BRNO UNIVERSITY OF TECHNOLOGY
VYSOKÉ UČENÍ TECHNICKÉ V BRNĚ

FACULTY OF CHEMISTRY
MATERIALS RESEARCH CENTRE

FAKULTA CHEMICKÁ
CENTRUM MATERIÁLOVÉHO VÝZKUMU

ADVANCED MATERIALS FOR ORGANIC PHOTONICS

POKROČILÉ MATERIÁLY PRO ORGANICKOU FOTONIKU

SUMMARY OF DOCTORAL THESIS

AUTOREFERÁT DIZERTAČNÍ PRÁCE

AUTHOR: D.E.A. IMAD OUZZANE

AUTOR PRÁCE

SUPERVISOR: Prof. Ing. MARTIN WEITER Ph. D.

VEDOUCÍ PRÁCE

BRNO 2014

Abstract:

Among low molecular organic materials, diphenyl-diketo-pyrrolopyrrole (DPP) derivatives used earlier as dyes are of high interests in modern technologies. The study of their optical properties related to their chemical structure will provide more information on the later relationship and comfort the high potential of DPP derivatives in the making of more performant smart materials. An overview of their chemical and physical properties is described at the theoretical part and followed by the state of the art in the field of interest concerning this thesis. The three main processes studied in this work are: The classic absorption and emission, the two photon absorption (TPA) and the amplified spontaneous emission (ASE). The results will be discussed and summarized in two parts: The first concerning the one and the two photon absorption and the second the amplified spontaneous emission.

Keywords:

Two photon absorption, amplified spontaneous emission, light absorption, threshold, cross section, thin films, diphenyl-diketo-pyrrolopyrrole derivatives, time resolved fluorescence, laser, thin films.

Abstrakt:

V oblasti nových nízkomolekulárních organických materiálů patří deriváty difenyldiketopyrrolopyrrolu (DPP), používané dříve jako barviva a pigmenty, k objektům vysokého zájmu pro jejich potencionální aplikace v moderních technologiích. Studium jejich optických vlastností ve vztahu k jejich chemické struktuře umožní využití jejich vysokého potenciálu ve vývoji pokročilých inteligentních materiálů. Přehled chemických a fyzikálních vlastností DPP derivátů a zhodnocení současného stavu řešené problematiky jsou uvedeny v teoretické části této práce. Tři hlavní procesy studované v této práci jsou: klasická absorpce a emise, dvoufotonová absorpce (TPA) a zesílená spontánní emise (ASE). Výsledky budou diskutovány a shrnuty ve dvou částech: první zahrnuje první dvě výše zmíněné oblasti a druhá problematiku zesílené spontánní emise.

Klíčová slova:

Dvoufotonová absorpce, zesílená spontánní emise, absorpce světla, deriváty difenyldiketopyrrolopyrrolu, časově rozlišená fluorescence, laser, tenké vrstvy.

Contents

1 Introduction

Intelligent packaging, organic photovoltaic cells (OPV), printed radio-frequency identification (RFID), organic memories, organic sensors, flexible batteries, organic thin film transistor (OTFT) displays backplanes to look at flexible displays, electroluminescence (EL), organic light emitting diode (OLED) among other smart objects are part of actual organic and printed electronics association (OE-A) field and main interest of research in chemistry like in physics. Organic electronics stands for a revolutionary way of making electronics: thin, lightweight, flexible, produced at low cost, better recyclable, enabling single use, ubiquitous electronic devices and new applications. Polymer light-emitting diodes (PLEDs) are perfect candidates as they enhance low operating voltage, film forming abilities via spin coating, tunable luminescence properties, potential full-color flat panel and flexible displays as well as easy fabrication at low cost [1, 2]. Polymer, containing chromophore subunit, prepared by polycoupling reaction recently appeared into another progressive area which is nonlinear optics (NLO), concretely two-photon absorption (TPA). Interest in non-polymeric materials such as DPP derivatives for the use in OLED technology and NLO is increased and was already demonstrated. Their advantageous properties such as high quantum yields, recyclability, lifetime and thermic resistance, non-toxicity, low cost fabrication and tunable emissive luminescence makes them ideal candidates for the purpose of these processes.

This work focuses mainly on the optical study and the synthetic development of new DPP derivatives suitable for devices to be used in photonic applications. These materials were substituted with electro-withdrawing and/or electro-donating chemical groups in specific positions and their physical property changes were observed. The aim of this thesis is to compare several DPP derivatives and the effect of their distinct substituents on their optical properties to

determine their relevance in modern applications for advanced devices. The results obtained should provide us with crucial information for the preparation of new type of DPP derivatives with enhanced characteristics.

2 State of the art

Organic photonics is an interdisciplinary and innovative research field with many materials systems and application areas resulting also in strong interactions between academic institutions and industry. In the **Figure 1** bellow we see a general map of photonics materials represented in green circles and their applications in blue rectangles.

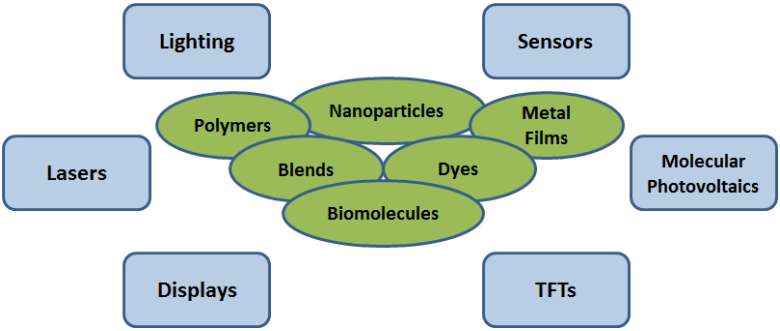


***Figure** 1: Photonics materials and applications* [3].

This field focused earlier mostly on optical telecommunications and began with the invention of the laser in 1960 [4]. It covers all technical applications of light over the whole spectrum from ultraviolet over the visible to the near-, mid- and far-infrared. It covers a huge range of science and technology applications, including laser manufacturing, biological and chemical sensing, medical diagnostics and therapy, display technology, electroluminescent diodes, optical modulators, optical amplifiers and optical computing.

