatives. Study provided comparison of asymmetrical D-π-A with symmetrical D-π-A-π-D, both alkylated either with ethyl-acetate or ethyl-hexyl-acetate.

It was demonstrated, that D-π-A-π-D type molecules always exhibited better photovoltaic and mobility parameters. Comparison of 2-ethyl-hexyl acetate and ethyl-acetate N−alkylationolubilizing chains showed that shorter solubilizing chain provides better molecular planarity, and therefore higher charge carrier mobility. The effect of the solubilizing chain was more significant for asymmetrical molecules, where a 2-ethyl-hexyl acetate chain led to destabilization.

Diphenyl amino building blocks in the structure are in general susceptible to rotation (intermolecular π–π interaction is weaker) and thus high charge carrier mobility is barely reachable. If $PC_{70}BM$ was used as the acceptor, all parameters of the solar cell improved, except from the fill factor. This effect demonstrated that lower mobility of the donor material is probably the most limiting factor for all four thiophene-free materials. However, considering the generally lower lifetime of organic solar cells and their possible disposal by incineration, the absence of sulphur (thiophene-free material) makes theman environment friendly alternative for solar cells.

Evaluation of personal contribution

Author performed the research of the actual situation and designed the experimental part.

Author prepared the samples and performed complete optical characterization, in extent going beyond the published results. Author prepared the samples for AFM microscopical analysis and for OFET measurements, which were performed by co-authors to verify the thin film homogeneity and to calculate the charge carrier mobility.

Author prepared substrates for organic solar cell prototypes. Author studied behaviour of studied materials in interaction with commonly used acceptors $PC_{60}BM$ and $PC_{70}BM$ and perform the optimization of donor:acceptor ratio.

Author evaporated aluminium cathode layers using MBraun vacuum system located in the inert atmosphere nitrogene glovebox MB-200B MBRAUN.

Author optimized the method of thin film deposition suitable for particular materials. Samples preparation took place in the clean room class C, to prevent the dust and particles from disrupting the thin layer. Samples before the encapsulation of the structures were manipulated within the nitrogen atmosphere of the glovebox. Author performed the encapsulation of the samples in the inert atmosphere.

Author performed electrical characterization of the prepared samples, measurements of current voltage characteristics with a a Keithley 2601B electrometer in the dark and under irradiance of 1 sun (100 mW/cm2) and a standard AM 1.5 spectrum, simulating sunlight after passing through the atmosphere provided by AAA solar simulator (LOT Oriel). Author calculated performance parameters from the measured data. Author evaluated the results and discussed influence of the molecular structure on the parameters of the power conversion.

Author formulated the complete paper.

3.3.6 P6: Reducing Recombination Processes in the Inverted-Solution-Processed Small-Molecule Solar Cells by the Inserted Fullerene Cathode

Aim of this brief paper was to describe the effect of inserted layer of fullerene (C60) on the cathode of inverted $DPP(TBFu)_2$ based OSC. It was demonstrated, that 10 nm thin layer of fullerene reduces recombination processes, which are the main reasons of the low fill factor at inverted $DPP(TBFu)_2$ based devices.

Inserted layer of C60 led to rapid increase of fill factor together with slight increase of short circuit current and therefore increase of the efficiency for both inverted and regular devices based on $DPP(TBFu)_2$ donor material. For inverted devices, obtained efficiency reached contemporary record value.

Evaluation of personal contribution

Author participated on designing the experimental part. Author partially prepared and characterized samples. Author prepared substrates for organic solar cell

prototypes. Author optimized the method of thin film deposition of the active layer. Sample preparation took place in the clean room class C, to prevent the dust and particles from disrupting the thin layer. Samples before the encapsulation of the structures were manipulated within the nitrogen atmosphere of the glovebox. Author performed the encapsulation of the samples.

4 CONCLUSION

Two groups of the new diketopyrrolopyrrole derivatives, diphenylamino stilbene DPP and thiobenzofuran DPP, were studied with respect to their potential use in organic photovoltaics. Author performed extensive study of optical and electrical properties of pure materials and study the structure-property relationship of DPP based materials. Series of prototypes of organic photovoltaic devices were prepared, their performance optimized and influence of molecular structure on solar cell performance was discussed.

