Time Table

July 11, Monday

Time	Programme
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Time	Programme
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12th International conference „Electronic and Related Properties of Organic Systems“

ERPOS-12

ERPOS-12

12th International Conference

ELECTRONIC AND RELATED PROPERTIES OF ORGANIC SYSTEMS

Book of Abstracts

July 11-13, 2011
Vilnius
LITHUANIA

12th International Conference

ELECTRONIC AND RELATED PROPERTIES OF ORGANIC SYSTEMS

ERPOS-12

July 11-13, 2011

Vilnius, LITHUANIA

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Foreword

The international conferences “Electronic and Related Properties of Organic Systems” provide a forum for interdisciplinary communication between chemists, physicists and technologists with the purpose to discuss innovative research and development in organic semiconductor materials and devices. The ERPOS conferences were initiated by researchers from the Institute of Organic and Physical Chemistry of the Wroclaw University of Technology, Poland, in 1974. Since then most of the ERPOS conferences were held in Poland, however, some of them were arranged outside Poland, for instance, in Capri (Italy), Prague (Czech Republic), Cargèse (France).

The present conference (ERPOS-12) held in Vilnius, Lithuania, July 11-13, 2011 is the 12-th in the series of these international events devoted to the rapidly developing field of organic electronics and optoelectronics. Therefore the programme of the conference contains the following topics: Dynamics and Coherent Spectroscopy, Excited States and Optical Nonlinearity, Transport Phenomena, Nano- and Bio-Systems, Devices.

I am grateful to the members of the Organizing Committee for their valuable contribution and for many helpful suggestions. On behalf of the Organizing Committe, I am also very grateful to the Research Council of Lithuania for its support as well as sponsoring companies: „Light Conversion“, „Standa“, „Ekspla“, „Eksma Optics“, „Altechna“ and „LaboChema“. The value of the conference depends crucially on the input from all participants, therefore, I thank you all for coming and contributing to the ERPOS-12. I am looking forward to lively discussions and a vivid exchange of information.

Leonas Valkunas
Chairman, ERPOS-12

Conference programme

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12 July
TUESDAY

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Nano-, Bio-systems

12 July
TUESDAY

18:00 – 20:00 POSTER SESSION II

Devices

Transport Phenomena

Excited States, Optical Nonlinearities

ORAL PRESENTATIONS

“MAKING THE MOLECULAR MOVIE”: FIRST FRAMES…COMING FEATURES

R. J. Dwayne Miller[1,2]

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One of the great dream experiments in Science is to watch atomic motions as they occur during structural changes. In the fields of chemistry and biology, this prospect provides a direct observation of the very essence of chemistry and the central unifying concept of transition states in structural transitions. From a physics perspective, this capability would enable observation of rarified states of matter at an atomic level of inspection, with similar important consequences for understanding nonequilibrium dynamics and collective phenomena. This experiment has been referred to as "making the molecular movie". Due to the extraordinary requirements for simultaneous spatial and temporal resolution, it was thought to be an impossible quest and has been previously discussed in the context of the purest form of a gedanken experiment. With the recent development of femtosecond electron pulses with sufficient number density to execute single shot structure determinations, this experiment has been finally realized (Siwick et al. Science 2003). Previously thought intractable problems in attaining sufficient brightness and spatial resolution, with respect to the inherent electron-electron repulsion or space charge broadening, has been solved. With this new level of acuity in observing structural dynamics, there have been many surprises and this will be an underlying theme. Several movies depicting atomic motions during passage through structural transitions relevant to condensed phase dynamics will be shown (Sciaini et al. Nature, 2009, Ernstorfer et al. Science 2009, Eichberger et al Nature 2010). The primitive origin of molecular cooperativity has also been discovered in recent studies of molecular crystals. These new developments will be discussed in the context of developing the necessary technology to directly observe the structure-function correlation in biomolecules ¾ the fundamental molecular basis of biological systems. The future is even brighter with the advent of a new concept in relativistic electron guns that will open up direct observation of atomic motions in solution phase to gas phase systems with femtosecond time resolution to watch even the fastest atomic motions. Some of the important scientific problems to be addressed with ultrabright electron sources will be discussed to give an impression of the potential impact of this emerging field.

STRONG AND LONG MAKES SHORT: STRONG-PUMP STRONG-PROBE SPECTROSCOPY

M. F. Gelin[1*], D. Egorova[2], W. Domcke[1]

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We discuss a recently proposed time-domain spectroscopic technique [1,2], which is based on strong pump and probe pulses. The strong-pump strong-probe (SPSP) technique provides temporal resolution which is not limited by the durations of the pump and probe pulses.

By numerically exact simulations of SPSP signals for a series of multi-level vibronic models, we show that the signals exhibit electronic and vibrational beatings on timescales which are significantly shorter than the pulse durations. We demonstrate that SPSP can successfully be applied to molecular systems both in the gas phase and in a condensed phase. A possibility is shown to distinguish between the ground electronic state and excited electronic state contributions to SPSP signals. The influence of the excited state absorption on SPSP signals is discussed in detail.

Our results suggest the possible application of SPSP spectroscopy for the real-time investigation of molecular processes which cannot be temporally resolved by pump-probe spectroscopy with weak pulses.

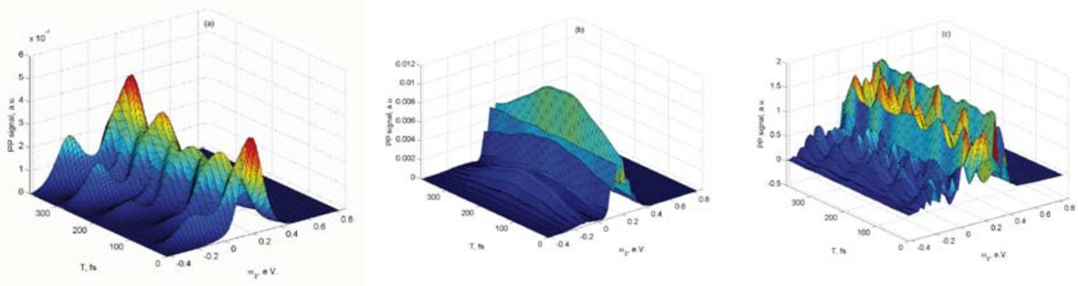

Figure 1. SPSP signal S(ω,T) excited and detected by short and weak (a), long and weak (b), and long and strong (c) pulses. ω is the carrier frequency of the probe pulse, and T is the pump-probe time delay.

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[1] M. F. Gelin, D. Egorova, W. Domcke, J. Phys. Chem. Lett., **2**, 114 (2011).
[2] M. F. Gelin, D. Egorova, W. Domcke, J. Phys. Chem. B, ASAP article, (2011).

QUANTUM MASTER EQUATIONS FOR NON-LINEAR RESPONSE OF COMPLEX MOLECULAR SYSTEMS

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In recent years, two-dimensional (2D) coherent spectroscopy [1] developed first in NMR, has been brought into optical and near infra-red domains. The 2D Fourier transformed spectrum completely characterizes the third order non-linear response of a molecular ensemble in amplitude and phase, providing thus the maximal information accessible in a three pulse experiment. Since its first experimental realization it has yielded many important insights into the properties of small molecules, polymers and even large photosynthetic aggregates [2-4]. One of the most interesting revelations was the identification of long living electronic coherences in energy transfer dynamics of photosynthetic proteins [5]. This has stimulated a renewed interest in the properties of energy transfer in biological systems and its quantum nature.

Most 2D experiments are well described by the third order semiclassical light-matter interaction response function (perturbation) theory. Response functions of model few level systems with pure dephasing (no energy transfer between the levels) can be calculated using second cumulant in Magnus expansion [6] and expressed in terms of the energy gap correlation function (EGCF). For a Gaussian bath this result is exact, and the EGCF of the electronic transitions thus determines fully both the linear (absorption) and the non-linear spectra. For energy transferring systems, such as Frenkel excitons in photosynthetic complexes [7], the exact response functions cannot be constructed in this way (by second cumulant). Photosynthetic complexes are relatively large and the proper methods to simulate finite timescale stochastic fluctuations at finite temperatures [8] carry a substantial numerical cost. They can be readily implemented only for small systems [9]. Practical calculations thus require some type of reduced dynamics where only electronic degrees of freedom (DOF) are treated explicitly. A convenient form of reduced dynamics, master equations, is realized by deriving kinetic equations for the reduced density matrix (RDM) averaged over the DOF of the bath.

It was demonstrated that RDM master equations derived by projection operator technique reproduce the linear response [10]. For higher order response, however, the same approach neglects bath correlation between different time intervals of molecule photo-induced evolution separated by interaction with laser pulses. In other words RDM master equations does not properly account for the non-equilibrium state of the phonon bath present after the second and the third laser pulse. This neglect can lead to a complete loss of the experimentally observed dynamics in simulated 2D spectra, such as in the case of the vibrational line shape modulation of a single electronic transition [11]. This modulation interplays with simultaneous effect of electronic coherence. Accounting reliably for bath correlations among intervals is therefore of utmost importance for interpretation of the role of quantum coherence in natural light-harvesting.

In this presentation, we will show that the exact third order response function of a multilevel molecular system with pure dephasing can be calculated by certain generalization of RDM master equations. We introduce special parametric projection operators that enable us to derive distinct equation of motion for each time interval of the response function. These parametric projectors offer a systematic approach to improvement of current master equation method by incorporating bath correlation effects into the calculation of non-linear response in energy transfer systems. Provided the optical coherences in the first interval can be assumed independent of each other (secular approximation), the parametric projectors can be used to derive corresponding master equations for the so-called population interval of the non-linear response function even in presence of relaxation [13]. Such equation contains a usual second order quantum master equation term and a correction which describes correlation between the optical coherence and population dynamics. We will present numerical results confirming the effect. Similarly, new equations are constructed in the second coherence interval to complete the non-linear response, and to enable simulation of the interplay of the non-equilibrium bath and electronic coherence effects.

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SIMULATION STUDY OF 2D SPECTRUM OF MOLECULAR AGGREGATES COUPLED TO CORRELATED COLORED BATH

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Currently developed two-dimensional (2D) spectroscopy provides a window into microscopic quantum dynamics of photoexcitations with a femtosecond time resolution [1,2]. Recently observed oscillatory dynamics of 2D spectra of photosynthetic pigment-protein complexes [3,4] raise the fundamental questions of how to disentangle various origins of these oscillations, which may include quantum beats, quantum transport, or intra-molecular vibrations.

We study the dissipative effects induced by the bath on photoexcited non-equilibrium electronic states. It is demonstrated that the bath induces three types of phenomena: (i) noise-assisted irreversible transport and damping, (ii) correlated-noise-induced support of electronic coherences and (iii) colored-noise-induced vibrational wavepacket beats. These microscopic effects are directly mapped onto two-dimensional spectroscopy signals. We develop methods how to unravel the combined non-linear spectrum and isolate different effects. The insights are demonstrated using simulations of the 2D spectra of photosynthetic Fenna-Matthews-Olson (FMO) aggregate (representative spectrum is shown in Figure 1), which has well-resolved exciton resonances, and a circular porphyrin hexamer, whose linear absorption spectra show vibrational progression. We use a generic exciton Hamiltonian coupled to a bath, characterized by an unique spectral density: bath-induced noise has smooth, while the intra-molecular vibrations create δ-shaped spectral densities. We show how various scenarios of correlated molecular fluctuations lead to some highly oscillatory cross-peaks. Molecular vibrations cause progression of diagonal peaks in the 2D spectrum and make their corresponding cross-peaks highly oscillatory. We, thus, demonstrate that bath fluctuations and molecular vibrations of realistic molecular aggregates are highly entangled in 2D spectroscopy and additional applications of coherent control and density matrix tomography is needed in separating different effects.

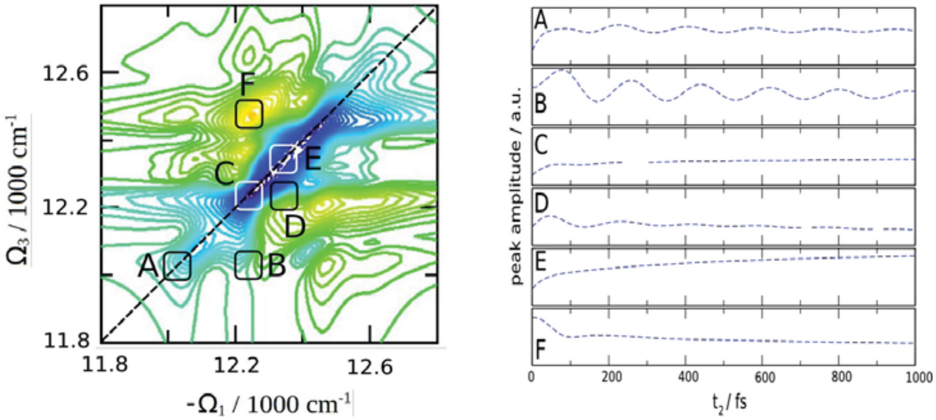

Figure 1. 2D rephasing spectrum of FMO aggregate (left); time-evolution of selected peaks (right).

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THEORY OF QUANTUM COHERENCE IN EXCITATION TRANSFER IN ORGANIC MATERIALS: SOME OLD SOLUTIONS TO PUZZLING PROBLEMS

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Theoretical approaches to the description and identification of quantum coherence in the transport of quasiparticles and the transfer of excitation in organic materials will be described. The phenomena play crucial roles in biological processes such as photosynthesis and industrial processes such as photo-imaging. It will be shown how some old, perhaps forgotten, tools can address these issues efficiently and naturally.

EXCITON DYNAMICS IN SEMICRYSTALLINE FILMS OF POLY(3-HEXYLTHIOPHENE) STUDIED BY 2D ELECTRONIC SPECTROSCOPY

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Conjugated polymers show great potential for development of solution-processable low cost and large area solar cells. Photovoltaic cells made of regioregular poly(3-hexylthiophene) (P3HT) blended with fullerene derivatives show nearly 100% internal quantum efficiency but the mechanism of efficient charge separation is not understood yet. Two-dimensional electronic (2DE) spectroscopy has been developed recently and is capable of revealing correlations between optical transitions that occur in different time intervals.

We will report a 2DE study of P3HT films. The 2DE spectra were recorded with site-selective excitation in the low energy tail of the absorption spectrum (Fig. 1). They are dominated by a positive absorptive signal associated with ground-state bleaching and stimulated emission. We observe spectral dynamics on a time scale of 20 femtoseconds which is attributed to electronic relaxation in a disordered H-aggregate formed by strong electronic coupling between conjugated chains with π-stacking. Broadband excitation using 15 fs pulses shows oscillations of the 2D signal amplitude which survive up to a picosecond and indicate a persistent vibrational coherence.