The following part of this chapter is dedicated to the physical and chemical background of low molecular organic compounds, mostly DPP derivatives involved in this study. The second part deals with the physical characterization of these materials focused on their spectroscopic study. The luminescence of DPP derivatives will be investigated throughout modern photo-processes which will be hereby introduced and described.

2.1 Organic photonics

Organics photonics is an interdisciplinary and innovative research field involving many materials like dyes, nanoparticles, polymers, metal films and biomolecules. The increasing interest towards organic materials is mainly justified not only by actual economy and ecological threats but also for advantageous processing properties and hereby resumed in **Table 1** where MBE stands for molecular beam epitaxy and MOVPE for metal-organic vapor phase epitaxy.

***Table 1**: Comparison of inorganic and organic electronics and photonics.*

Inorganic Materials	**Organic Materials**
Materials	
Hard, fragile	*Soft, molecular, flexible*
Material Processing	
Vaccum deposition *Ultra high temperatures*	*Solution processing, low temperature*
Fabrication Equipment	
MBE, MOVPE	*Spin coated, printing*
Cost	
Highly specialized, expensive *Difficultly recyclable*	*Simple, inexpensive* *Recyclable*

Polymers play an important role in the development of materials for photonics in industries because they are relatively inexpensive and can be functionalized to achieve required optical, electronic or mechanical properties. They can possess useful optical properties such as electroluminescence, photoluminescence, or nonlinear optical properties [5]. The Polymer based display technology is based on the discovery of conjugated polymer electroluminescence [6].

Among many other organic materials, DPP derivatives are also highly suitable for electro-optical applications [7] as they provide many advantages and we shall present them in following chapter.

2.2 Diphenyl-diketo-pyrrolopyrrole derivatives

Lately interest towards DPPs increases in the field of organic photonics because of their great fluorescent properties. **Figure 2** illustrates the basic chemical structure of these organic chromophores where the R_1 and R_2 positions can be differently substituted with whether a withdrawing or a donating group [8] knowing that in symmetrical DPPs R_1=R_2 and R_3=R_4.

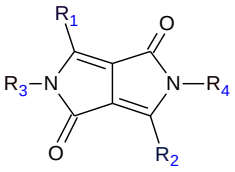


***Figure 2**: Basic structure of diketo-pyrrolopyrrole derivatives.*

They constitute recent industrial important class of highly efficient dyes [9] because of their outstanding chemical and physical properties such as a high melting point unusual for such a low molecular weight molecule relative to standard pigments.

2.3 New types of DPP derivatives

Common strategy to develop materials with desired properties for organic electronics applications is to combine various building blocks and transform them into new sophisticated molecular structures with enhanced properties. The incorporation of polar groups into these organic chromophores causes a redistribution of the electronic density in the ground states like in the excited one. This can strongly affect their absorption and fluorescence properties [10]. New types of DPP derivatives were synthetized considering that in position R_3 and R_4 seen in **Figure 3** could be other subsequent substituents than only alkyl (or acyl) solubilizing groups. The blue arrows represent electron withdrawing group whereas the green arrows represent electron donating groups (attraction towards the arrow's head).

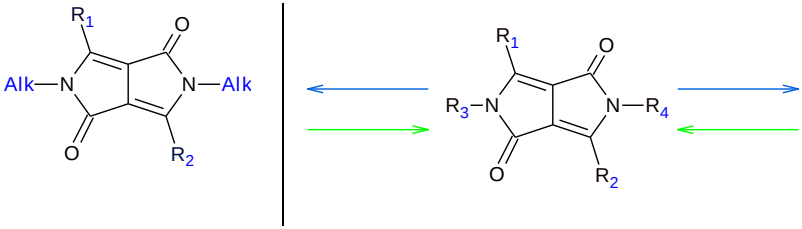


***Figure 3**: (left) Classical DPP derivatives with solubilizing alkyl groups in position R_1-R_2. (right): New types of DPP electron withdrawing or donating effects of pendent groups in amine position R_3-R_4.*

It has been proved that diketo-pyrrolopyrroles (DPP) can serve as an efficient base structure for organic solar cells materials [11]. Although originally developed as an industrial pigment, it has drawn attention for its strong light absorption, photochemical stability and extended π-conjugated system.

2.4 Optical study of organic material

In this chapter we introduce the optical and theoretical background involved in this doctoral thesis and used further for determining particular optical properties of the molecules investigated. All of the materials presented will be subject to specific optical studies according to their properties.

2.4.1 Linear absorption and fluorescence emission

During light excitation, photons are absorbed by the atom or molecule and therefore an electron is promoted from the ground state S_0 to the upper transition allowed excited state S_1 of higher energy. Following the Franck-Condon principle [12] which states that since electronic motions are much faster than nuclear motion, electronic transitions occur most favorably when the nuclear structure of the initial and final states are most similar [13]. There are two processes (**Figure 3**) that emit light from a molecule and therefore also two transitions:

-The first is fluorescence (represented above in green-arrow downwards) which corresponds to the spontaneous emission of a photon and a transition of the molecule's electron from the excited state S_1 to the ground state S_0.

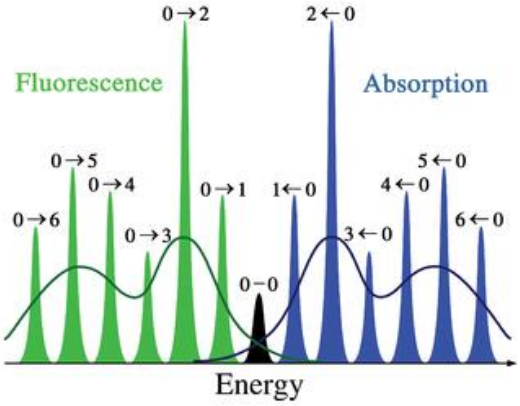


***Figure 4**: Schematic representation of the absorption and fluorescence spectra [32].*

-The second emitting process much slower is the phosphorescence corresponding to the transition from the triplet state T_1 to the electronic ground state S_0.