Effect of side solubilizing chain presence and type was described. It was demonstrated for diphenylamino stilbene DPP that shorter, ethyl acetate solubilizing chain led to better thin film morphology and higher charge carrier mobility within the bulk. Therefore all OSC parameters connected with mobility were improved. For thiobenzofuran DPP, ethyl hexyl, ethyl-hexyl acetate, and diethyl acetal solubilization group were compared and it was showed that ethyl-hexyl acetate group led to a formation of an appropriate bulk-heterojunction without the thermal annealing, which indeed is advantageous for potential industrial use.

Besides materials, application based research is also closely connected with area of organic materials. Alternative methods of optimization and thin film deposition were studied with regard to diketopyrrolopyrrole materials.

Among methods of solar cell optimization, gradual annealing was studied and it was described that slow increase of temperature can lead to improve of thermal stability and performance of studied devices. As an alternative to commonly used PEDOT:PSS, MoO_3 hole transporting layer was introduce and it was demonstrated that with studied devices from TBFu based DPP, MoO_3 led to better stability of the BHJ/HTL interface. Low efficiency of small molecules based inverted solar cells was improved by evaporated layer of fullerene on the cathode, which solved problem with low fullerene population on the cathode and thus increased efficiency of inverted solar cell, mainly via the fill factor.

As deposition methods, next to the commonly used spin coating, within this work vacuum deposition and spray deposition were used. Advantage of vacuum deposition is creation of precise layer and possibility to deposit insoluble materials. On the other hand, spray deposition is solution-based method which allows fast large scale production. Homogenized spray deposition enables to reach more precise layer. Both methods were used and optimized for diketopyrrolopyrrole material.

Results were published within 7 scientific papers and 11 conference contributions. 6 chosen publications are integral to this thesis.

5 REFERENCES

[1] RYAN, James W., Thomas KIRCHARTZ, Aurélien VITERISI, Jenny NELSON a Emilio PALOMARES. Understanding the Effect of Donor Layer Thickness and a MoO 3 Hole Transport Layer on the Open-Circuit Voltage in Squaraine/C 60 Bilayer Solar Cells. *The Journal of Physical Chemistry C* [online]. 2013, 117(39), 19866-19874. DOI: 10.1021/jp406472t. ISSN 1932-7447. Available from: http://pubs.acs.org/doi/10.1021/jp406472t

[2] ZHANG, Hui, Congxu WANG, Xiao LI, Jianli JING, Youyi SUN a Yaqing LIU. The effect of processing conditions on performance of small-molecule organic solar cells. *Solar Energy* [online]. 2017, 157, 71-80. DOI: 10.1016/j.solener.2017.07.043. ISSN 0038092X. Available from: http://linkinghub.elsevier.com/retrieve/pii/S0038092X1730628X

6 CURRICULUM VITAE

Personal information

First name(s) / Surname(s)	**Jana Vrchotová (Honová)**
Birth	02.06.1987, Ostrava

Education and training

Dates	**06/2011 – onwards, distance form since 9/2015**
Title of qualification	**Studying doctoral degree in Physical chemistry**
Principal subjects/occupational skills covered	Optical and electrical characterisation of new advanced materials. Spectroscopic methods, physics, microelectronics. Thesis: Organic materials for molecular electronics
Name and type of organisation providing education and training	Brno University of Technology, Faculty of Chemistry
Activities and awards	Vulcanus in Japan scholarship holder 09/2011 – 08/2012 Vulcanus in Japan internship Brno Ph.D. Talent scholarship holder ECME 2013 (London) poster presentation Ossila OSC workshop 2013 (Sheffield) Chemistry and life 2013 (Brno) given speech ISFOE 2014 (Moscow) conference + summer school of organic electronics, poster presentation, Best poster price Chemistry and life 2014 (Brno) given speech Chemistry and life 2015 (Brno) given speech IFSOE 2015 (Thessaloniki) poster presentation

Dates	**06/2006 – 06/2011**
Title of qualification awarded	**Bachelor and Master degree in Physical and applied chemistry**
Principal subjects/occupational skills covered	Physical chemistry, analytical chemistry, advanced organic materials, spectroscopic methods, coloristics and colorimetry, surface treatment, physics of vacuum Bachelor thesis: Organic materials for photovoltaic conversion of solar energy Master thesis: Correlation between structure and properties of diketopyrrolopyrrole derivatives
Name and type of organisation providing education and training	Brno University of Technology, Faculty of Chemistry