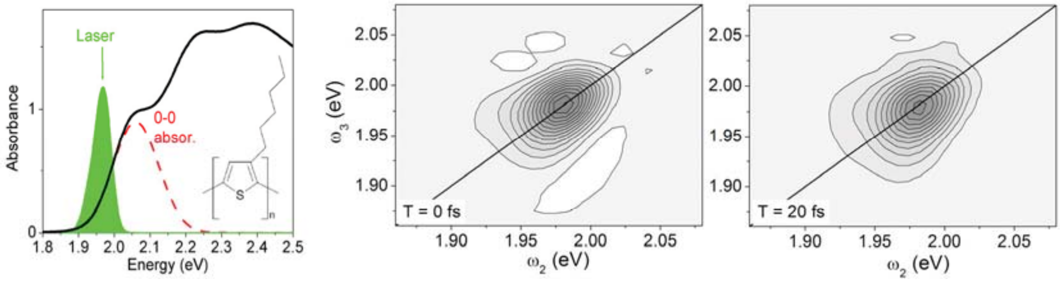

Fig. 1. Left panel shows the absorption spectrum of P3HT film (solid line), the 0-0 vibronic band of absorption (dashed line) and the spectrum of the 36 fs laser pulse used for measurements. Central and right panels show the absorptive part of 2DE spectra recorded at population times of T=0 and 20 fs after excitation, the dark area on the diagonal is a positive signal attributed to ground-state bleaching and stimulated emission.

COHERENTLY-CONTROLLED TWO-DIMENSIONAL ELECTRONIC SPECTROSCOPY

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Optical two-dimensional photon-echo spectroscopy (2D-PE) is realized with shaped excitation pulses allowing the coherent control of two-dimensional spectra [1]. This development enables probing and manipulation of state-selective quantum decoherence and phase (time-) sensitive couplings between states. The designed femtosecond 2D-PE spectrometer with two pulse shapers is based on a passively stabilized four-beam interferometer with diffractive optic and allows heterodyne detection of the PE-signals with a long-term phase stability $> \Lambda/100$ in the VIS [1] and a temporal resolution of ≤ 10 fs. The first two-dimensional spectra of solvated dye (Rhodamine 101/MeOH) measured with unshaped and shaped pulses found in optimization experiment [2] exhibit significant differences [1]. By excitation with phase-shaped pulses having periodic modulation that matches the vibrational frequency of the molecule (220 cm^{-1}) we detected a long-lived phase memory ($T \geq 80$ ps) at room temperature (see Fig. 1). The induced phase memory appearing as a modulation of the 2D-spectrum along the ω_τ axis (Fig. 1 B), where τ is the delay between the excitation pulses, has a clear resonant nature with respect to the modulation frequency in the phase of shaped pulses.

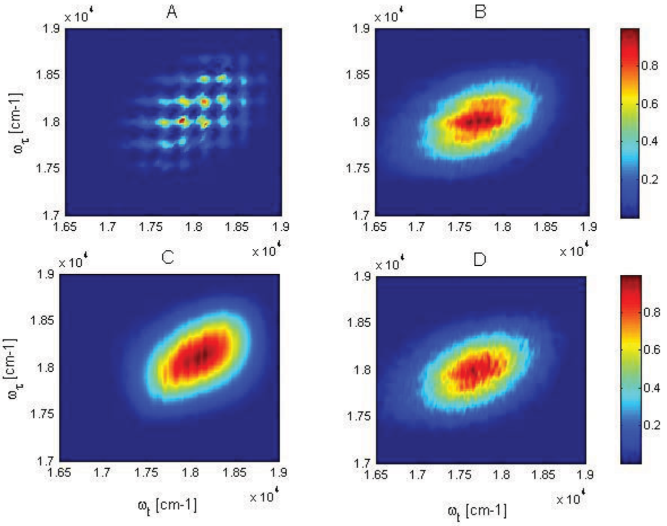

Figure 1. 2D-PE power spectra obtained using phase-modulated excitation pulses at waiting times T = 0 (A) and 40 ps (B). The lower panel shows corresponding spectra measured with unshaped pulses.

Theoretical modeling based on the conventional third-order response theory (Loring & Mukamel, [3]) perfectly reproduces experimental 2D-spectra at small waiting times ($T \leq 1$ ps; see Fig. 1 A); however, at long waiting times the presence of experimentally-observed induced phase memory cannot be reproduced. Possible physical mechanisms, not accounted for in the Loring-Mukamel theory, are discussed.

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TWO-COLOR TWO DIMENSIONAL ELECTRONIC SPECTROSCOPY STUDY OF SELF-ASSEMBLED PORPHYRIN NANOTUBES

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During recent years electronic two-dimensional (2D) spectroscopy has been established as a powerful tool in investigating artificial and biological multichromophoric systems [1]. The special advantage of the technique lies in its ability to obtain dynamic and spectroscopic information with simultaneous time and frequency resolution that is not limited by the uncertainty principle related to the ultrashort laser pulses used in the experiments. In addition, since three excitation pulses are used to produce four wave mixing signal, parameters of each pulse can be manipulated separately (polarization, pulse shape, etc.). This allows to acquire results with unprecedented detail, unraveling previously unavailable insights in functionality of molecular systems.

Recently we have added one more dimension to the technique, namely ability to perform experiments in two substantially different spectral regions, when only the cross peaks are measured. Two-color 2D (2C2D) spectroscopy technique opens new possibilities of getting information about correlations (couplings) and detailed dynamics between these regions.

Here we present the 2C2D spectroscopy study of zwitterionic meso-tetra(4-sulfonatophenyl) porphyrin ($TPPS_4$) aggregates. Under acidic conditions (pH 1-2) $TPPS_4$ molecules self-assemble into cylindrical J-aggregates with nanotube diameter of ~18 nm and length of up to several micrometers [2]. The absorption spectrum of the aggregates is dominated by two excitonic bands originating from shifted monomer B and Q bands. Two color laser spectra are tuned to cover both bands separately (Figure 1). From single color experiments homogeneous linewidths of excitonic bands are determined. In addition intraband excitonic relaxation and frequency memory loss is studied. By measuring cross peaks between two spectral regions in two-color experiment we investigated ultrafast energy transfer between B and Q excitonic bands. Additionally correlation of intraband frequencies, which distribution is dictated by the inhomogeneous broadening, during energy relaxation between B and Q bands is examined.

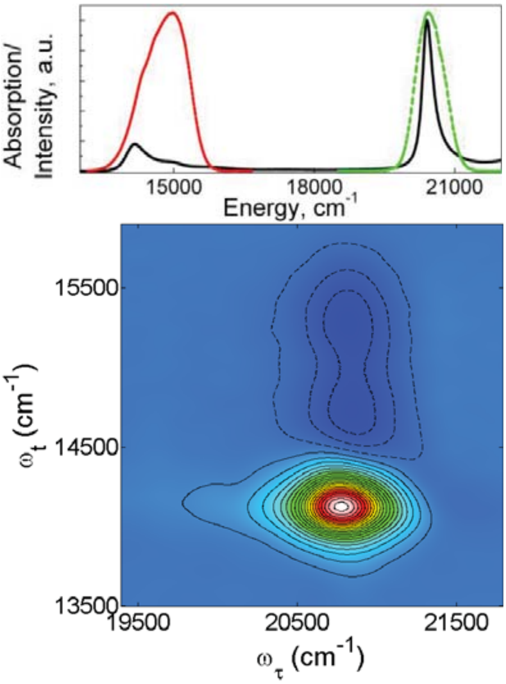

Figure 1. Top - $TPPS_4$ absorption spectrum and two laser spectra covering absorption bands, bottom - 2C2D spectrum of $TPPS_4$. Solid line contours show positive features corresponding to emissive signals and dashed line contours show negative signals corresponding to absorptive features as excited state absorption.

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ULTRAFAST EXCITON AND CHARGE DYNAMICS IN ISOLATED AND INTERACTING CARBON NANOTUBES

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Carbon nanotubes (CNTs) are promising materials for optoelectronic devices like, photovoltaic elements, photodetectors and sensors [1]. To fully exploit their potential, insight into the dynamics of exciton transport, exciton dissociation and charge transport is needed. In the device environment, these phenomena are largely controlled by extrinsic factors, like, structural defects and interactions with other pi-conjugated systems (polymers, electron acceptors, CNT aggregates). Due to the high intrinsic mobilities for both charges and excitons, the extrinsic factors can influence exciton and charge dynamics on a very short time scale. Here, we present recent results on ultrafast charge and exciton dynamics in CNTs by transient absorption spectroscopy with down to 10 fs instrumental resolution. Samples are chirality enriched CNTs from density gradient ultracentrifugation, either isolated or in small aggregates. In isolated CNTs, we find that exciton migration is diffusive, and therefore essentially limited by the defect density. In small CNT bundles after resonantly pumping the lowest excitonic resonance S_1, we observe ultrafast inter-tube exciton transfer towards CNTs with lower optical bandgaps. If the S_1 energies of the interacting CNT are close to kT (between the (6,5) and (7,5) chiralities), then an equilibrium exciton density is reached in less than 10 fs. If the S_1 energetic separation is larger (between the (6,4) and the (6,5) chiralities), then complete exciton transfer is found within less than 10 fs [2]. The dynamics of the excitonic populations on the exciton "donor" and "acceptor" chiralities are traced via the transient bleach of the respective exciton resonances, see figure 1. Coherent effects, superposing the population dynamics on this very short time scale (figure 1a), are separated by a numerical method [3]. The result is shown in figure 1 b. Horizontal cuts yield pump-probe dynamics at constant probe energies which allow to visualize a delayed population transfer from the (6,5) towards the (7,5) tube (figure 1c). When pumping small CNT aggregates with high excess energy, then a large fraction of the excitons is dissociated into free carriers. These carriers cause distinct features in the transient absorption spectra in the S2 spectral region, which allow a tracing of charge carrier dynamics (recombination and localization) on a sub-picosend to picosecond time scale.

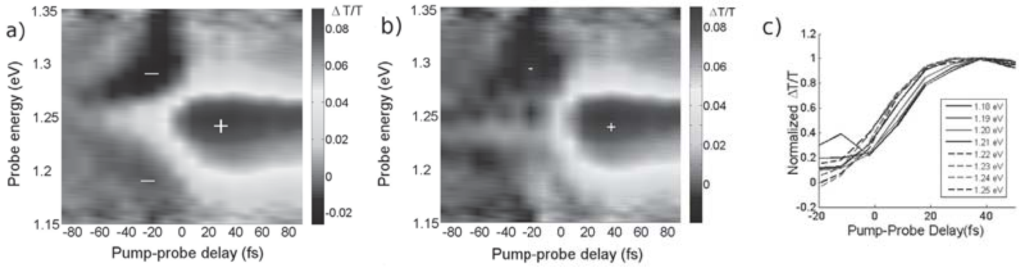

Figure 1. a) Time-resolved pump-probe spectrum of the transient ground state bleach of small CNT aggregates after resonantly pumping the (6,5) tubes at 1.25 eV with 20 fs pulses. The spectrum shows strong coherent effects (spectral oscillations) at negative pump-probe delays. b) isolated population contribution to a). c) horizontal cuts through b) for probe energies dominated by the bleach of the (6,5) tubes (dashed lines) and of the (7,5) tubes (solid lines).

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NONLINEAR ABSORPTION AND REFRACTION IN METAL-CONTAINING CHROMOPHORES, NANO-OBJECTS AND BIO-DERIVED MATERIALS

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Materials with optimized nonlinear absorption are needed for numerous applications including those where the nonlinear absorption is used to excite luminescence (eg in two-photon microscopy) as well as those where no light emission is required (e.g. in two-photon induced photochemistry or optical power limiting). Nonlinear refraction, on the other hand, is needed for photonic applications such as all-optical switching. Understanding the interrelations between the nonlinear absorption and refraction of various materials requires systematic studies of wide wavelength range dispersion of both parameters, i.e. both the real and the imaginary parts of the cubic susceptibility $\chi^{(3)}$ or molecular hyperpolarizability γ. We use the technique of Z-scan, employing a tunable femtosecond laser system as a light source. These studies have been carried out for many years in Canberra at the ANU (see eg [1-3]) and have now been initiated at the Wroclaw University of Technology.

An example of dispersion of the complex hyperpolarizability γ is shown in Figure 1. We have investigated many molecules containing metal atoms such as highly conjugated metal acetylide compounds, coordination complexes or clusters, and dendrimers. We also performed some studies on bio-derived materials such as DNA. More recently, we have started measurements of the cubic nonlinearity in nano-objects such as colloidal inorganic nanoparticles.

In general, there is no simple way to relate the two-photon absorption spectra (imaginary part of γ) to the spectral dependence of the nonlinear refraction (real part of γ). Failures of attempts to make use of Kramers-Kronig based approaches indicate that even in typical two-photon chromophores some role may be played by one–photon transitions and by two-photon induced cumulative effects. We find that the NLO behavior of some metal-containing clusters and of lanthanide-doped nanoparticles may be completely dominated by effects related to one-photon transitions and excited state absorption.

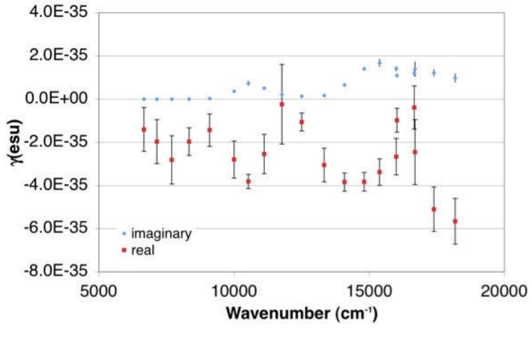

Figure 1. An example of the dispersion of the complex hyperpolarizability of an organic chromophore obtained from femtosecond Z-scan measurements. This is one of the first results obtained using the new tunable femtosecond laser system (a Quantronic Integra regenerative amplifier with a Quantronic Palitra optical parametric amplifier) in Wroclaw.

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EXCITON DYNAMICS IN SEMICONDUCTING CARBON NANOTUBES

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We report femtosecond transient absorption spectroscopic study on the (6, 5) single-walled carbon nanotubes and the (7, 5) inner tubes of a dominant double-walled carbon nanotube species. We found that the dynamics of exciton relaxation probed at the first transition-allowed state (E_{11}) of a given tube type exhibits a markedly slower decay when the second transition-allowed state (E_{22}) is excited than that measured by exciting its first transition-allowed state (E_{11}). A linear intensity dependence of the maximal amplitude of the transient absorption signal is found for the E_{22} excitation, whereas the corresponding amplitude scales linearly with the square root of the E_{11} excitation intensity. Theoretical modeling of these experimental findings was performed by developing a continuum model and a stochastic model with explicit consideration of the annihilation of coherent excitons. Our detailed numerical simulations show that both models can reproduce reasonably well the initial portion of decay kinetics measured upon the E_{22} and E_{11} excitation of the chosen tube species, but the stochastic model gives qualitatively better agreement with the intensity dependence observed experimentally than those obtained with the continuum model.

Three-pulse photon echo peak-shift measurements were also performed for the same nanotubes embedded in polymer matrix at room temperature. We found a striking dependence of the peak shift on the excitation intensity. Numerical simulations based on the interacting boson model demonstrate that the intensity dependence originates from a highly nonlinear optical response initiated by exciton-exciton annihilation.