Good lasing properties would require a low concentration of dye molecules and non-competing processes like phosphorescence or non-radiative transitions. The triplet state has a long lifetime and if it is at lower energy than the singlet one, it competes with the populating of the excited state S_1 and therefore lowering the quantum yield of the fluorescence.

2.4.2 Nonlinear and two photon absorption (TPA)

The difference between one-photon absorption (OPA) and two-photon absorption (TPA) lies in that OPA depends linearly on the light intensity, whereas TPA involves the simultaneous interaction of two photons and so it increases with the square of the intensity. Since this process depends on the simultaneous absorption of two infrared photons, the probability of two-photon absorption by a fluorescent molecule is a quadratic function of the excitation radiance.

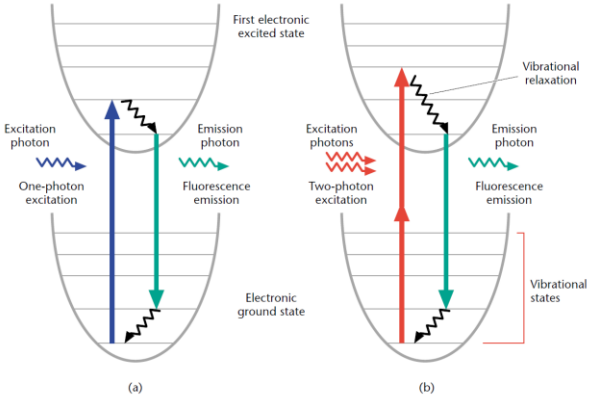


***Figure 5**: Jabloński diagram of one-photon (a) and two-photon (b) excitation, which occurs as fluorophores are excited from the ground state to the first electronic states[14].*

The general scheme for the two photon absorption compared to the single photon absorption process is represented in **Figure 5**. After either excitation process, the fluorophore relaxes to the lowest energy level of the first excited electronic states via vibrational processes. The subsequent fluorescence emission process for both relaxation modes is nearly similar.

2.4.2.1 Two photon absorption and two photon absorption cross section

The double photon excitation has recently attracted much interest since a number of technical applications can be derived from the fact that the TPA cross section depends quadratically on the intensity of the exciting light and that fundamental excitations can be reached by applying half the wavelength, thereby considerably increasing the penetrability of materials and tissue [15].

It is experimentally much simpler to alter the laser power than to prepare many samples with different concentrations. In that case we get final expression in **Equation 1**:

$$\sigma_{2PE(NEW)} = \sigma_{2PE(STD)} \frac{c_{STD}}{c_{NEW}} \frac{S_{NEW}}{S_{STD}} \frac{n_{STD}}{n_{NEW}} \quad (1)$$

The slope *S* is obtained from the plot of integrated fluorescence intensity vs. the square of average laser power P^2 (W.s^{-1}).

2.4.3 Amplified spontaneous emission

Amplified spontaneous emission (ASE) [16] arises where the emitters are non-interacting and the spontaneous emission from one emitter is amplified as it propagates through a region containing an ensemble of other emitters [17].

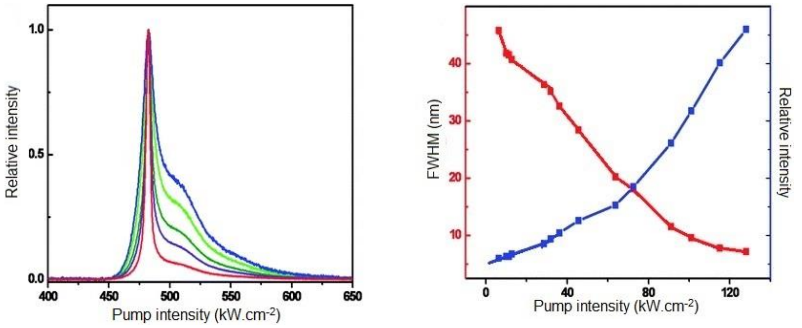


***Figure 6**: a) The ASE phenomenon represented as the fluorescence emission function of the increasing exciting pump power. b) The full width at half maximum representing the narrowing of the emission range wavelength with the increasing exciting energy [18].*

The amplified spontaneous emission [19] is represented in **Figure** 6. Spontaneously stimulated fluorescence emission of optically pumped thin films

leads to the spectral narrowing of fluorescence spectrum of organic luminescent dyes dissolved in polymer films as a potential source of monochromatic light.

2.4.3.1 Net gain

Laser beam is produced by excited dye molecules (pumped molecules) that undergo spontaneous emission producing photons resonating as coherent monochromatic directional light. The gain was measured and obtained with **Equation 2** by keeping all settings constant changing only the shape of the beam along the x axes and measuring the ASE's intensity for different values of x.

$$I_{\mathrm{ASE}} = \frac{A_{(\lambda)} I_{(P)}}{g_{(\lambda)}} \left(\mathrm{e}^{g(\lambda) l} - 1 \right) \qquad (2)$$

Where I_{ASE} is the Amplified spontaneous Emission intensity at a sample edge, $A(\lambda)$ $I(p)$ defines the spontaneous emission proportional to the pump energy, l is the length of the pump stripe, and g(λ) is the net gain coefficient.
DPP derivatives with different chemical structure were selected accordingly to the process studied and their physical properties were determined with methods that shall be described in following chapter.

3 Experimental part

At first, we shall present the chemical structure of the molecules under optical investigation, their synthesis and chemical determination, followed by the optical methods, experimental settings and devices used for their optical study.

3.1 DPP materials studied

Diphenyl-Diketo-Pyrrolopyrrole derivatives commonly referred to as DPPs can be easily modified by chemical substitution in position R_1, R_2, R_3 and R_4 (**Figure 7**) modifying their electronic properties by effect of electro-donating (blue arrows) and electro-attracting (green arrows) pendent groups.