Activities and awards	5/2010-7/2010 research fellowship, Carl von Ossietzky University of Oldenburg Speech Chemie je život 2009 (Brno) – 2nd price Speech Chemie je život 2010 (Brno) – 2nd price Passed with honours Received deans award Nominated for Česká hlava (Gaudeamus) prize

Work experiences

Dates	**9/2015 – ongoing, maternity leave since 2/2018**
Occupation or position held	**Development testing engineer - senior**
Main activities and responsibilities	Development and reliability Testing of Electronic Throttle Body. Pending between Budweis and Stuttgart. Acquisitions for new customer, customer project testing and technical support ,platform project testing, DRBFM, FMEA, 8D, Ishikawa, time and capacity planning, cost calculations, worldwide support.
Name and address of employer	Robert Bosch spol. s r.o. Roberta Bosche 2678, 370 04 České Budějovice, Czech Republic

Dates	**10/2012 – 7/2015**
Occupation or position held	**Researcher – PhD student, full time**
Main activities and responsibilities	Optical and electrical characterisation of new advanced materials. Spectroscopy, microelectronics
Name and address of employer	Materials research cente Purkynova 464/118, 612 00 Brno, Czech Republic

Dates	**01/2012 - 08/2012**
Occupation or position held	**Intern**
Main activities and responsibilities	Development of improved electrolyte for lithium-ion battery for electromobile. Physical and chemical properties modelling, calculations, experimental work.
Name and address of employer	Mitsubishi Chemical Corporation 1-1 Marunouchi 1-chome, Chiyoda-ku, 100-8251 Tokyo, Japan

Dates	**06/2008 -07/2011**
Occupation or position held	**Intern, part-time (100 hours per month)**
Main activities and responsibilities	Control quality of purchased parts - Aging simulation tests, chemical analysis, colorimetrics, thermal analysis, communication with suppliers
Name and address of employer	SKODA AUTO a.s. Laboratories and dimension center, Vaclava Klementa 869, 293 60 Mlada Boleslav, Czech Republic

ABSTRACT

Organic electronics is a dynamic rapidly growing industry. Therefore the research of novel materials for organic electronics is an important challenge both in terms of materials performance and economy of the final product, while the environmental impact is also important. Diketopyrrolopyrrole derivatives are materials with a great potential for organic electronics exploitation. This thesis is focused on optical and electrical characterization of diketopyrrolopyrroles, an assessment of their potential applications in organic electronics and suggestions, how to optimize their performance.

Theoretical part of this thesis describes state of art in organic electronics with focus on the field of diketopyrrolopyrrole based materials. Subsequent results part summarizes important results and contains brief introduction to the enclosed publications, including evaluation of author´s personal contribution to particular publications. Results part consists of 6 scientific articles, integral to this thesis, thematically connected with area of organic electronics, new diketopyrrolopyrrole based materials and their applications.

Formally the thesis is, based on article 42 paragraph 1b of The Study and Examination Rules of BUT, designed as thematically arranged set of published works and works accepted for publication.

ABSTRAKT

Organická elektronika je dynamické, rychle se rozvíjející odvětví. Studium nových materiálů pro organickou elektroniku je důležitým úkolem jak z hlediska výkonnosti budoucích zařízení a ekonomičnosti procesů, tak z hlediska vlivu jejich používání na životní prostředí. Deriváty diketopyrrolopyrrolu patří mezi zajímavé materiály, které jsou v posledních letech studovány s ohledem na využití v organické elektronice. Dizertační práce je zaměřena na studium těchto materiálů a jejich jak optickou, tak i elektrickou charakterizaci. Součástí je také zhodnocení jejich potenciální aplikace v organické elektronice a návrhy optimalizace jejich výkonu.

Teoretická část práce popisuje současný stav na poli organické elektroniky zaměřený na materiály na bázi diketopyrrolopyrrolu. Následující výsledková část shrnuje podstatné výsledky práce a obsahuje stručný úvod k přiloženým publikacím, včetně zhodnocení vlastního přínosu autora k jednotlivým publikacím. Výsledková část dále sestává ze 6 vědeckých publikací, které jsou nedílnou součástí této práce a jsou tématicky propojeny v oblasti organické elektroniky, nových materiálů na bázi diketopyrrolopyrrolu a jejich aplikací.

Z formálního hlediska je práce na základě čl. 42 odstavce 1b Studijního a zkušebního řádu VUT koncipovaná jako tematicky uspořádaný soubor uveřejněných prací a prací přijatých k publikaci.