ENHANCING PHOTOSENSITIVITY OF CARBON NANOTUBES BY MODIFICATION WITH METAL CONTAINING BLOCK COPOLYMERS

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Carbon nanotubes exhibit highly promising potentials in applications such as optoelectronics, advanced composites, sensing, and biomedics. They have been demonstrated to be the key materials in various optoelectronic devices such as field effect transistors, photo switching, light sensing, and light emitters. In order to disperse carbon nanotubes in solution, chemical modification of nanotube surface or surfactants have to be used. Here, we report the use of a multifunctional metal containing block copolymers for dispersing carbon nanotubes and modification of their photosensitivity. **Ru-b-Py** (Figure 1) was synthesized by reversible addition-fragmentation chain transfer polymerization. The block copolymer contains pyrene moieties in one block and ruthenium terpyridine isothiocyanate complexes in another block, which function as anchoring groups and photosensitizers, respectively. After mixing **Ru-b-Py** with multiwalled carbon nanotubes in DMF, the dispersion was stable for more than 5 days. The nanotube dispersion was drop casted on an ITO substrate with patterned electrodes, and the photoconductivity of individual nanotube was measured with a conductive atomic force microscope with and without illumination of light. It was observed that the photocurrent response of the copolymer:nanotube composite at different wavelength agreed well with the absorption spectrum of carbon nanotube modified with **Ru-b-Py**. This strongly suggests that the enhancement of photoconductivity of the block copolymer-nanotube composite is due to the ruthenium complex sensitizers, which strongly absorbs between 500-700 nm. This new approach in modifying carbon nanotubes allows us to fine-tune the optical and electronic of carbon nanotubes and related materials with similar structures, such as graphenes.

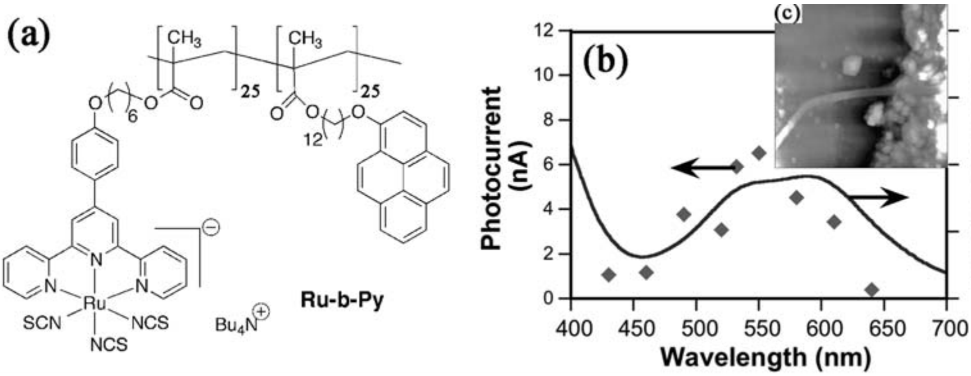

Figure 1. (a) Structure of the multifunctional block copolymer; (b) photocurrent response and optical absorption spectrum of the copolymer:carbon nanotube composite; (c) AFM micrograph of carbon nanotube functionalized with **Ru-b-Py** at the edge of an ITO electrode (full scale = 2 μm).

ULTRAFAST EXCITATION ENERGY TRANSFER AND THE MECHANISM OF NON-PHOTOCHEMICAL QUENCHING IN PLANT PHOTOSYNTHESIS

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The success of photosynthesis relies on two ultrafast processes: excitation energy transfer in the light-harvesting antenna followed by charge separation in the reaction center. LHCII, the peripheral light-harvesting complex of Photosystem II, plays a major role. At the same time, the same light-harvesting system can be ‘switched’ into a quenching state, which effectively protects the reaction center of Photosystem II from over-excitation and photodamage. In this talk I will demonstrate how LHCII collects and transfers excitation energy. Using single molecule spectroscopy we have discovered how LHCII can switch between this light-harvesting state, a quenched state and a red-shifted state. We show that the switching properties between the light-harvesting state and the quenched state depend strongly on the environmental conditions, where the quenched state is favoured under ‘NPQ-like’ conditions. It is argued that this is the mechanism of non-photochemical quenching in plants.

TUNEABLE ORGANIC NANODOTS AS A BIOCOMPATIBLE AND NATURE-FRIENDLY ALTERNATIVE TO QUANTUM DOTS FOR NANOPHOTONICS

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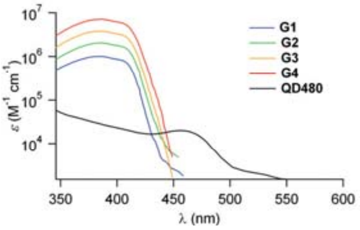
Among inorganic nanomaterials, semiconductors quantum dots (QDs) have gained a lot of popularity as photonic nano-objects due to their unique optical and electronic properties. These include record excitation cross-sections, luminescence tuneability (by varying the size and/or composition), photostability, multicarrier generation…. These nanoparticles have thus been heralded as major nanotools for imaging (including bioimaging) purposes as well as for the elaboration of nanostructures for optoelectronics. However, these inorganic systems suffer from several drawbacks such as toxicity, dispersity, blinking … and raise a number of questions with respect to environmental and safety issues (clearance, biodegradability…).

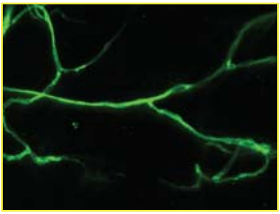
In order to address theses issues and concern about potential hazards of nanosciences, we have implemented an innovative approach towards a novel class of biocompatible and eco-friendly soft purely *organic nanodots*. These fully organic nano-emitters of controlled nature are obtained from a rational and bottom-up route and differ in both their design and in the origin of their luminescent/optical properties from QDs. Our route is based on the control, at the single nano-object level, of the optical responses via the design of covalent assemblies of highly confined chromophores in hierarchical architectures of defined structure in which interactions are controlled.

This led to tuneable nano-objects which can outperform semiconductor quantum dots in terms of brightness by orders of magnitude [1], show cooperative enhancement of nonlinear absorption cross-sections, and allow fast intra- and inter-nanodot excitation energy transfer in films [2]. These tuneable organic nanodots have been proved to be of major interest as single nano-objects for in vivo imaging [3] as well for sensitive detection of explosives [2].



Comparison of excitation efficiencies (and brightness) between blue emitting *nanodots* and analogous quantum dot QD480.

Tuning the luminescence color of organic *nanodots* .



I*n vivo* two-photon imaging of blood vessels of *Xenopus laevis* tadpole, after intracardiac injection of green-emitting water-soluble nanodot.

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BIO-ORGANIC INTERFACES FOR NEURONAL PHOTOACTIVATION

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A key issue toward the realization of retinal prosthetic devices is a reliable transduction of the information carried by light into specific patterns of electrical activity at the level of the networks involved in visual information processing. In this perspective, soft organic materials offer a unique chance in coupling artificial sensors with neuronal tissues [1]. We recently reported [2] the successful interfacing of an organic blend with a network of primary neurons. We show that primary neurons can be successfully grown onto the polymer layer, without affecting the optoelectronic properties of the active material and the biological functionalities of the neuronal network. Moreover, action potentials can be triggered in a temporally reliable and spatially selective manner by shining short pulses of visible light. Our results lead to a new generation of neuronal communication and photo-manipulation techniques, thus paving the way to the development of an artificial retina based on organic photo-detectors and other neuro-prosthetic interfaces.

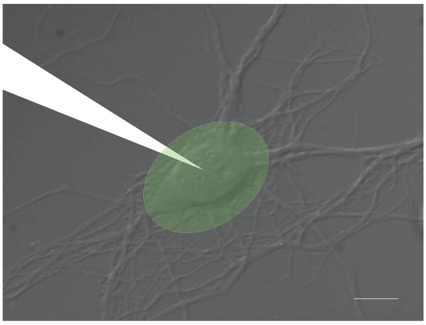

Figure 1. Hyppocampal neurons cultured on polymer substrate and schematic representation of the optical stimulation paradigm. Scale bar, 10μm.

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EFFECTS OF METAL NANOPARTICLES ON ENERGY SPECTRA AND OPTICAL PROPERTIES OF DIFFERENT ASSEMBLIES

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The unique optical properties of localized surface plasmons are the subject of considerable interest due to perspective applications including the surface-enhanced Raman scattering, biosensors, enhanced photoluminescence, bio-molecular tagging and optical data storage devices. Some effects are connected with the existence of the strong resonant interaction between the plasmon states and electronic states of other components of the assembly. Due to the giant dipole transition moment of the surface plasmon excitation the mixing of the plasmon states with electronic states of other entities leads to significant changes of properties of the composite system: shift of electron levels, enhancement of optical transitions etc. In this report, the formation of hybrid states between the surface plasmon and electronic states are considered for two types of low dimensional systems.

Firstly, the effects of the resonant interaction between an exciton in a quantum well and a localized plasmon in a metal nanoparticle are studied. It is shown that 1) if the exciton energy level is lower than that of the plasmon, the exciton-plasmon interaction may result in the localization of the exciton as a whole in the vicinity of the nanoparticle; 2) near the resonance between the exciton and the plasmon levels a giant (by several orders of magnitude) increase of the oscillator strength of the localized exciton transition is possible [1].

Secondly, we studied the electronic spectra and optical parameters of the light harvesting complexes LH2 of the photosynthetic purple bacterium *Rhodopseudomonas acidophila,* which interacts with the plasmon excitation of a metal nanoparticle. Our attention was concentrated on the studying of a ring consisting of eighteen closely interacting BChl molecules (B850) with the absorption band around 850 nm. The electronic excited states of this ring are coherently delocalized over eighteen BChl molecules (so they are Frenkel's excitons). The formation of the hybrid state of the metal nanoparticle and molecules of the ring causes the shift of electronic levels, the change of the polarization and strong enhancement of optical transitions. The value of the enhancement of the transitions increases for nanoparticles with the plasmon frequency close to the frequency of optical transitions for the ring. The effect of the location of the metal particle relative to the ring has been considered. The interaction of LH2 complexes with metal nanoparticles containing a dielectric inclusion (metallic nanoshells) was studied as well. The dielectric inclusion allows one to change the plasmon frequency in wide region and, in this way, to approach the resonance with excitonic levels (and thus, to reach greater enhancement of the light absorption by the complexes). The enhancement of the oscillator strength may be increased by a factor of several tens.

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HIGHLY EFFICIENT ORGANIC DEVICES

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Organic semiconductors with conjugated electron system are currently intensively investigated for optoelectronic applications. This interest is spurred by novel devices such as organic light-emitting diodes (OLED), and organic solar cells. For both devices, high efficiency is a key parameter for many applications. I this talk, I will discuss some of the recent progress on highly efficient OLED and solar cells, in particular results using doped transport layers [1]. Surprisingly, doping (for raising the conductivity) has been largely ignored till now in organic devices, in contrast to classical silicon technology where controlled n- and p-type doping has always been a standard technique needed for virtually all devices.

The concept of molecular doping allowed to realize green OLED devices with the highest efficiencies reported so far [2], well exceeding the efficiency of current inorganic GaN LED! The devices were pin-devices where the emitting layer is embedded between a p-doped hole transport layer and an n-doped electron transport layers. It has been shown that these pin-structures can also achieve extremely long lifetimes. White OLED have recently achieved very high efficiencies of 90lm/W [3], significantly higher than fluorescent tubes, opening the path to a new form of high-efficiency area lighting devices.

The doping concepts can be applied in organic solar cells as well. Here, the use of electrically doped transport layers is helpful for an optimized optical design since it yields large freedom in the choice of window layer thickness, this making it easy to put the absorber layers in the electric field maximum in the cavity [4]. Also, doped layers are a key point in efficient charge recombination junctions for tandem solar cells: It has been shown that a pn-junction is an excellent recombination contact causing very small voltage loss. Recently, we have achieved solar cells with certified efficiency exceeding 8% on larger area.

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EFFECT OF CHARGE TRAPPING DOPANTS ON THE CURRENT AND EFFICIENCY OF POLYFLUORENE-BASED LEDS

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Doping of the emissive layer of organic light-emitting diodes has been mostly used to tune their emission colour and to increase the electroluminescence efficiency. In the first case, the process relies on the energy transfer from the host (which, in most cases, is the charge transporting material) to the guest molecules. In the second case, the increase of efficiency may result from an exciton confinement or due to the use of phosphorescent dopants in order to harvest the triplets. The presence of the guest or dopant has usually a detrimental effect on the charge transport, via charge localization or disorder, and leads also to an increase of the dopant emission with respect to its contribution to the photoluminescence spectrum, as a result of on-site exciton formation promoted by that charge localization.

In this study we use dopants with a wider gap than the host polymer, thereby avoiding energy transfer from the host to the guess and promoting instead the reverse energy transfer process. In this case, any on-guest formed exciton would be transferred to the host. The dopants were chosen to induce either hole or electron trapping.

In this particular case, we have selected TPD, PBD and OXD-7 as charge trapping dopants and PFO, F8BT and a blend of PFO/F8BT as host materials. TPD, having a ionization potential (Ip) of 5.4 eV will act as hole trap, while PBD (electron affinity, EA, of 2.6 eV) and OXD-7 (EA= 2.8 eV) are expected to act as electron traps. We have studied the concentration effect of these dopants on the current of hole-only devices and on the efficiency of the LEDs fabricated with such composites. For instance, in the case of the LEDs based on the PFO/F8BT blend, a significant increase of the efficiency occurs at low level concentration of both hole and electron trap dopants.

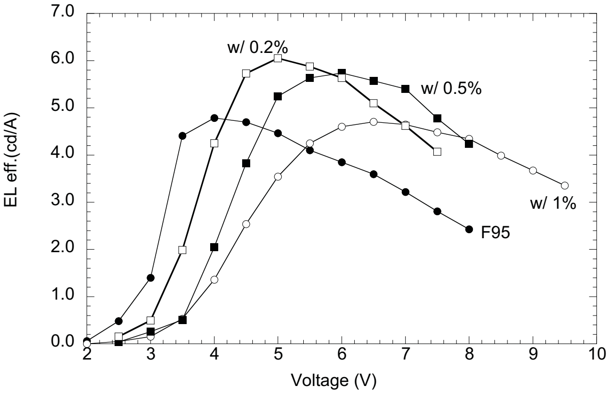

Figure 1. This figure shows conference logo. Note that only one figure is allowed.

Figure 1. Electroluminescence (EL) efficiency of devices based on a blend of PFO (95%, by weight) and F8BT (F95 blend) with various contents of TPD and OXD-7 (used in the same concentration, by weight).