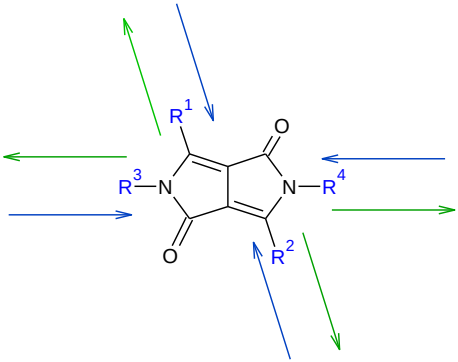


***Figure 7**: General scheme of DPP derivatives and pendent group's electronic effects.*

The main task of this work was to investigate the optical properties of organic low molecular materials like newly synthetized diphenyl-diketo-pyrrolopyrrole derivatives and to correlate these results with their chemical structure for further optimization. These molecules present potential advantages like high efficiency, versatility in their application (flexibility, transparency), low weight, cheap production and environmental friendly [20].

3.2 Structural characterization

The synthesis, nuclear magnetic resonance and the mass spectrometry measurements were done in France at the University of Rouen under the direction of Professor Jean-Philippe Bouillon with the collaboration of Dr Jozef Krajčovič.

3.3 Absorption and emission spectra

The referred UV-Vis absorption spectra in solution were recorded using Varian Carry 50 UV-Vis spectrometer. Fluorescence measurements were also driven with:

- Excitation and fluorescence emission were made with a Thermo Spectronic AMINCO Bowman Series 2 luminescence spectrometer (model FA-357).
- Excitation and fluorescence emission were confirmed with a Fluorolog Spectrofluorometer via an excitation source composed with a 450 W xenon lamp and its power supply, inside a housing, a single-grating excitation monochromator, a T-format sample compartment with excitation reference detector, a single-grating emission monochromator and an emission photomultiplier tube with photon-counting detection.
- A LASER class IV was used as a strong excitation source, mainly for the amplified spontaneous emission and the two photon absorption experiments. The LASER was coupled with and Andor Shamrock SR-303i spectrograph iStar ICCD camera for the fluorescence spectra determination.

3.3.1 Lifetime fluorescence measurements

The fluorescence lifetime was measured using Andor Shamrock SR-303i spectrograph and Andor iStar ICCD camera. The samples were excited by first, second and third harmonic from EKSPLA PG400 Nd:YAG laser (1064, 532, 355 nm) with a 10Hz repetition rate. The temporal resolution of the system is approximately 25 ps.

The fluorescence lifetime was also measured with the Fluorocube: NanoLED wavelength from 260 nm up to 740 nm with working frequency of 1 MHz.

3.3.2 Fluorescence quantum yield determination

The fluorescence quantum yields (ΦF) in solution were calculated according to the comparative method [21], where for each test sample gradient of integrated fluorescence intensity versus absorbance F=f(A) is used to calculate the ΦF using two known standards. The fluorescence quantum yields were also measured with a *Quanta*-φ integrating sphere part of the Fluorolog Spectrofluorometer from Horiba.

3.4 Two photon absorption study

The incoming energy from the laser had to be lowerd to afford accurate measurment. The samples were placed before collecting hyperbolic mirrors placed before Andor ICCD camera and pumped with a laser beam emitted by a Nd-YAG LASER from EKSPLA.

3.5 Amplified spontaneous emission study

We mixed the DPP derivative with poly(methyl methacrylate) (PMMA) and polystyrene (PS) to form thin films by spin coating meant to be used as a laser media. The sample was placed before collecting hyperbolic mirrors placed before Andor ICCD camera and pumped with a laser beam emitted by a Nd-YAG LASER from EKSPLA. Thin layers were made by spin coating (1500tr/min, during 1min.) a mixture of 4mg of DPP mixed with 158mg of polystyrene (PS) solubilized in 1mL of chloroform. The thin layers samples were dried and placed on a sample holder at normal room temperature.

4 Main Results

The two photon absorption like the amplified spontaneous study of the following DPP derivatives will lead to new perspectives in modern applications. Results concerning their optical characterization previously presented will be discussed throughout following chapters.

4.1 One photon absorption and fluorescence emission study

DPP derivatives were developed with various structural modifications making them interesting as advanced materials for modern optical and electronic technologies. The substituted pyrrolinone nitrogens with alkylated or acylated substituents allowed their solubility enabling wet solution based processing.

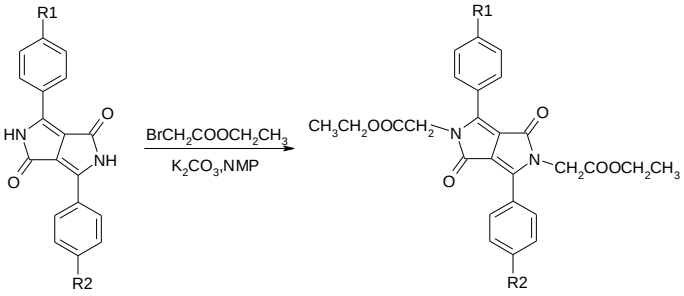
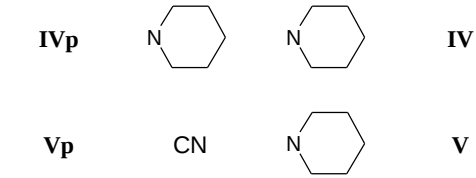


***Figure 8**: Synthesis reaction of N-Alkylated DPP derivative.*

***Table 2**: DPP derivatives involved in the one and two PA study.*

Symbol	R_1	R_2	Symbol
Ip	H	H	**I**
IIp	CN	CN	**II**
IIIp	H		**III**



For the purpose of the one photon absorption study we have chosen symmetrically and unsymmetrically differently substituted DPP derivatives (**Table 2**) with donor or withdrawing groups on para position of pendent phenyls.

Dimethyl sulfoxide (DMSO) was found to be the only common solvent able to dissolve all compound presented here above. Contrary to more usual N nucleophilic substitution on alkylhalogen [16], we applied in this case (**Figure 8**) the substitution on ethyl bromoacetate.