Acknowledgments This work was partially supported by FCT-Portugal and FEDER under the contract PTDC/QUI/65474/2006

ELECTRIC FIELD CONFINEMENT EFFECT ON CHARGE TRANSPORT IN ORGANIC FIELD-EFFECT TRANSISTORS

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Organic semiconductor films offer a huge potential for the emerging flexible large-area electronics because they allow for a low cost of device fabrication and a low-temperature processing of semiconductor layers compatible with flexible plastic substrates. The charge-carrier mobility is the critical factor that limits the efficiencies of modern optoelectronic devices and it is usually attributed to the non-crystalline (disordered) nature of conventional organic semiconducting films, so the charge transport is controlled by localized states disordered in space and energy. Therefore, apart from the endeavor to optimize the structure-property relations of organic functional layers, it is of paramount importance to improve understanding the conceptual premises of the electrical transport mechanisms in realistic organic electronic devices.

Dependence of the charge mobility on electric field is of particular interest as it bears on the fundamental nature of charge transport in organic semiconductors. In contrast to perfect organic crystals with band-type transport, the charge mobility in amorphous organic solids typically considerably increases with electric field in a Poole-Frenkel fashion. The latter is a consequence of inherent energetic disorder and thermally-activated hopping charge transport through the manifold of localized sites in organic semiconductors with Gaussian density-of-states distribution. There were several hopping transport models suggested to describe adequately the field-dependent charge-carrier mobility in realistic organic semiconductor devices like organic field-effect transistors (OFET). Notably, so-called Extended Gaussian disorder model has been recently suggested using both numerical computer simulations [1] and analytical theory [2], and predicts a similarly strong increase of the charge mobility with increasing both the carrier concentration and the electric field.

A limitation of existing models is that they tacitly assume an idealized amorphous system where energetic disorder is homogenously spread over an organic semiconducting film. In all previous treatments of the charge transport in disordered organic solids the electric field was also assumed to be homogenous within the film. This might not always be true in polydomain films where transport is controlled by spatially limited grain boundaries constituting the major potential barriers for charge transport. In the present paper [3] we demonstrate the influence of strong local lateral electric fields, which are much higher than the spatially averaged field, on the effective charge mobility by the comparison of OFETs with and without grain boundaries made from the same active organic material (silylethynyl-substituted pentacene). We show that the strong field inhomogeneity, being experimentally observed by scanning Kelvin probe microscopy, emerges when the charge accumulation layer is formed and it is due to a sharp difference between local conductivities within grains and at grain boundaries. This has an immediate impact on the electric field dependent charge transport controlled by grain boundaries and we account for this within an extended disorder model to describe quantitatively puzzling field dependence of the OFET mobility observed in organic semiconductors with poly-domain morphology.

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ENHANCEMENT OF LIGHT OUTCOUPLING EFFICIENCY IN OLEDS BY EMPLOYING NANO STRUCTURED HOLE TRANSPORT MATERIALS

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The major advantages of organic light emitting diodes (OLEDs) in the application field of lighting or display are the self emittance of the materials, resulting in brilliant colours, a large viewing angle and a high power efficiency [1,2]. However, the excellent device performance is strongly limited by a low light outcoupling, because of the high refractive index of organic materials and the optical confinement due to internal reflection. Following the classical ray-optics theory, 80% of the light produced inside a conventional OLED is lost [3-4]. Several strategies were developed in the last years, e.g. by using micro-cavity effects [5] or inserting an hole-transport layer between anode and emitter, which reduces the injection barriers for holes by creating an intermediate electronic step.

In this contribution, we report on a novel route to increase the outcoupling efficiency in OLEDs. We present an OLED configuration featuring a nano-structured hole-conductor layer showing a reduced refractive index. The layers constitute a foam with pore sizes in the nanometer range using the “Principle Of Supercritical Microemulsion Expansion” (POSME) [6]. The potential of this method, especially for forming bulk nanofoams, becomes evident in scanning electron microscopy (SEM), indicating pore sizes with a maximum in the nanometer range (100 nm). We demonstrate that embedding such low-index nanoporous hole-transport layers in OLEDs improves their efficiency substantially. Thus, this approach can in principle lead to OLEDs with super high efficiency.

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ORGANIC-ORGANIC HETEROEPITAXY OF RED-, GREEN-, AND BLUE-EMITTING NANOFIBERS

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In recent years, heteroepitaxy of organic-organic nanostructures has been demonstrated as a valuable technique to explore the full potential of organic semiconductors for optoelectronic applications. Crystalline and highly ordered heterostructures with different morphology and molecular orientations can be realized by heteroepitaxy starting from conjugated oligomers, aimed at tailoring their optical properties and transport characteristics [1-4]. Para-hexaphenyl (p-6P) and sexithiophene (6T) are good model systems for heteroepitaxy as well as important oligomers for device applications, and hence, several studies have been conducted on the p-6P/6T material couple.

Here we show by combining optical, structural, and morphology investigations that organic-organic heteroepitaxy can be used to produce multilayered organic nanofibers with high crystallinity, well-defined epitaxial relationship along different materials' phases, sharp molecular azimuthal order, and long-range morphological homogeneity [5]. Directed growth of sexithiophene on a para-sexiphenyl fiber template on muscovite mica results in highly crystalline and oriented hetero-nanostructures with molecules laying parallel to the substrate, yielding strong optical polarization anisotropy in a broad band of wavelengths. Achievement of broad band optical waveguiding in blue, green, and red spectral regions could enlarge the horizon of potential applications of epitaxial organic nanofibers. Organic nanofibers featuring optical waveguiding and random lasing could enable the realization of active photonic sensors with high sensitivity. Moving from single (blue) band operation of pure p-6P fibers to the triband operation based on heteroepitaxial p-6P/6T fibers would then allow for increasing sensing capabilities and data volumes.

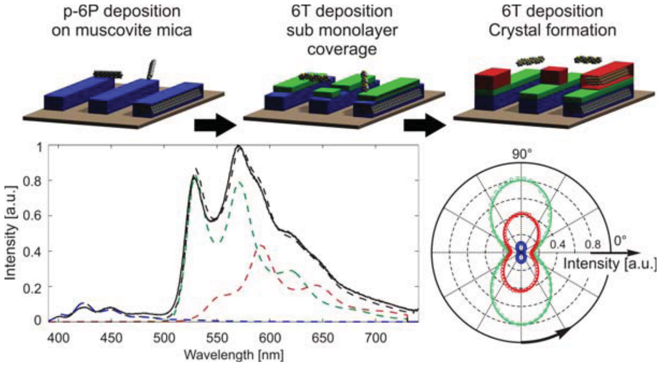

Figure 1. Highly polarized emission in the red, green and blue spectral range obtained by organic-organic heteroepitaxy of p-6P/6T nano-fibers.

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ORGANIC FIELD EFFECT TRANSISTORS CONTAINING BISTABLE MATERIALS

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Properties of multistable materials has been matter of increasing interest in recent years because of emerging prospects of their use in electronic and/or photonic systems such as switches, memories, etc. The switching between stable positions (orientations of dipoles in ferroelectric materials, structures of molecules in photochromic systems, etc.) can be activated by, e.g., mechanical, optical or electric stimuli, resulting in controlled changes in optical or electrical parameters of the systems (cf. Fig. 1).

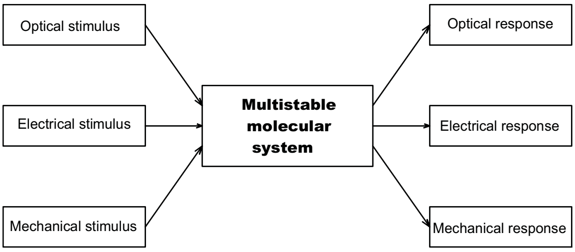

Figure 1. Scheme of a molecular switch employing optical, electrical or mechanical stimuli with optical, electrical or mechanical detection of response.

This contribution focuses on application of bistable (switchable) materials as elements of organic field effect transistors (OFETs). Possible archtectures of the systems will be discussed. In particular, results obtained on OFETs containing organic photochromic molecules dispersed in the active elements of the transistors (either semiconductor or gate insulator) will be presented, and the mechanism of the switching will be elucidated.

The results presented in the contribution have been obtained within framework of cooperation supported by the European Commission through the Human Potential Programme (Marie-Curie RTN BIMORE, grant No. MRTN-CT-2006-035859),

ORGANIC LIGHT-EMITTING FIELD-EFFECT TRANSISTORS

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In the organic electronics the greatest progress has been made so far in the technology of manufacture of organic light emitting diodes (OLED) with selective emission of visible light as well as white light. In the field of organic field effect transistors (OFETs), one of the main applications foreseen for them is their use as switching elements for OLEDs in the flexible active matrix displays [1]. Both OLEDs and OFETs still suffer from the lack of technology for their integration into functional systems. New idea leading to combination of OLEDs and OFETs properties into one, multifunctional devices is the organic light emitting field effect transistor (OLEFET) [2].

The OFETs is a three-electrode devices that couple the electrical characteristics of a FET to the controlled radiative recombination of the electrons and holes injected in the channel via the drain and source contacts. The charge carriers injection and radiative recombination processes are controlled by both the drain and gate voltage. The LEFETs have several advantages in comparison to OLEDs because the gate electrode enables higher degree of the control of the processes influencing on device efficiency like: charge injection, electron and holes balance and generation of light. Moreover in the ambipolar LEFETs the concentration of the charge carriers able to form excitons can be much higher than in the OLEDs [3,4].

The aim of this study is the presentation of the principles of OLEFET operation and the deeper analysis of the influence of device architecture (horizontal [4-6] and vertical [7-9]) on work parameters of the devices. Moreover either the recent developments in the field of materials science or some technical progress will be shown, which both are critical issues in obtaining of efficient OLEFETs.

Acknowledgements
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CHARGE-TRANSPORTING POLYMERS AND MOLECULAR GLASSES FOR OPTOELECTRONIC APPLICATIONS

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Organic charge-transporting polymers and molecular glasses are widely used in (opto)electronic devices, such as electrophotographic photoreceptors, light-emitting diodes, solar cells, organic thin film transistors [1].

In this presentation the resent results of the work on the synthesis and properties of charge-transporting polymers and molecular glasses performed in the author's laboratories are reviewed. We use carbazole as of the main building block in the design and synthesis of charge-transporting polymers and molecular glasses. Carbazole is a cheap raw material, carbazolyl group easily forms stable charge carriers, different substituents can be introduced into carbazole ring and multifunctional materials can be obtained. We prepared charge-transporting polymers by chain growth (photo)polymerization of oxiranes, oxetanes, thiiranes, vinyl ethers bearing different electroactive groups [2] also by polycondensation and polyaddition of bifunctional electroactive monomers [3].

We also prepared hole-transporting molecular glasses belonging to the families of condensed aromatic amines [4], hydrazones [5], enamines [6], ethynylenes, stilbenes and electron-transporting materials belonging to the families of thioxanthenes and aromatic imides [7]. The ionization potentials of hole-transporting materials range from 4.80 to 5.80 eV. Time-of-flight hole drift mobilities in the amorphous films of 2,7-substituted derivatives of carbazole [8] and carbazole-based enamines [6] exceed 10^{-2} cm^2/V. Electron mobilities in the layers of bay-substituted perylene diimide derivatives exceed 10^{-3} cm^2 V^{-1} s^{-1} at high electric fields [9]. Changing the linking topology of carbazolyl moieties to the core of perylene bisimides has furnished materials with complementary semiconducting properties. Glass-forming stable free radicals have appeared to be very effective ambipolar organic semiconductors [10]. 3-(9-Carbazolyl)carbazoles and 3,6-di(9-carbazolyl)carbazoles are effective host materials for blue organic electrophosphorescent devices. The triplet energies of these materials approach 3.0 eV. Using these host materials, blue phosphorescent OLEDs having efficiencies of up to 15 %, 31 cdA^{-1}, and 28 lmW^{-1} were demonstrated [11]. Some of the recently synthesized high-triplet-energy glass-forming hosts have appeared to be effective ambipolar semiconductors [12]. They were successfully used for the development of single layer electrophosphorescent devices.

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TIME-RESOLVED FLUORESCENCE MEASUREMENTS OF EXCITON DIFFUSION IN ORGANIC SEMICONDUCTORS

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Exciton diffusion plays an important role in many organic semiconductor devices, including lasers, light-emitting diodes and solar cells. In lasers and light-emitting diodes exciton diffusion can lead to exciton-exciton annihilation and hence loss of light emission. Hence it is an undesirable process. In contrast, in solar cells the fact that the excitons are strongly bound makes diffusion to a heterojunction an essential and critical step in the operation of an organic solar cell.

In spite of its importance, exciton diffusion in organic semiconductors has received much less attention than charge transport, and there is limited understanding of the factors controlling it. We have developed and applied time-resolved fluorescence techniques to learn about exciton diffusion in organic semicondcutors. In one approach we measure time-resolved luminescence as a function of excitation density, and extract the bimolecular component of the decay, leading to the exciton diffusion constant.

An alternative approach is to study films of a range of thicknesses on a quencher. Exciton diffusion means that the light-emission from thinner films decays faster than that from thicker films – the additional decay being due to exciton diffusion to the quencher. This is a simple one-dimensional diffusion problem, enabling the exciton diffusion constant to be determined. Results for a range of materials including poly(3-hexylthiophene) will be reported and their implications discussed.

CHARGE CARRIER SEPARATION AND TRANSPORT DYNAMICS IN P3HT:PCBM BLENDS

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Blends of conjugated polymers and fullerene derivatives are the key materials for fabrication of plastic solar cells. Close to 100% efficiency of the exciton dissociation into charge pairs and reduced charge carrier recombination determine relatively high efficiency of the blend-based devices. Carrier mobility is on of the key parameters determining operation efficiency of the blend-based solar cells. We have recently demonstrated that the initial carrier mobility in neat conjugated polymers is several orders of magnitude higher than its stationer value [1]. Therefore charge carriers pass short distances, typical of carrier motion in solar cells, much faster than one would expect on a base of the stationer mobility values.

Here we investigate carrier mobility and the corresponding drift dynamics in a well known blend combination, Poly (3-Hexylthiophene) (P3HT) and soluble fullerene [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM). We look at the carrier transport with a a TREFISH method previously used on a neat polymer devices [1]. This technique based on an electric field induced second harmonic (EFISH) generation allows us to bridge the time scales between measurements such as CELIV and time of fight (in the microsecond regime) to terahertz and transient absorption (to the picosecond regime).

Our results demonstrate decreasing in time mobility in blends. However, mobility dynamics in blends is significantly different than in neat polymers. The difference is related to the different mechanisms of the charge carrier generation when charge carriers are separated by electric field in neat films, while initial charge separation in blends occurs by the electron transfer from excited polymer to PCBM. Initial mobility at 2 ps in blend was of the order of 10^{-2} cm^2/Vs, which decreased to the order of 10^{-4} cm^2/Vs at 2.5 ns for high voltages. The excess energy produced due to initial preparation of nonequilibrium distribution of charge carriers inside distributed density of states result in a high mobility immediately after excitation, which reduces in time during the carrier localization at low energy sites. The recorded time of fight measurements show that the mobility continues to further decrease to the order of 10^{-8} cm^2/Vs.

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MODEL OF THE CHARGE CARRIER MOBILITY IN CONJUGATED POLYMERS

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Conjugated polymers are important candidates for future molecular-scale electronic devices. Thus, investigation of the charge carrier transport mechanism in these materials on molecular level attracts considerable research interest. Since the polymer chains are usually twisted, kinked, possess many chemical defects, and have rather disordered mutual positions and orientations, disorder plays a key role in the description of the charge carrier transport. Moreover, properties of polymer semiconducting matrices are often modulated by different additives and supplementals, which further increase conformational and energetic disorder of the polymer matrix. A classical model of charge transport in disordered organic solids was developed by Bässler [1]. It is based on the quasi-classical charge carrier hopping among point sites with Gaussian distribution of energies reflecting an energetic (diagonal) disorder. The jump rates among these sites are described by means of the Miller–Abrahams relations.

We have modified this model in order to extend the description for the hole transport in polymers. First of all, point sites have been substituted by polymer chains. Thus, the hole transport involves both the on-chain motion through the conjugated system and hopping between adjacent chains. Quantum mechanical description of the on-chain charge carrier transport is based on the solution of the Schrödinger equation with the tight-binding Hamiltonian. The proposed model takes into account the electrostatic interaction of the hole moving on the polymer chain with dispersed polar additive. The same model is used for determination of the hole states near the valence band edge, which are involved in the inter-chain hopping transport. Unlike quantum mechanical description of the intra-chain charge carrier motion, the inter-chain hopping is modeled using the quasi-classical Marcus approach, taking into account the thermalization of the charge carrier between any subsequent jumps.

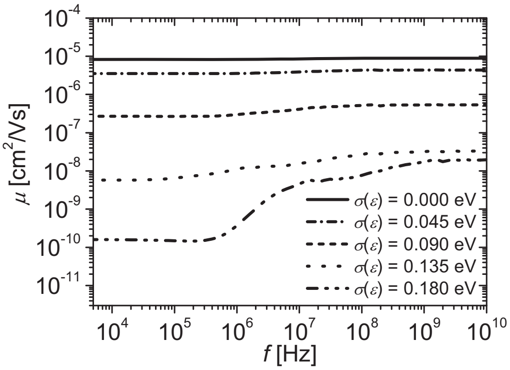

Figure 1. Frequency dependence of the hole mobility $\mu(f)$ in MEH–PPV doped by a polar additive calculated for various values of the energetic disorder $\sigma(\varepsilon)$.

Our model made it possible to calculate the charge carrier mobility as a function of the value of the energetic disorder produced by the dispersed polar additive, external electric field frequency, temperature, and charge carrier concentration. The obtained results show a very strong dependence of the charge carrier mobility on the energetic disorder. Thus, the charge carrier transport may be readily influenced by the presence of the dispersed polar additive. Doubling of the value of the energetic disorder leads to a decrease in the inter-chain hole mobility by up to several orders of magnitude (see Fig. 1). While the mobility in the polymer with a low value of the energetic disorder is frequency-independent, for higher values of the energetic disorder there is a significant increase of the mobility with the frequency. Unlike Bässler model, the calculated temperature dependence of the mobility shows essentially Arrhenius–type behavior with a moderate sub-Arrhenius deviation at the low additive concentration and the low-temperature saturation at the high additive concentration. Finally, the charge carrier mobility in polymers doped by polar additives shows a strong dependence on the carrier density, which can be explained by means of the filling of the trap states at higher charge carrier densities.

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POLARON DYNAMICS IN POLYMERS DOPED WITH POLAR ADDITIVES

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The presence of the excess charge in molecular crystals results in a change of the equilibrium configurations of the nuclei in the time scale of vibronic relaxation. Electronic polarization, molecular vibronic polarization, lattice polarization, etc., create a molecular polaron (MP), which is mainly formed in consequence of the interactions of an excess charge carrier localized on a given molecule with the IR-active vibrations of the molecule itself and the nearestneighbor molecules (molecular vibronic polarization). The formation energy of molecular polaron is typically about 0.15 eV; 60% of the value comes from the formation of the ionic state of the charged molecule and the rest results from the interactions with surrounding molecules. Lattice deformations and the polarization of lattice vibrations are usually low.

In polymers ("soft lattices") the situation is quite different. The main contribution to the polaron binding energy comes from the polymer chain deformation; a moving charge carrier causes a deformation of the macromolecule and atoms shift to new positions in the charged molecule to preserve the minimum of potential energy. Charge carriers moving by hopping are self-trapped in potential wells formed by local chain distortion. The sum of the deformation (during the localization of the charge) and "redeformation" (during the escape process of the charge) energies (reorganization energy, λ) is typically 0.55 eV for poly[methyl(phenyl)silylene] (PMPSi). The changes in atom positions and vibration frequencies, as well as charge redistribution move together with the charge carrier. The contribution of the charge-vibration (phonon) coupling is only about 20% of the overall polaron binding energy E_p ($E_p \cong 0.5\ \lambda$), which follows mainly form the molecular deformation.

Presence of polar species changes the reorganization energy. For example, the reorganization energy of PMPSi increases from 0.55 to 0.64 eV upon addition of 1-(benzamido)-4-nitronaphtalene (BANP). On the molecular level, three factors, the electronic coupling (electron transfer integral) between individual segments of the macromolecule, the reorganization energy (λ) and the effective length of the electron transfer (L), are important for the charge transport. The Marcus theory [1] can be used for the calculation of the rate constant of the charge hopping. For the same L in both systems, PMPSi and PMPSi+BANP, the ratio of the mobilities is proportional to the ratio of the rate constants and was determined from quantum chemical calculations to amount to ca. 3. Experimentally, using the microwave technique [2], the ratio of the "one-chain" mobilities was found as 2.5 ÷ 3 (note that the mobility weakly depends on BANP concentration). The same situation was found in 3D (macroscopic) samples. With BANP, the mobility of the doped PMPSi is lower; it decreases from $2\text{x}10^{-4}$ cm^2/Vs for undoped sample to $5\text{x}10^{-5}$ cm^2/Vs for the doped sample (3.6 mole% of BANP, measured at the electric field $F = 1.6\text{x}10^5$ V/cm and at room temperature). Using quantum chemical calculations for inter-chain hopping the mobilities were found to be $7\text{x}10^{-5}$ cm^2/Vs ($\lambda = 0.55$ eV) and $3\text{x}10^{-5}$ cm^2/Vs ($\lambda = 0.65$ eV). This result is also in a good agreement with experimental data.

In conclusion we can state that the charge carrier transport in PMPSi is of the polaron type, polaron binding energy being about 0.26 eV. In presence of polar species in the vicinity of the polymer chain, the value of the reorganization energy increases and the charge carrier mobility decreases.

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RECOMBINATION OF THE CHARGE CARRIERS IN THE ORGANIC STRUCTURES

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Usually, in low mobility organic materials the bimolecular Langevin recombination is observed. It is caused by the probability for charge carriers to meet in coordinate space, hence it is depending on the charge carrier's transport. This type of recombination limits further development possibilities of the organic materials. However, recently slower recombination process in low mobility organic materials was observed [1], extending the area of the application of such materials.

In this work we are presenting:

- methods for testing of the presence of Langevin recombination – the analysis of current transients in the cases of photo-generated charge carriers extraction, double injection and space charge limited current;
- reasons and features of Langevin recombination reduction – the influence of the random potential, nanostructuring etc.[2,3];
- the experimental results of reduced Langevin recombination in lamellar structure of RR-PHT, bulk heterojunction P3HT/PCBM et al.

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SPECTRAL DIFFUSION IN SINGLET AND TRIPLET STATES OF POLY(PARA-PHEYNELENE)-TYPE POLYMERS

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We have employed quasi continuous fluorescence and phosphorescence spectroscopy within a temperature range between 10K and 500K to monitor the spectral diffusion of singlet and triplet excitons in a series of π-conjugated polymers. [1] We investigated (i) how spectral diffusion is controlled by the degree of energetic disorder present in the amorphous film (that is reflected by the inhomogeneous broadening of the photoluminescence spectra), and (ii) how this process depends on the range of the electronic coupling (by comparing singlet exciton diffusion via long-range Förster transfer against triplet exciton diffusion by short-range Dexter transfer).[2] The fluorescence spectra bear out a bathochromic shift upon cooling the sample down to a critical temperature below which the shift saturates. This is a signature of spectral relaxation. Random walk theory applied to excitation transport within a Gaussian density of states distribution is both necessary and sufficient to rationalize the experimental results in a quantitative fashion. The same behaviour is observed for triplets in weakly disordered systems, such as in a polymer containing platinum in the main chain and a ladder-type poly-phenylene. In contrast we observe a hypsochromic shift of the phosphorescence spectra below a characteristic temperature for triplets in systems with at least moderate energetic disorder. Monte-Carlo simulations prove that the hypsochromic shift is caused by frustration of triplet exciton relaxation because thermally activated exciton jumps that otherwise promote spectral diffusion become progressively frozen-out. The frustration effect is controlled by the jump distance, and thus it is specific for triplet excitations that migrate via short range coupling among strongly localized states as compared to singlet excitons.

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LOCAL FIELD OPTICAL CONTROL OF CHARGE TRANSPORT IN MOLECULAR TUNNELLING NANOJUNCTIONS

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Molecular conduction nanojunctions have been under intense study for some time. Recently one of the authors and collaborator investigated a class of molecules in molecular tunneling junctions characterized by strong charge-transfer transitions into their excited state [1]. Within steady-state consideration they have shown that when such molecular wire connects between two metal leads, weak optical pumping can create an internal driving force for charge flow between the leads. In this work we, first, extend the consideration [1] to strong optical pulse fields, second, apply the theory to studies of coherent control of nanojunction transport and third, take into account the local field and non-Markov effects.

The model of a molecular nanojunction is similar to that of Ref.[1]. We consider a molecular bridge represented by its highest occupied and lowest unoccupied orbitals, HOMO and LUMO, respectively. The corresponding Hamiltonian includes both the standard electron-transfer coupling that gives rise to net current in the biased junction, energy transfer between the molecule and electron-hole excitations in the leads, and the molecule-radiation field coupling. Using, first, a Markov approximation, we have derived a closed system of equations for the expectation values of binary (populations and a polarization) and tetradic (exciton populations) variables of the annihilation and creation operators for electrons in the molecular states [2].

We have proposed an optical control method using chirped pulses for enhancing and controlling charge transfer in unbiased molecular junctions where the bridging molecule is characterized by a strong charge-transfer transition. We have shown that a single-electron transfer can be realized using adiabatic rapid passage. When the energy transfer is absent, the optical control problem for inducing charge transfer with linearly chirped pulse can be reduced to the Landau-Zener transition to a decaying level.

Furthermore, the effects of local field for realistic junction geometry and non-Markov response of the molecule are taken into account within finite-difference time-domain (FDTD) and non-equilibrium Green functions equation-of-motion formulations, respectively [3]. Non-Markov response enables us to describe broadening of molecular states induced by hybridization with states in the contacts. The point is that in realistic molecular junctions such hybridization is non-negligible, since molecules are usually chemisorbed on at least one of the contacts. We find that contrary to symmetric behavior of incoming laser pulse (pump) relative to the sign of the chirp, duration of the corresponding local field pulse depends on the chirp sign, which results in asymmetric operation of the pump. In the non-Markov situation the most effective charge pump regime is at finite positive bias, rather than at equilibrium as one may expect from Markov consideration [2].

The proposed control mechanism is potentially useful for developing novel optoelectronic single-electron devices with optical gating based on molecular nanojunctions.

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SINGLE MOLECULE SPECTROSCOPY TO MONITOR ENERGY TRANSFER IN MACROMOLECULES AND AGGREGATES

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Since the end of 1990-s methods of single molecule spectroscopy are used for studying organization and electronics properties and in particular energy transfer in conjugated polymers, aggregates, light-harvesting antennas etc at single molecule/particle/antenna level. Already the early works showed that large conjugated polymer macromolecules potentially consistent of hundreds of chromophores often show “single-molecule features” like e.g. fluorescence blinking [1]. This exiting phenomenon was explains in terms of very efficient energy funneling to just several so-called emitting sites – low energy traps [2]. Since then the energy-funneling concept in nano-objects has become a paradigm without, however, having any solid experimental method to evaluate quantitatively the extent of energy transfer.

In fact assessment of energy transfer is not trivial at all. We have shown that to make any conclusions about energy funneling it is not enough just to observe blinking. It is vitally important to measure the absolute fluorescence brightness [3] (fluorescence intensity/excitation power) to make sure that the whole particle/chain is actually participating in the light absorbing and emitting process. The striking example is the conjugated polymer MEH-PPV. Its single chains have been a “role model” in terms of energy transfer – energy funneling over hundreds or even thousands of chromophores was believed. We observed domination of non-emissive regions (“dark matter”) in high-molecular weight MEH-PPV chains imbedded in standard polymer hosts like PMMA and PS, which, of course, completely changed the picture [4].

Blinking effect uses photogenerated long-living energy traps to make energy transfer visible. Therefore, the drawback is that it allows seeing mostly the energy transfer from chromophores to the trap, but generally tells very little about the energy transfer between the chromophores themselves the nano object consists of.

How to observe internal energy transfer without implementing traps? While in ensemble spectroscopy the method is to monitor fluorescence anisotropy, analogues technique at single molecule level did not exist until recently. Two-dimensional polarization single-molecule imaging recently introduced by us [5] allows addressing energy transfer and internal organization of chromophores in an individual nano-object without having any specially added energy traps. In this method fluorescence intensity of a single object excited by linearly polarized light is measured as a function of both the excitation polarization angle and the angle of the analyzer installed in front of the detector. Recent advances in the data analysis give us strong hope that that we are coming closer to the primary goal - developing a “ruler” for energy transfer or a way to tell the percentage of energy which has actually been funneled in an individual system. The method will be illustrated on conjugated polymers, molecular J-aggregates and natural light-harvesting systems.

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PROTON TRANSFER REACTION AS MECHANISM FOR CONTROLLING ELECTRICAL TRANSPORT IN SINGLE MOLECULE JUNCTION

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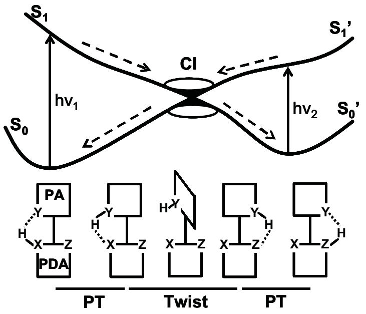
Electrical transport in molecular junction, where single molecule is bound to metal or semiconductor electrodes, has been of great interest recently. Molecular junction represents a prototype system to investigate nonequilibrium physics at the nanoscale and, furthermore, may provide the building blocks for future nanoelectronic devices in the field of molecular electronics. An important aspect in this respect is the possibility to influence and control the conductance of a molecular junction by external parameters.