***Table 3**: The spectroscopic properties of I - V in DMSO (* dm^{-3} mol^{-1} cm^{-1}).*

DPPs	λ_A (nm)	$\varepsilon(\lambda_A)$ *	λ_F (nm)	ϕ_F	$\Delta\lambda_{Stokes}$ (nm)	τ_F (ns)
I	460	15800	519	0.56±0.18	59	7.34±0.08
II	480	13300	557	0.72±0.03	77	6.50±0.04
III	516	32200	601	0.12±0.02	85	1.17±0.02 6.7±1.2
IV	540	45100	603	0.45±0.02	63	3.45
V	541	42300	654	<0.01	113	0.217±0.002 3.72±0.10

The derivatives have shown bathochromic and hyperchromic shift of OPA and bathofluoric shift of one-photon excited fluorescence (OPEF) with respect to parent molecules **Ip** invoked above containing piperidino electron donating substituent.

With results provided earlier (**Table 3**), we have chosen proper *N*-substituted derivatives **I** – **V** as candidates for the following two photon absorption study.

4.2 Two photon absorption

Five alkylated soluble DPP derivatives **I** – **V** with polar substituents in para position of pendant phenyls were synthetized and their absorption like emissive properties were determined earlier. The TPA cross section shall be determined in order to compare these DPPs derivatives according to their chemical structure. In order to validate the power-squared dependence of the fluorescence signal we determined the logarithmic dependence of the fluorescence on the incident intensity $\log F = m \log I$ for all of the studied materials.

***Table 4**: Slope (m) in the logarithmic plot of fluorescence (F) versus the incident light intensity (I) logF = m logI (Rh B and Rh 6G being respectively Rhodamine B and Rhodamine 6G).*

	Rh B	Rh 6G	I	II	III	IV	V
Slope	2,00	1,99	1,95	1,97	2,01	1,98	-

As can be seen from **Table 4** the deviation from perfect power-squared dependence did not exceeded ±2.5% indicating two-photon events in the ranges used for the analysis. Most of the compounds under study showed fluorescence caused by two-photon absorption in DMSO. Although unsubstituted N precursor **Vp** has shown significantly higher ϕ_F, its TPA was rather small in DMSO (σ_{2PA} = 0.66 ±0.13 GM). A comparison of OPEF and TPEF spectra of **II** in DMSO at concentration of 1.10^{-5} mol l^{-1} is shown in **Figure 9**.

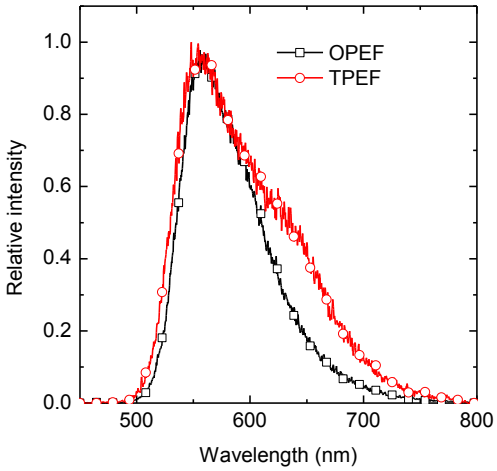


***Figure 9**: Normalized OPEF and TPEF spectra of **II**.*

The TPEF spectrum shows increased intensity at longer wavelengths near 650 nm compared to OPEF spectrum. Less pronounced, but detectable differences were also found for **III** and **IV**.

4.2.1 Two photon absorption cross section

The results of two photon experiments in DMSO are summarized in **Table 5**. Among the five compounds under study three ones either do not show any TPEF (**V**), or their one photon absorption does not significantly match the half of the only available excitation wavelength 1064 nm (**I**, **II**). Very high value of TPA cross section (1400±300 GM) was achieved for **III** which is hardly explainable considering piperidino group as only electron-donor and the central diketo-pyrrolo-pyrrole unit as a simple acceptor in D-π-A-π schematic pattern.

***Table 5**: Cross-section of two-photon absorption, emission and related parameters in DMSO.*

DPPs	λ_{2PF} (nm)	σ_{2PA} (GM)[a]	ε (532 nm) (dm^{-3} mol^{-1} cm^{-1})	σ_{2PE} (GM)
I	520	2,1±0,4	320	1,7±0,3
II	555	2,4±0,5	3500	1,7±0,3
III	594	1400±300	26000	170±30
IV	598	44±9	45000	20±4
V	-	-	-	-

The TPA cross-section of **IV** (44±9 GM at 1064 nm in DMSO) is more than an order of magnitude lower than for *N*-alkylated DPP derivative with both piperidine substituents replaced by diphenylamino groups.

These five *N*-alkylated DPP derivatives presented in this chapter were studied optically in liquid state and have demonstrated nonlinear absorption properties corresponding to their TPA and enhanced strong two-photon cross section. They have also provided precious information on possible more appropriate chemically structured DPPs.

4.3 DPP derivatives thin layers

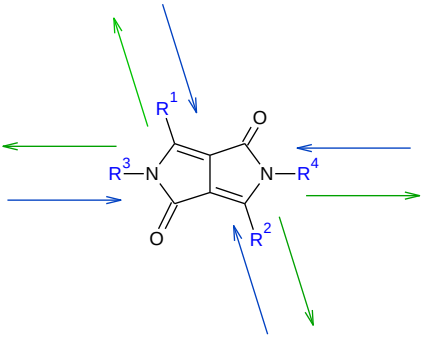
Luminescence of DiketoPyrroloPyrrole (DPP) derivatives in solution was described in previous chapter [22] and enhance large wavelength range tunability, high quantum yields and good chemical thermo stability.

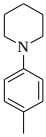
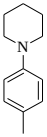
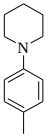
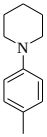
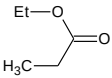
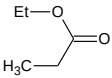
4.3.1 DPP derivatives used for the ASE study

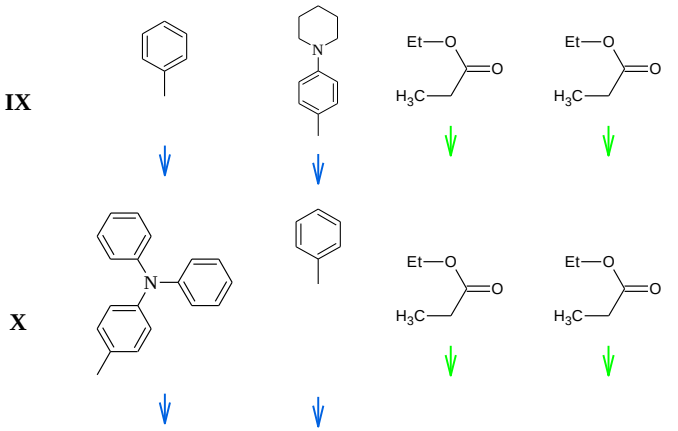
In this work we studied the luminescence in thin layer of *N*-Alkylated DPP derivatives differently substituted on para position of phenyl with electro donating functionalizing groups, demonstrated a good stabilization of the ASE phenomenon

in polystyrene (PS) matrix and tried to compare the effect of their side groups on its amplified emission. In **Table 6** are represented the DPP derivatives which underwent amplified spontaneous emission and for which were collected data results are discussed below.