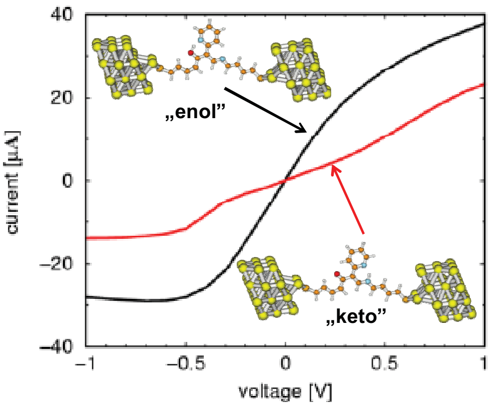
Recent theoretical studies show that in molecule which subjects to intramolecular proton transfer reaction [1] - (a), the various tautomeric forms (“enol” and “keto”, for instance) can realize different conductance states of a molecular junction [2] - (b). The reversibility of such reaction has recently been proven experimentally [3].

In the presentation, the results of theoretical investigations of proton transfer reaction in a molecular junction triggered by static or optical external fields will be discussed as a mechanism to control electrical transport. In particular, the possibility to switch a molecular junction reversibly by an optical excitation or by external electric fields will be emphasized.

(a)



(b)



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SUPER-DIFFUSIVE EXCITON TRANSPORT IN J-AGGREGATES

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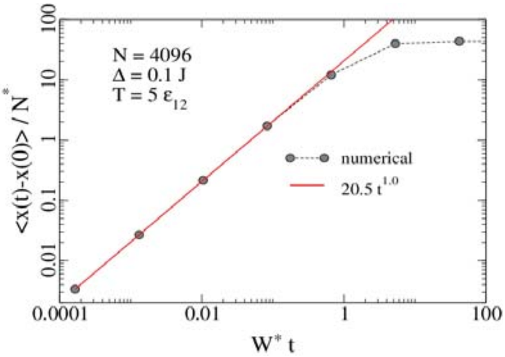
We study theoretically the quasi-particle (electron, hole, or exciton) transport in a quasi-one-dimensional disordered systems, such as molecular aggregates, conjugated polymers, DNA, etc. The diffusion is considered as incoherent hopping between quasi-particle localized states, induced by weak coupling to phonons of the host, into which the system is embedded (a glassy matrix in the case of an aggregated systems, or the natural aqueous environment of the DNA). We argue that the hidden energy structure of the Lifshits tail of the density of states (DOS) [1], introduced in Ref. [2], provides a characteristic activation energy ε_{21}= 0.4J(Δ/J)1.36 [2,3] for the transport where Δ is the degree of disorder and J is the nearest neighbor hopping. There exist two regimes of transport in such systems. At temperatures T < ε_{21}, the quasi-particle transport is diffusive, while at T > ε_{21}, the diffusion is determined by hops via higher-energy band states of the system [4], not by hops over the highly localized DOS tail states. Because of that, the quasi-particle transport has more than one characteristic length scales and reveals a super-diffusive behavior - (Lévy flights).



The figure shows a super-diffusive behavior of the mean displacement <x(t) – x(0)> of the exciton created initially in the leftmost eigenstate of the DOS tail. The simulation has been performed with linear aggregates of size N = 4096 subjected to a disorder Δ = 0.1 J, and embedded into a host at the temperature T = 5 ε_{12}. The typical spread of the DOS tail wave functions, N*≈30, and the typical rate of hopping between these states, W*, are used as units for the mean displacement and time, respectively. Full circles represent numerical data points, while the straight red line is the best linear fit. We observe almost perfect ballistic motion of the exciton for W*t<1. The deviation of the numerical results from the fit for larger times can be attributed to finite size effects.

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TUNING OF TRIPLET ENERGY AND TRIPLET INTERACTIONS IN ORGANIC SEMICONDUCTORS

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The spin state plays a major role in organic electronic devices such as organic light emitting diodes, solar cells, or spintronic devices like spin valves. However, little is known how to control the energy of singlet and triplet level in organic materials. Moreover, on the level of devices the knowledge about interactions between triplets and charge is limited. Thus one is far away from the ultimate goal of controlling these processes.

We report a joint theoretical and experimental study of electronic properties of a class of triphenylene based polyaromatic hydrocarbons. We succeeded with suppression of aggregation by appropriate substitution of the triphenylene core. The influence of substitution on the energy levels is investigated by DFT theory. Upon chemical modification of the triphenylene core the singlet-triplet energy gap can be reduced by 0.4 eV. This is spectroscopically verified. As a demonstration of the potential of the materials Ir(III) doped phosphorescent OLEDs are tested and limits of the performance are investigated. We achieve efficiencies above 30 Cd/A for simple green emitting two layer devices.

In the second part of the contribution we will present a study of triplet dynamics in Ir(III) doped amorphous organic semiconductors. To tune triplet processes in these materials and devices we vary the Ir(III) dye, the used matrix and the processing conditions, i.e. solution vs. vacuum processing. We investigate triplet - triplet annihilation and charge (polaron) - triplet annihilation by time resolved spectroscopy and current voltage characteristics. The current in the devices is space charge limited. The annihilation constants clearly reveal a dependence on the chemical nature of the Ir-dye and the structure of the used matrix.

the format shown below.

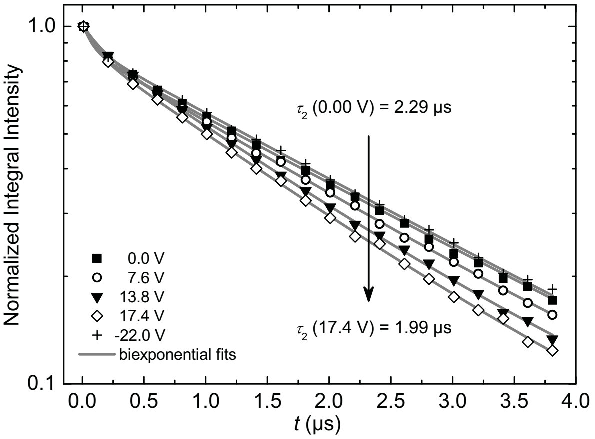

Fig. 1. Normalized (integral) intensity of 5% IrC6Red doped in MeOTPD as a function of time. The second time component τ_2 of the biexponential decay fits decreases with higher voltage (hole density), whereas a negative electric field (no hole current) has no perceptible influence on intensity decay.

ONE DIMENSIONAL J-AGGREGATES: DEDUCING THE LEVEL STATISTICS AND MICROSCOPIC GEOMETRICAL STRUCTURE FROM OPTICAL SPECTRA

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One of the current dreams in the field of molecular optics is the full understanding of nature's way to harvest and use photonic energy, which ultimately could enable the development and design of highly efficient functional optical devices using molecular arrangements as building blocks. One of the crucial elements of such photonic assemblies are the “wires” which transport the energy between the different functional units of the devices. Nice synthetic model systems for these wires are found in the low dimensional J-aggregates, which show a variety of intriguing optical phenomena. This presentation will focus on the electronic and geometrical structure of two representatives of this class of nanomaterials as derived from a combination of optical spectroscopies and theoretical considerations. In particular it will be shown that modeling the absorption and linear dichroism spectra allows one to deduce the microscopic structural aspects of self assembled TPPS4 (meso-tetra(4-sulfonatophenyl)porphyrin) tubular J-aggregates.

In addition, recent optical experiments will be discussed which measure the local distribution of exciton levels in disordered cyanine-dye-based molecular nanoaggregates. The observation of a Wigner−Dyson-type level spacing distribution provides direct evidence of the existence of level repulsion of strongly overlapping states in the molecular wires, which is important for the understanding of the level statistics, and therefore the functional properties, of a large variety of nanoconfined systems.

CONCENTRATION QUENCHING OF AMPLIFIED SPONTANEOUS EMISSION IN BAY-SUBSTITUTED PERYLENEDIIMIDES

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Excellent chemical and thermal stability, robustness against photodegradation accompanied by close to unity emission quantum efficiency and superior charged carrier mobility enabled perylenediimide (PDI) compounds to penetrate application areas of laser dyes, organic field-effect transistors, electrophotography, photovoltaics etc [1]. Unsubstituted PDIs and those substituted at the imide nitrogen position feature planar backbone, which facilitates face-to-face molecular arrangements in a solid state resulting in remarkable concentration quenching of emission [2]. The concentration quenching drastically reduces emission efficiency, increases threshold of amplified spontaneous emission, and therefore severely limits lasing applications of the PDIs. Recently, PDI derivatives substituted at the bay position with electron donating and electron accepting groups were introduced [1,3,4]. The bay-substitution enabled tuning electronic transitions and carrier and exciton transport properties. In particular, introduction of electron donating groups enhanced electron transport and tuning of emission wavelength [3]. Additionally, the bay-substitutents induce distortion to the perylene core and owing to the steric hindrance provide possibility of altering molecular packing in the solid state. This allows tailoring exciton migration processes and thus concentration quenching.

In this work, optical properties of a series of PDI derivatives with electron-accepting bay-substituents were investigated. The unsubstituted PDI derivative was also studied as a reference. The impact of bay-substituents on absorption and fluorescence spectra, emission quantum yield, emission lifetime, amplified spontaneous emission and photodegradation was thoroughly evaluated. To reveal the excitonic properties the PDI derivatives were investigated in dilute solutions, neat solid films and polymer films doped by PDI at various concentrations (0 – 8 wt%).

The bay-susbtitution was found to significantly alter radiative and nonradiative decay rates. In particular, bromo and 2,4-di(trifluoromethyl)phenyl substituents resulted in a usual increase of nonradiative decay rate with increasing PDI concentration in a polymer matrix due to concentration quenching effects. As opposed to this, the PDI derivatives with more polar bay-substituents expressed reduced nonradiative decay rate with increasing concentration, which had a direct impact on the amplified spontaneous emission. Although the unsubstituted PDI demonstrated the lowest threshold of amplified spontaneous emission it also featured the strongest concentration quenching of emission, whereas the PDI possessing bulky bay-substituents and higher threshold of amplified spontaneous emission showed minimal concentration quenching. To determine the connection between the torsion of particular bay-substituent with regard to the perylene core and the emission quenching induced, quantum chemical calculations of the geometry and electronic states of the PDI derivatives were performed. The calculations carried out in the framework of density functional theory (DFT) at the B3LYP/6-311G level revealed differences in torsion angles and torsional activation barriers of the different PDI bay-substituents upon the excitation. The significant reduction of the emission quenching was explained in terms of enhanced steric repulsion between the perylene core and more branched and bulky bay-substituents.

Our results infer that the bay-substitution by the bulky groups efficiently reduces concentration quenching of emission in PDI derivatives, and therefore, might serve in the design of PDI-based light emitters with improved efficiency.

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INSPIRATIONS FOR EO POLYMER DESIGN GAINED FROM MODELING OF CHROMOPHORE POLING BY LANGEVIN DYNAMICS

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Over last two decades there is a stable interest to make use of organic molecular materials in a wide variety of NLO applications [1]. One of the possibilities to create a material for these applications, like EO modulators, is polymer with dispersed NLO active chromophores. In general there are two types of such systems “host/guest” systems with NLO active chromophores admixed in polymer matrix and so called “grafted” polymers where chromophores are covalently bounded to polymer. To act in an NLO material chromophores must be acentrically aligned, what is generally achieved by applying an electric poling field. The NLO efficiency depends on dipole moment, molecular hyperpolarizabilities, concentration of the chromophores and external poling field strength. Calculating, from first principles, the extent of the alignment and via this NLO efficiency has proven to be challenging. One approach to solve this problem is pure analytic statistical mechanics treatment [2], what could be enhanced by Monte Carlo (MC) statistical mechanical modeling[3,4]. The chromophore molecules usually have been treated as point dipoles embedded in some kind of realistic molecular shape prolate spheroid. From our point of view, at short intermolecular distances model of interacting point dipoles is not appropriate representation for electrostatic interactions of chromophores. Another disadvantage of these MC based statistical mechanical methods is impossibility to get some insight in poling (relaxation) dynamics. Fully atomistic molecular modeling with classical force field molecular dynamic (MD) methods allows observing the time evolution of a system [5]. Unfortunately, in case when host and chromophores are represented at atomistic level, MD approach requires huge amount of computations. One of the solutions is to reproduce the motion of the molecules of interest (chromophores) using Langevin dynamics (LD). This method simulates the effect of molecular collisions and the resulting dissipation of energy that occur in real host, without explicitly including host molecules. In this contribution, we would like to present results of our LD simulations of the model systems. In the case of modeling “host/guest” NLO polymers chromophores have rotational and translational freedom. Restricting translational movement of chromophores allows us to model “grafted” NLO polymers. Chromophore load, dipole moment and poling field impact on extent of alignment and poling / relaxation dynamics of model systems obtained by LD simulations will be presented. In general, both prototypical systems according to our simulations behave similar, except formation of dipolar chromophore chains in case of “host/guest” model (see fig.). Formation of such chains has positive effect on polar order stability and in some cases could yield in “ferroelectric” behavior of polymer. On a basis of these results we would like to come forward with some inspirations for EO polymer design.

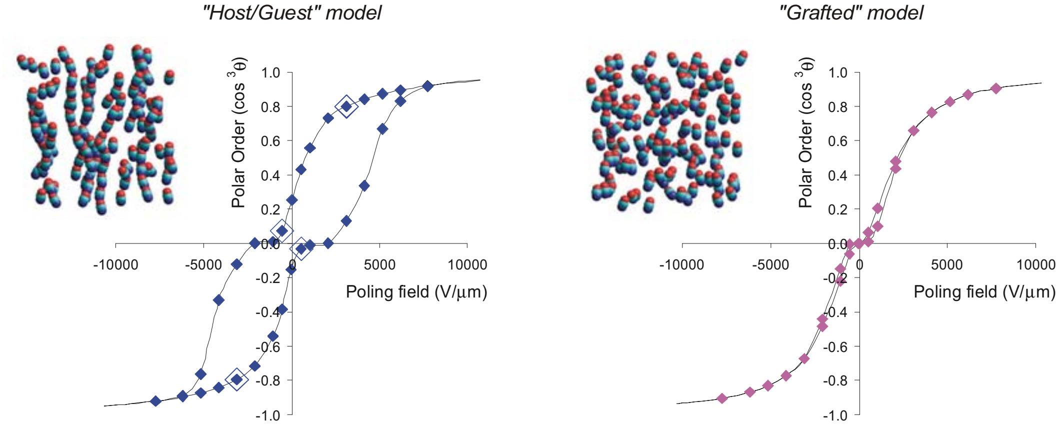

Figure 1. LD simulation of polarization:

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HELICAL SUPERSTRUCTURE AND CHARGED POLARONS CONTRIBUTIONS TO OPTICAL NONLINEARITY of 3-NITROANILINE

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Origin of the optical nonlinearity of 3-nitroaniline (m-NA) , the model compound in nonlinear optics, is still the subject of intensive theoretical [1] and experimental [2] studies. At room temperature (RT) m-NA is in the rotative phase due to the phenyl ring fluctuations [3], the -NO$_2$ group reorientations [4] and the 180^o jumps of NH$_2$ group protons [3]. The motions are connected with the anomalous m-NA contraction along the *b* crystallographic axis [4]. Bearing in mind the motions (dynamic disorder) we have proposed the "hop and turn" model to explain the sign reversal of crystal polarity at RT with the switching on/off the 980 nm diode laser beam [2] , the reversal similar to that resulting from the electrooptic Pockels effect [5].

To explain the NIR influence on the m-NA crystal it has been suggested that the NIR radiation excites the overtones of -NH$_2$ stretching vibrations and induces the intermolecular proton transfer along the asymmetric N H…O hydrogen bond. The proton transfer couples with the radical anions (charged polarons) electronic transitions lying in the NIR region what increases the polaron population (autocatalysis) [6,7].

The "hop and turn" model consists in the reorientational motions of phenyl ring and both substituents, especially of the NO$_2$ group, leading to the instantaneous helical superstructure (conformational chirality) around the crystallographic *a* axis shown in (Fig. 1 of Ref. 2). Along this helix the polaron hoppings could occur. The relevance of radical anions to the m-NA optical nonlinearity results from their first hyperpolarizability β larger than that of the neutral molecule [8]. It is in line with the newly emergent spintronics, according to which the circularly polarized light is absorbed in different way by the spin-down and spin-up electrons inducing the circular dichroism (CD) spectra and the optical nonlinearity [9]. m-NA crystallizes in the orthorhombic space group Pca2$_1$ (mm2 or C$_{2v}$) thus does not belong to the chiral space groups [10].

This work [11] was undertaken to check the hypothesis of conformational and/or induced chirality of the m-NA molecule and crystal both experimentally by CD spectra records and theoretically by the CD spectra ab initio quantum chemical calculations . The calculations were performed at the DFT B3LYP level with SVP basis of Ahlrichs [12] using ORCA 2.7.1 package [13].The energy of maxima and minima positions observed in the CD spectra of m-NA solution, KBr pellet and single crystal are in satisfactory agreement with the calculated ones for neutral molecule and radical anion. The last spectrum resembles better the experimental spectra of solids then the theoretical spectrum for neutral molecule. We conclude that the helical arrangement enables the polaron circulation inducing magnetic dipole moments. Thus both helical superstructure and charged polarons contribute to the m-NA crystal optical nonlinearity as well as to its electric (low) conductivity [2,11].

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EXCITED-STATE SYMMETRY BREAKING AND GROUND-STATE SYMMETRY LOWERING IN BRANCHED ICT CHROMOPHORES

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Organic molecules with intramolecular charge-transfer (ICT) character are widely studied in view of their potential applications in the fields of polarity sensing, organic electronics and photovoltaics, nonlinear optics, to name a few. ICT molecules are typically characterized by the presence of one or more electron-donor (D) and electron-acceptor (A) groups, connected by π-conjugated structures. The simplest case is represented by so-called push-pull chromophores, but more extended, branched structures, with multiple D and A groups have recently attracted attention for their enhanced nonlinear optical responses and light-harvesting capabilities. Branched ICT molecules comprise quadrupolar structures (with A-π-D-π-A or D-π-A-π-D motif), octupolar molecules (with $A(-\pi-D)_3$ or $D(-\pi-A)_3$ motif) and more involved dendritic structures of different size and generation. In order to exploit branched ICT molecules for specific tasks, a good understanding of their excited states is needed. In fact, depending on the strength of the coupling among the different molecular branches, either localized or delocalized excited states can be expected, with important consequences on the material properties and behavior. On the other hand, the nature itself of molecular excited states is strongly affected by the molecular environment.

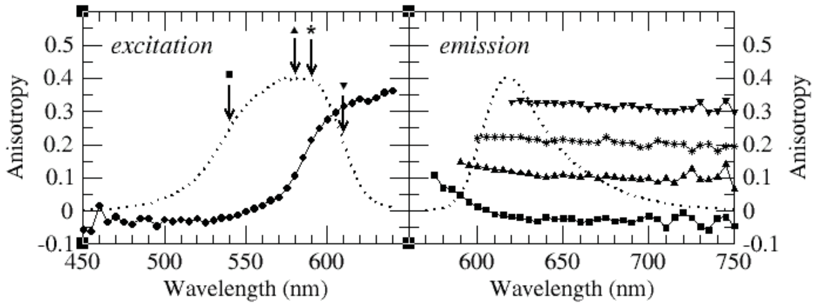

Figure 1. Fluorescence anisotropy spectra of Crystal Violet in glassy propylene glycol at 190 K. Left: Excitation anisotropy spectrum, which is independent of the emission wavelength. Right: Emission anisotropy spectra obtained by exciting at different wavelengths (540, 580, 590, 610 nm), as indicated by the arrows in the left panel. In both panels, dashed lines report representative excitation and emission spectra, as a guide to the eyes.

In this contribution we investigate the optical spectra of some representative octupolar ICT molecules. A careful analysis of the spectra collected in environments of different polarity leads to a detailed understanding of the nature of the excited states of octupolar dyes, and of the subtle effects of disorder induced by polar solvation in ICT chromophores. Based on a thorough experimental spectroscopic investigation, we propose original models for multibranched ICT chromophores that account for few essential electronic states coupled with molecular vibrations and polar solvation [1,2]. Our approach *quantitatively* reproduces the evolution of linear and nonlinear optical spectra with the solvent polarity, accounting for the observed solvatochromism and for solvent-induced inhomogeneous broadening. Fluorescence anisotropy spectra collected in glassy solvents shed light on some controversial issues, in particular the difference between symmetry breaking in the excited state and disorder-induced symmetry lowering in the ground state, and their relation to so called "red-edge effects". At the best of our knowledge, this is the first time that fluorescence anisotropy spectra of ICT chromophores in matrices of different polarity have been calculated, taking into account vibronic coupling, solvation effects and inhomogeneous broadening [3].

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MONITORING THE OPTICAL SPECTRA OF DYE MOLECULES SPATIALLY SELF-ORGANIZED IN THE BODY OF SILICA THIN FILM

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Creation of material with a controlled response to light has a large potential in different applications (optical switches, chemical sensing, drug release, light-powered molecular machines) due to of the non-contact manipulation of the material. Really, such processes can induce small changes on the nanoscale that cause a change in the material properties. Applying the technique of sol-gel synthesis we can be combining inorganic and organic materials to create composite materials with attractive properties. In such frame, the sol-gel synthesis plays a key role, as it provides a low cost tool to obtain mechanically and optically stable organic-inorganic hybrid materials.

We have demonstrated the strategies of functionalization 2D hybride micelle templated silica films with dye molecules which arrested *in situ* self-organization in the different chemically regions of the quasicrystalline structure and post-synthesis approaches for derivatizing the exposed surfaces of the materials. A simple one-pot synthesis has been used to prepare structured inorganic-organic hybrid films. As a result, the dye molecule is orienting to the pore wall with the hydrophobic dendrimer extending into the interior of the micelle.

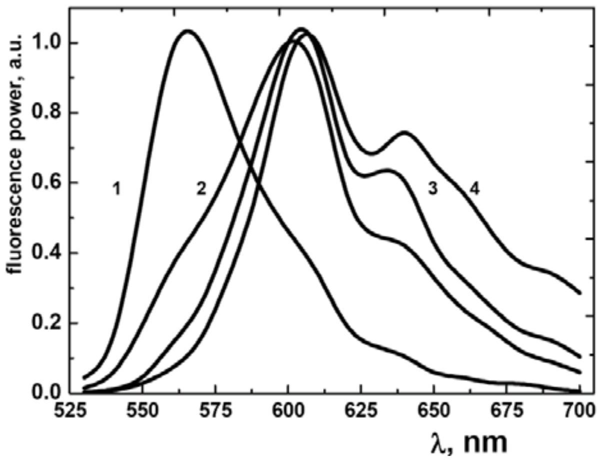

Figure 1. Evolution of fluorescence spectra R6G arrested in the body of mesoporous silica film at various concentrations: 1 - below 0,5mol/l; 2 - 4 above the 0,5 mol/l

Here, we highlight results of monitoring of optical and fluorescence spectra of laser dyes with different nature of the charge state (Rhodamine, Eosin, Pyromethene) and various concentrations encapsulated in micelle templated mesostructured silica films. Unusual optical manifold of spatial localization of the dyes and existence of the concentration limit of dyes in micellar space deliberated in the body of mesoporous silica was shown, that is accompanied by the increasing changes of absorption and fluorescence spectra with a formation of ionic pairs of dye and appearance of absorption spectra of the ionic pair due to the centers of monomolecular absorption. For example (Fig.1), at excess of the amount of cation dye R6G in a hydrophobic core more than two, formations of excimers and excimer fluorescence with the characteristic spectrum and lifetime at the simultaneous quenching of the monomolecular fluorescent spectrum is experimentally observed. We monitored synchronous suppression of the basic band R6G at 565nm and the relative increase of the band of excimer luminescence at 610nm and exciton emission at 670nm. On the possible exciton nature of emission R6G in mesostructured silica film at the highest concentration specifies coincidence of the given spectrum with bulk spectrum. Physical nature of the optical manifold can be related to amount of organic cations self-organized in the hydrophobic micelle core with their counterion in the hydrophilic micelle shell. At excess of the admissible concentration, the formation of the ionic dye pairs in the interface silicate walls – micelle shell and occurrence of an absorption spectrum of the ionic pair take place.

It is set that at exceeding of a number of molecules in the hydrophobic region of a micelle results in forming of excimers and excimer fluorescence with characteristic a spectrum and lifetime at a simultaneous quenching of spectra of the monomolecular fluorescence. This study also demonstrates strategies of self-assembly of spatially separated donor and acceptor molecules in a nanostructured optically transparent continuous thin film. Such approaches can be expandable to a wide variety of donor and acceptor molecules for both photoinduced and electron energy transfer.

DETERMINATION OF THE ENERGY STRUCTURE OF THE ORGANIC MOLECULES IN THIN FILMS

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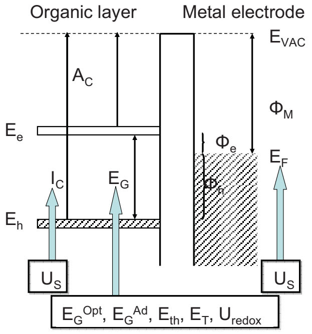
The fundamental part to design effective sandwich type organic films, i.e., electrode/organic layer(s)/electrode is knowledge of energetic parameters of materials [1]. An ionization potential and energy gap directly affect such important electronic processes as charge carrier generation and transport. These parameters are useful to create the energy diagram both of a material and structure electrode/organic layer/electrode. In order to have complete energy diagram of thin film structure the values of the work functions of electrodes are necessary as well. In order to characterise energy gap several parameters are applied such as an optical energy gap E_G^{Opt}, an adiabatic energy gap E_G^{Ad}, a transport gap E_T, a threshold of quantum efficiency of intrinsic photoconductivity E_{th}.

The value of the optical energy gap E_G^{Opt} is usually measured as the energy, where the normalized absorption and fluorescence spectra intersect or from electromodulated absorption spectra [2]. Besides the difference between the oxidation and reduction potentials U_{redox} corresponds to the energy gap [3].

In order to determine the adiabatic energy gap E_G^{Ad}, one must measure the charge carrier energies after their vibronic relaxation to the molecular polaron states. In this work we present one of the methods to determine the threshold of intrinsic photoconductivity in low molecular organic thin films. It is the dependence of quantum efficiency of intrinsic photoconductivity E_{th} [1,2].



The value of transport band is applied as difference between the values of the HOMO and LUMO of a material [4]. In this work the values of the HOMO and LUMO levels are calculated according to the RHF *ab initio* calculations with basis set 6-31G** by Gaussian G09W software package.

Kelvin probe technique is applied to determine the values of the ionization potential of the organic layer and the values of the work function of the electrodes [4].

In this work the values of the energy gaps, local trapping states and ionization potentials of the thin films of indandione [5] and carbazole derivatives [6] were determined by the methods mentioned above. The intercorrelation of all parameters characterisizing the energy gap will be presented.

According to results of the electronic state parameters of indandione derivatives with different electron acceptor and electron donor groups and carbazole derivatives in thin films and Fermi levels of electrodes, the diagrams and terms of charger carrier injection from Au, Al, Ni, Cu and ITO electrodes will be presented.

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TWO-PHOTON INDUCED FLUORESCENCE IN ORGANIC NON-LINEAR OPTICAL SINGLE CRYSTAL DCNP

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Organic compound 3-(1,1-dicyanoethenyl)-1-phenyl-4,5-dihydro-1H-pyrazole (DCNP) (cf. Fig.1) crystallizes in a noncentrosymmetric monoclinic space group Cc and has optimal molecular arrangement for efficient electro-optic (Pockels) effect.

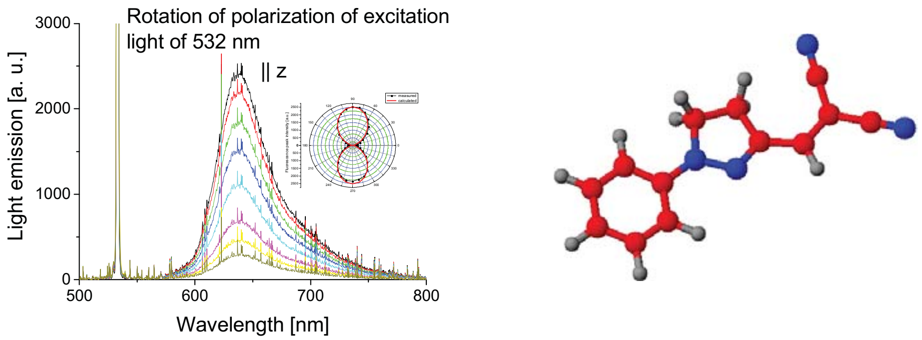

Figure 1. Fluorescence spectra of DCNP single crystal excited by 532 nm pulsed light with polarization rotation and chemical structure of DCNP (C13H10N4) molecule.

The measurements confirmed its large electro-optic coefficient r_{333} = 8.7x10^{-11} m/V at 633 nm ($\chi_{333}(-\omega;\omega,0)$=-2.3x10^{-9} m/V) [1]. The interest in fluorescence measurements of DCNP was stimulated by the observation of an intense reddish luminescence emerging from the crystalline sample of the title compound when illuminated with 7 ns pulses of Nd:YAG laser working at 1064 nm wavelength. Two-photon absorption and reabsorption of SHG light have been considered.

Analysis shows that the mechanism of fluorescence excitation occurs via second harmonic generation (SHG) light of infrared pulse at 532 nm and its subsequent absorption. In order to reveal the detailed mechanism of this process we performed characterisation of fluorescence properties of DCNP crystal. We measured emission and excitation spectra of the crystal under various conditions of excitation as well as in function of temperature down to T = 77 K. Unusual temperature dependence of the fluorescence spectra has been measured. The pronounced luminescence anisotropy (cf. Fig. 1) has been determined on single crystal. The properties of DCNP crystal are compared with properties of its constituent molecules in various solid (polymeric or LC) matrices. Quantum chemical calculations of energies of excited states for single DCNP molecule were performed by semi-empirical GRINDOL method [2]. Possibility of J-aggregate formation in solution and crystal are discussed.