***Table 6**: DPP derivatives involved in the amplified spontaneous emission study.*



DPP	R_1	R_2	R_3	R_4
VI			C_7H_{15}	C_7H_{15}
VII			C_4H_9	C_4H_9
VIII				



The *N*-alkylation of these DPP had minor impact on the values of the emission or the absorption spectra but helped with their solubility in polar solvent. This was accompanied by the hypsochromic shift and blurring of the vibration structure. In this study we could observe this same behavior of the shift in absorption in the solid state of DPP **VII** compared to the other non-symmetric derivative DPP **IX** and **X**. DPP **VIII**, **IX** and **X** were *N*-acylated with the same substituents but only DPP **IX**, **X** possesses the same non-symmetry of pendent groups R_1 and R_2.

4.4 Amplified spontaneous emission study

Among other materials, the light amplification in PMMA doped DPP derivatives have been studied [23] and the photopumping of its thin films leaded to the narrowing of the full width at half maximum (FWHM) of the emission spectra while increasing the incoming pump intensity. The results demonstrated that these dye molecules are potentially good candidates to be used as organic laser dyes as we have proven an accurate lasing threshold rate leading to their amplified spontaneous emission (**Figure 10** curve in green).

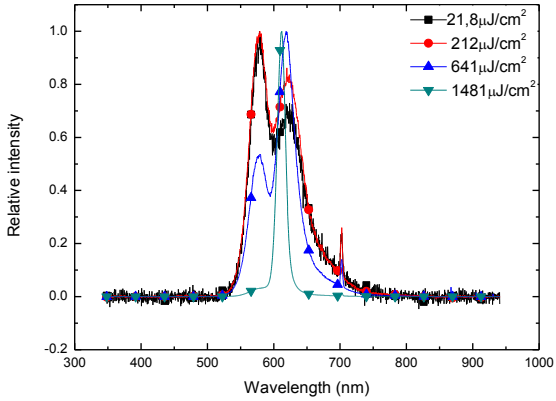


***Figure 10**: Normalized emission intensity of DPP **VII**-PS collected, at the waveguide edge with a determined excitation stripe and at increasing pump intensities.*

In this experiment the light emitted from the edge of the film at constant pump strip length but growing income energy was measured. Higher incoming intensity gets the emission maxima narrower at λASE = 612 nm and the FWHM value decreases from 100 nm to 16 nm. Same experimental mode was used to determine the maximum ASE emission value for DPP **VI**, **IX**, **VIII** and **X** and was

determined respectively at λASE= 602 nm, 626 nm, 659 nm and 641 nm.

Light amplification by stimulated emission of radiation in a resonator is determined by these means [24]: 1st- the narrowing linewidth emission, 2nd- light output consist of a beam, 3rd- clear threshold in both the output power and the linewidth, 4th- light emission is characteristic of the specific gain medium and resonator.

By plotting the dependency of the full width at half maximum and the total emission intensity integrated over all wavelengths versus the growing pump intensity we could determine the threshold corresponding to the start of the lasing process. From these two curves we could calculate and estimate the threshold energy for DPP **VII** with ρ_{th}= 28 μJ/cm^2. Higher values of threshold were determined for DPP **VI** and **IX** respectively ρ_{th}= 63 μJ/cm^2 and ρ_{th}= 79 μJ/cm^2.

Electron distribution is more homogeneous in case of planar molecules; this causes the increase in molar coefficient of absorption which in its turn increases the possibility of fluorescence. The phenyl torsion acting on the planarity of the molecule, influences its emission but comes also in account many other factors like the molar coefficient absorption, the stock shift, the quantum yield, the ability to radiationless processes, the donating or withdrawing effect of the substituents and the thin layer morphology favoring waveguiding which also improves ASE process.

4.4.1 Net gain of the ASE

When ASE occurs in a long narrow excitation region, most of the light is emitted out of the two ends of the region because light is highly amplified if it travels across the full length of the gain region. The pre-shaped laser beam is displaced along x axis between the edges creating a waveguide along it. We measured the emission spectra from waveguide's edges as the pump intensity and the pump stripe length varied. The net gain of DPP **VII** was calculated by changing the

excitation strip length (l) of the incoming beam and preceded the measurement at different pump energy. The emitted light was collected from the edges at different input pump energies. This allowed us to plot and fit the curves in **Figure 11** to determine the gain value at different pump intensity. It was reported that amplification saturated at higher pump intensities because of sample degradation.

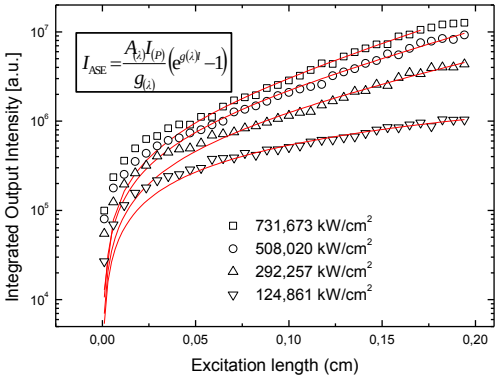


***Figure 11**: The calculated gain of DPP VII-PS at different pump intensities.*

The net gain was higher at high pump intensity and the output intensity increased exponentially at excitation lengths less than 2 mm. Gain saturation occurs as the pump stripe is increased, the gain coefficient is reduced and light is not amplified furthermore. The best photo stability was obtained by making films of mixture of DPP derivatives and polystyrene (PS), to exhibit light amplification by stimulated emission. The lowest threshold found was for the symmetrical push-push system DPP **VII** around 30 uJ/cm^{-1}. With one order magnitude above the lowest threshold found, these materials are very promising and enhance high perspectives in lasing and organic light emitting diode (OLED) technology.

5 Conclusion

This thesis is dedicated on their optical study related with their chemical structure to provide key information on DPP derivatives confirming their potential in the making of more performant modern smart materials. The main task was to provide conclusive results for their possible attractiveness in modern applied organic electronics and photonics by analysing their optical properties in the following three main fields: The one photon absorption, the two photon absorption and the amplified spontaneous emission.

5.1 One photon and two photon absorption

N-alkylated soluble DPP derivatives with polar substituents in para positions of pendant phenyls were synthesized, in order to make original non-alkylated DPP precursors better treatable. The compounds are non-planar with phenyl rings rotated out of diketo-pyrrolo-pyrrole plane. The degree of this rotation is decreased by the electron-donating substituents, while increased by the electron-withdrawing substituents, contrary to the density functional theory (DFT) predictions. The compounds show small solvatochromism of absorption and a moderate positive solvatochromism of fluorescence, if substituted by strong electron-donating substituent.

These *N*-alkylated DPP derivatives were studied optically and have demonstrated nonlinear absorption properties corresponding to their TPA and enhanced strong two-photon cross section. To afford these results we had to determine earlier the most suitable DPP derivatives and the appropriate concentration range of the solutions involved in the measurement as well as the appropriate excitation (laser) and detection (Andor camera) settings.

The two photon excitation fluorescence (TPEF) was used to obtain the two photon absorption (TPA) cross sections (σ_{2PA}) values. A considerably high value of σ_{2PA}

was obtained for mono piperidino substituted derivative **III** (1400 GM at excitation wavelength 1064 nm), making DPP derivatives promising materials for the applications based on the two-photon excitation.

5.2 Amplified spontaneous emission (ASE)

Organic thin films of DPP derivatives mixed with polymer were made and their amplified spontaneous emission was studied. For this purpose, the best stoichiometry and thickness of the mixture and the most suitable polymer had to be determined before their optical study and lasing properties was made in evidence. With polymethylmethacrylate (PMMA) we managed to observe the spectral narrowing of the emitted light but the observation was restricted by the pronounced degradation of the film which limits the repetition of the experiment. The best photo stability was obtained by making films of mixture of DPP derivatives and polystyrene (PS), to exhibit light amplification by stimulated emission. The main goal was to characterize these derivatives made into thin layers to obtain their threshold intensity, which is the main parameter for lasing materials. Results obtained for the threshold measurement were higher in energy compared to other published results. The lowest threshold found was around 30 uJ/cm-1 for DPP VII (the symmetrical push-push system), which is only one order of magnitude higher than the state of the art. Therefore, these materials are very promising and enhance high perspectives in lasing and organic light emitting diode (OLED) technology. Using a more appropriate excitation wavelength would certainly give better threshold values as we conducted all our analysis at a lower absorption band of the DPPs studied.

The thesis brings new insight into the relation between the molecular structure of DPP and their related properties.

6 Literature

[1] WILLIAM, A. M.: Engineered films for display technologies; *J. Mater. Chem.* (2004), 14, 4-10. DOI: 10.1039/B310846P.

[2] KRAFT, A., GRIMSDALE, A. C., HOLMES, A. B.: Electroluminescent conjugated polymers-Seeing polymers in a new light; *Angewandte Chemie International Edition* (1998), 37, 4, 402–428. DOI: 10.1002/(SICI)1521-3773(19980302)37:4<402::AID-ANIE402>3.0.CO;2-9.

[3] D. D. C. BRADLEY, IC talk 2004.

[4] GOULD, G.: "The LASER, Light Amplification by Stimulated Emission of Radiation" in Franken, P. A., Sands, R. H. (Eds.): The Ann Arbor conference on optical pumping, the *University of Michigan* (1959), 128. OCLC 02460155.

[5] PAQUETA, C., KUMACHEVAB, E.: Nanostructured polymers for photonics; *Materials Today* (2008), 11, 4, 48–56. DOI: 10.1016/S1369-7021(08)70056-7.

[6] FRIEND, R., BURROUGHES, J., BRADLEY, D.D.C.: Nature paper (1990), Patent (1989).

[7] BEYERLEIN, T., TIEKE, B., FORERO-LENGERB, S., BRÜTTING, W.: Red electroluminescence from a 1,4-diketopyrrolo[3,4-c]pyrrole (DPP)-based conjugated polymer; *Synthetic Metals* (2002), 130, (2), 115–119. DOI: 10.1016/S0379-6779(02)00058-9.

[8] VALA, M., VYŇUCHAL, J., TOMAN, P., WEITER, M., LUŇÁK, Jr. S.: Novel, soluble diphenyl-diketo-pyrrolopyrroles: Experimental and theoretical study; *Dyes and Pigments* (2010), 84, 176-182. DOI: 10.1016/j.dyepig.2009.07.014.

[9] HERBST, M., HUNGER, K., *Industrial organic pigments*. (1993) VCH, Weinheim. Third Edition (2004) ISBN 3-527-30576-9.

[10] GRIFFITHS, J.: Colour and constitution of organic molecules; *Academic Press London* (1976), 281. DOI: 10.1002/col.5080030213.

[11] SANYIN, Q., WENJUN, W., JIANLI, H., CONG, K., YITAO, L., HE, T.: New Diketopyrrolopyrrole (DPP) Dyes for Efficient Dye-Sensitized Solar Cells. J. Phys. Chem. C, (2010), 114 (2), 1343–1349. DOI: 10.1021/jp909786k.

[12] FRANCK-CONDON Principle. 1996, 68, 2243. IUPAC Compendium of Chemical Terminology 2nd Edition (1997).

[13] Modern Molecular Photochemistry N.J. Turro.

[14] ENCYCLOPEDIA OF LIFE SCIENCES / & 2002 Macmillan Publishers Ltd, Nature Publishing Group / www.els.net.

[15] SAŁEKA, P., VAHTRASA, O., GUOA, J., LUOA, Y., HELGAKERB, T., ÅGRENA, H.: Calculations of two-photon absorption cross sections by means of density-functional theory; *Chemical Physics Letters* (2003), 374, 5–6, 446–452. DOI: 10.1016/S0009-2614(03)00681-X.

[16] GELINCK, G., H., WARMAN J., M., REMMERS M., NEHER D.: Narrow-band emissions from conjugated-polymer films; *Chemical Physics Letters* (1997), 265, 3, 320-326 (7). DOI: 10.1016/S0009-2614(96)01447-9.

[17] MCGEHEE, M., GUPTA, R., VEENSTRA, S., MILLER, E. K., DIAZ-GARCIA, M. A., HEEGER, A. J.: Amplified spontaneous emission from photopumped films of a conjugated polymer; *Physical Review B* (1998), 58, 11, pp. 7035-7039. DOI: 10.1103/PhysRevB.58.7035.

[18] YUANXIANG, X., HOUYU Z., FENG, L., FANGZHONG, S., HUAN, W., XIANJIE, L., YANG, Y., YUGUANG, M.: Supramolecular interaction-induced self-assembly of organic molecules into ultra-long tubular crystals with wave guiding and amplified spontaneous emission; Journal of Materials (2012), 4, 22, 1592-1597. DOI: 10.1039/C1JM14815J.

[19] SALBECK, J., SCHÖRNER, M., FUHRMANN, T.: Optical amplification in spiro-type molecular glasses;

Thin Solid Films (2002), 417, 1–2, 20–25. DOI: 10.1016/S0040-6090(02)00650-8.

[20] Safe Handling of Color Pigments (1993), Color Pigments Manufacturers Association Inc., Virginie, USA.

[21] WILLIAMS, A. T. R., WINFIELD, S. A., MILLER, J. N.: Relative fluorescence quantum yields using a computer-controlled luminescence spectrometer; *Analyst* (1983), 108, 1067-1071. DOI: 10.1039/AN9830801067.

[22] VALA, M., WEITER M., VYŇUCHAL, J., TOMAN, P., LUŇÁK Jr. S.: Comparative Studies of Diphenyl-Diketo- Pyrrolopyrrole Derivatives for Electroluminescence Applications; *Journal of Fluorescence* (2008), 18:1181-1186. ISSN: 1053-0509. DOI: 10.1007/s10895-008-0370-x.

[23] FUKUDA, M., KODAMA, K., YAMAMOTO, H., MITO, K.: Solid-state laser with newly synthesized pigment; *Dyes and Pigments* (2002), 53, 1, pp. 67–72. DOI: 10.1016/S0143-7208(02)00002-5.

[24] SAMUEL, D. W., NAMDAS, E. B., TURNBULL, G.: : How to recognize lasing; *Nature Photonics* (2009), Vol 3. DOI: 10.1038/nphoton.2009.173.

OUZZANE Imad

Formation

2009-2014 **University of Technology** **Brno**

Ph.D. studies: Spectroscopy of fluorescence of organic compounds for applications like solar cells, OLED, LASER, printed circuits, transistors, 3D Storage, Bio- sensors.

1995-2003 **Université des Sciences Exactes et Naturelles** **Reims**

DEA (Master 2): Organic Synthesis. Analysis technics and measurement:
U.V., IR, CPV, HPLC, GC, Nuclear Magnetic Resonance, mass spectroscopy.
Maîtrise de chimie (M.Sc.): Option Bio-organics, Hétéro-éléments and Chemistry of sugars.
Licence de chimie (Bc): Electronics.
DEUG A: Option: Informatics applied to laboratory technics.
Baccalauréat série S: Specialized in Physics and Chemistry.

Professional Experience

Scientific Research

2007-2013 **University of Technology** **Brno**

Publications: http://www.vutbr.cz/en/people/imad-ouzzane-104903/publikace.

2003-2004 **CNRS laboratory of Selective Reactions** **Reims**

Employee: Synthesis of Fluorinated Heterocyclic compounds.

2000-2003 **CNRS laboratory of Selective Reactions** **Reims**

Training course M.Sc. level: Chemistry of sugars Pr. Françoise Hénin :
Synthesis of bis-oxazolines.
DEA under the supervision of Pr. Jean-Philippe Bouillon :
Synthesis of monos and bis acylsilanes via Peterson's oléfination.

2000-2002 **Autonomà University** **Barcelona**

Erasmus Training course: Research laboratory with Pr. Marcial Moreno-Mañas.
Synthesis of recyclables palladium catalysator. (Asymmetrical synthesis).
Erasmus Training course: Research laboratory with Pr. Ramon Alibès Arques.
Synthesis of a nitrone biologically active. (Total Synthesis).

Professional Experience

Employment

2007-2014 **University of Technology** **Brno**

Research engineer and technician in LASER laboratory. Teaching classes for Master degree. Erasmus project responsible. Responsible of international training course for students passing M.Sc. Degree.

2005-2013 **Champagne** **Reims**

Recruitment responsible for wine harvesting. Organisation of the work and the logistic in Champagne.

2000-2014 **WEB-SR** **France**

Webmaster and designer for websites serving a company of champagne

1997-2002 **France** **Reims**

Teacher: Private lessons in Chemistry, Physics and Mathematics.Polyvalent receptionist and manager: Cinema Gaumont, formation as a projectionist (part time job).

Languages

French, Spanish, English, Czech :	Fluent
Catalan, Arabic, Slovak:	Understood
Russian, Polish:	Basics
Chinese, German:	Learning

Informatique:

Microsoft Offices, PHP, HTML, CSS, ChemDraw, OriginLab, Windows, Linux.

Centers of Interest

Languages, rugby, travelling, music, cinema…

Special acknowledgment

This work was written on a free linux operating system with free open source software:

Thanks to Apache Open Office (openoffice), Libre office, PDF Creator (pdfforge), PDF Split And Merge (pdfsam), ACD/ChemSketch, GNU Image Manipulation Program (gimp).