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POSTER PRESENTATIONS

DYNAMICS,
COHERENT SPECTROSCOPY

STIMULATED EMISSION FROM ORIGINAL GLASS FORMING ORGANIC COMPOUNDS

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Organic materials which can be used as a solid state laser material become more interesting in last decade. Till now nearly all systems consist of conjugated polymers [1,2] or polymers doped with organic molecules [3,4]. In most cases stimulated emission (SE) in such films is achieved by energy transfer from one compound (donor) to another (acceptor). It means that irradiated light is absorbed by donor and via energy transfer excite acceptor which emits light. Compatibility of optical properties of donor and acceptor molecules (overlapping of luminescence and absorption spectra) is one of the needs in such films. To overcome this problem we use organic molecules which emit SE by direct excitation by light. Glass state forming low molecular weight organic compounds from the solution would be additional advantage due to easier film processing.

In the work we have realized SE from glass forming styryl -4H-pyran-4-ylidene fragment containing derivatives with three acceptor groups: indene-1,3(2H)-dione, pyrimidine-2,4,6(1H,3H,5H)-trione, malononitrile. Samples were prepared on glasses by spin coating method from the dichloromethane solutions. Sample thickness was about 400 nm. SE was induced by Nd:YAG second harmonic 532 nm at pulse repetition 10 Hz and duration 0.5 ns. Stimulated emission was observed at red spectral region and full width at half maximum is 10 times less compared to spontaneous emission and reach ~10 nm. Chemical structure and emission spectra for the best compound with malononitrile (DWK1) as acceptor group is shown in Fig.1.

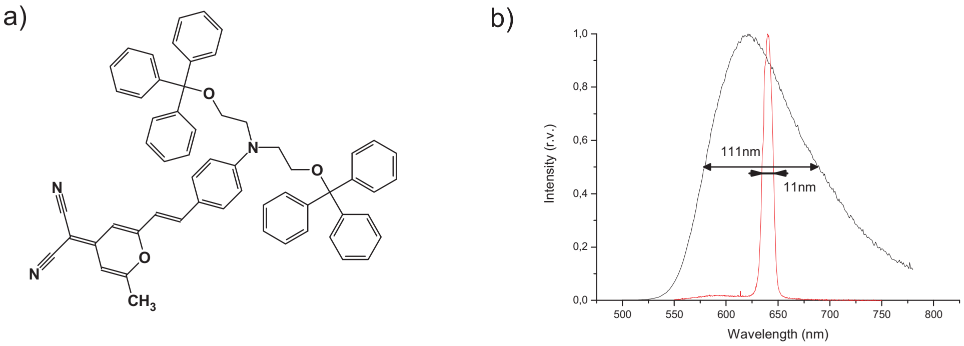

Figure 1. (a) Chemical structure of DWK1. (b) Spontaneous and stimulated emission of DWK1 molecules in thin film.

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LUMENESCENC PROPERTIES OF STYRYL-4H-PYRAN-4-YLIDENE FRAGMENT CONTAINING DERIVATIVES

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Organic molecules become more popular in electro-optical devices, like organic light emitting diodes (OLED). Glass forming low molecular organic compounds could be perspective due to easier synthesis and thin film processing from solution. Fluorescence decay time constants and fluorescence quantum yield are important parameters to estimate application possibility of organic compound in OLED device.

In the work we were studied the influence of acceptor and donor groups in glass forming styryl-4H-pyran-4-ylidene fragment containing derivatives (see Fig.1.) on fluorescence kinetics and quantum yield in solution and thin films. Dichloromethane was used as a solvent for preparation of both: solutions and thin films. The concentration of molecules in solution was between 10^{-6} to 10^{-5} mol/l. Thin solid samples were prepared by spin coating method. The thickness was from 400 to 600 nm. Picoseconds diode laser with wavelength 375nm and pulse duration of 70 ps was used as excitation source.

Fluorescence kinetics in solution consists of one exponential decay but in thin solid films at least of two exponential decays. The slowest process time constant is 1 to 2 nanoseconds and fastest one is several hundreds of picoseconds.

Also was measured quantum yield of all molecules in solution and thin films. In the solution quantum yield was in range of 0.32 - 0.42. Fluorescence efficiency decreases at least one order in the thin film. It could be due to high exciton quenching. The influence of molecular structures on fluorescence quantum yield and kinetics will be discussed.

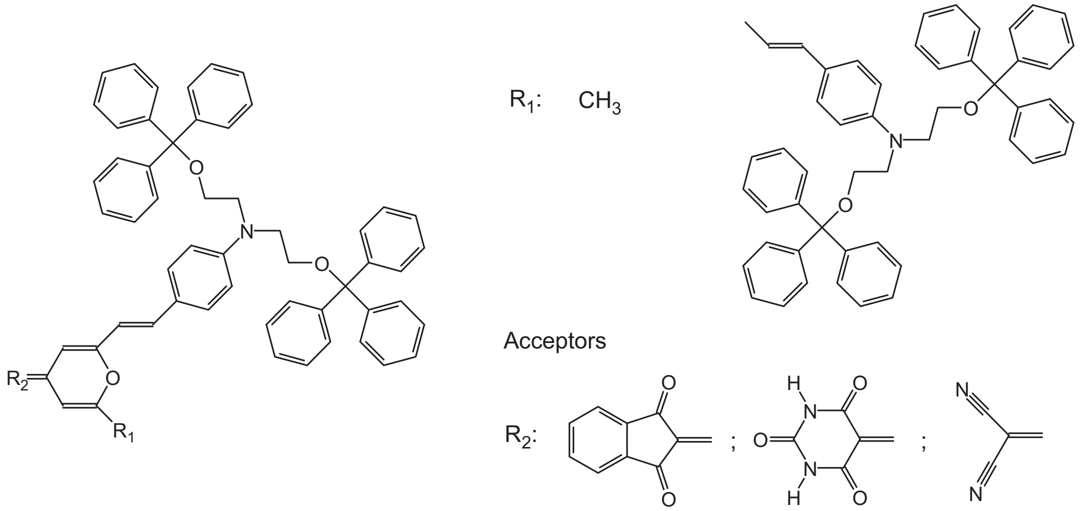

Figure 1. Chemical structure of styryl-4H-pyran-4-ylidene fragment containing derivatives.

ON PHOTO-OXIDATION OF TERRYLENE. CONTRIBUTION TO SINGLE MOLECULE STUDIES

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It is generally regarded that the most important reagent in photo-bleaching of single aromatic dyes is molecular oxygen in its excited singlet state [1]. The preliminary and required step for the oxidation reaction is creation of singlet oxygen and this reactive species is usually obtained after annihilation of the lowest excited triplet state (T_1) of a considered dye and the triplet ground state oxygen. Singlet oxygen can be detected by monitoring the characteristic phosphorescence emission with maximum at about 1270 nm.

In the present work we would like to contribute to the understanding of this preliminary step in photo-oxidation of terrylene [1-3], one of the most frequently used dye in the single molecule spectroscopic studies. To increase depopulation rate of terrylene molecules into the triplet T_1 state we doped terrylene into a 9,10-dibromoanthracene, which due to external heavy-atom effect may considerably affect the intersystem crossing ($S_1 \rightarrow T_1$) rate.

The singlet oxygen phosphorescence spectrum (with maximum at 1272.5 nm) and its excitation spectrum for the considered sample are presented below [4]. It is important to notice that the oxygen phosphorescence excitation spectrum is the same as the fluorescence excitation spectrum of one of two terrylene sites in considered matrix. It indicates specific requirements for singlet oxygen creation, like existence of a 1:1 complex between terrylene and oxygen molecules. According to quantum-chemical calculations a weak van der Waals complex, with binding energy 141 cm^{-1}, can be formed if oxygen molecule is located along the long axis of terrylene molecule, 0.3 nm apart, with the oxygen molecule axis inclined by 110^O [4].

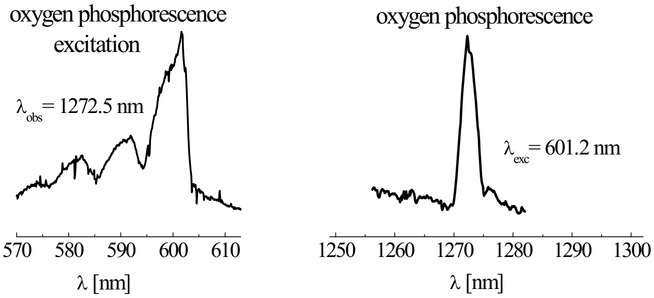

Figure 1. Oxygen phosphorescence and its excitation spectrum of an ensemble of terrylene molecules in 9,10-dibromoanthracene at 5 K.

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BIFUNCTIONAL TRIPHENYLAMINE DERIVATIVES FEATURING EMISSION ENHANCEMENT IN A SOLID STATE

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Triphenylamine (TPA) derivatives are the popular building blocks in material chemistry, the most extensively used as hole-transporting or electroluminescent materials for organic light emitting diodes (OLEDs) [1]. Recently, enhanced emission efficiency in a solid state for some of the TPA derivatives was demonstrated paving the way for their application in high efficiency light-emitting devices [2]. The possession of both transporting and emissive properties in the same TPA compound could favor its application in OLEDs as a bifunctional material. The reduction of a number of functional layers in multilayered devices by utilization of bifunctional materials is extremely attractive for fabrication of OLEDs by wet-casting technique, which is considered as simple and cost-effective alternative to widely exploited vacuum thermal evaporation systems.

In this work, fluorescence properties of a series of TPA derivatives known to possess excellent hole mobilities and having different number of 2,2-diphenyl and 2,2-di(4-methoxyphenyl) substituents were investigated. Absorption and fluorescence spectroscopy as well as fluorescence quantum efficiency and excited state lifetime measurements were employed to assess the optical properties of the TPA monomers and dimers in diluted and condensed phases.

An increase in the number of 2,2-diphenyl or 2,2-di(4-methoxyphenyl) substituents was found to cause significant enhancement (up to 10 times) of fluorescence efficiency of the TPA derivatives in dilute solutions. The 2,2-di(4-methoxyphenyl) substituents were determined to have more profound effect on the emission enhancement as 2,2-diphenyl substituents due to stronger electron-donating character. Further 5-10-fold enhancement of fluorescence quantum yield (up to 50-60%) was achieved by incorporating the TPA derivatives in a rigid polymer matrix at low concentrations. Although the diphenyl substituents were attached by using the conjugated ethenyl bridges to the TPA core, the maximum position of the fluorescence bands remained unchanged implying unaltered conjugation. The results indicate a stabilizing role of the peripheral groups inhibiting torsional motions of the phenyl rotors in the TPA compounds and causing the dramatic emission enhancement. This is well supported by the excited state lifetime measurements of the TPA derivatives clearly demonstrating the dominant ultrafast decay in dilute solution caused by the torsions of phenyl rotors and considerably prolonged decay in a solid state due to the suppression of the torsions. The revealed feature can be successfully exploited for designing the TPA-based nanostructures with aggregation-induced emission property. Enhanced emission in a solid state achieved through the suppression of the intramolecular torsions via aggregation is especially promising for the fabrication of OLEDs and fluorescence sensors [2].

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EXCITATION WAVELENGTH DEPENDENCE OF THE TRANSIENT SPECTRA OF PERIPHERAL LIGHT – HARVESTING COMPLEXES OF PHOTOSYNTHETIC BACTERIA

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Spectral variability of photosynthetic light-harvesting pigment-protein complexes arises either from excitonic interactions between pigment molecules or from their interactions with protein surrounding. Both these effects causing the shift of the absorption spectra can be well distinguished in peripheral light-harvesting complexes (LH2) of photosynthetic purple bacteria, the structure of which demonstrate a perfect ring-like symmetry [1] and, therefore, is considered to be a good modeling system for studies of excitonic properties of the spectra.

By exciting LH2 complexes from wild type *Rhodoblastus* (*Rbl.*) *acidophilus*, *Rhodobacter* (*Rba.*) *sphaeroides* and *Rhodovulum sulphidophilum* dependence of transient absorption spectra of B850 ring on the excitation wavelength was studied. Kinetics of the bleaching band was due to competition between energy transfer from B800 ring to the B850 ring and direct excitation of the upper excitonic subband of the B850 ring. The discrimination between these two pathways of the excitation relaxation/transfer reflects the difference in the timescale of both these processes. Indeed, the energy transfer from B800 to B850 ring has a time constant of the order of 1 ps [2] whereas excitation of excitonic band causes its instantaneous bleaching. The difference in the timescale of the transient spectra depending on the excitation wavelength made it possible to resolve the upper excitonic subband of the B850 ring [3].

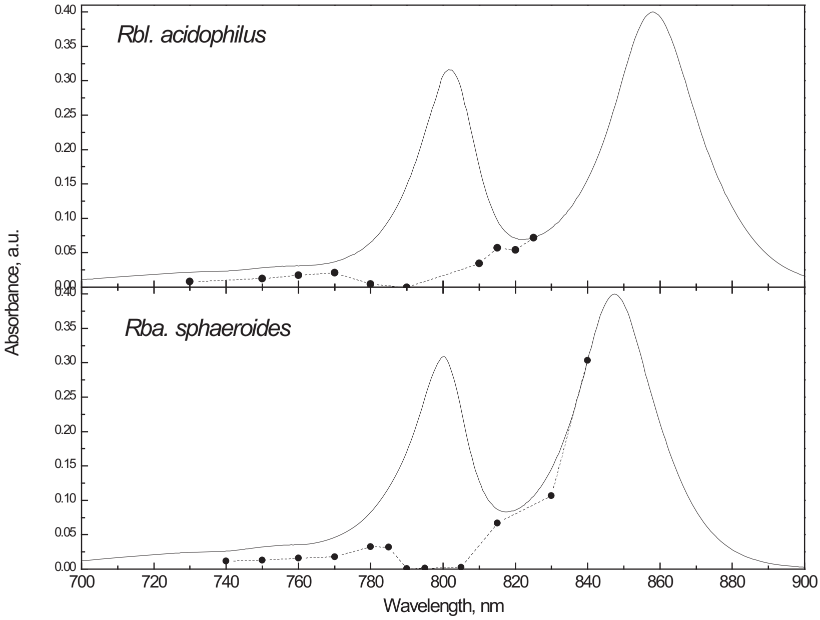

Figure 1. The absorption spectra of LH2 complexes isolated from *Rbl. acidophilus* and *Rba. sphaeroides*; dotted line represents the excitonic transition corresponding to the B850 ring.

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LOW TEMPERATURE EMISSION SPECTRA OF OPTICALLY NONLINEAR *N*-BENZYL-2-METHYL-4-NITROANILINE CRYSTAL

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The current search for new nonlinear optical materials for potential application in communications, medicine, electro-optic devices and holography focus on organic compounds. The knowledge about crystal structure, intermolecular interactions, dynamical disorder and electronic transitions is important to understand properties of solids. The optically nonlinear *N*-benzyl-2-methyl-4-nitroaniline (BNA) crystal reveals the high efficiency of second harmonic generation (SHG) which is almost 2 times larger than in the 2-methyl-4-nitroaniline (MNA) crystal [1], and widely tunable THz generation in 0.1 15 THz range [2].

The (BNA) non-centric [3] crystal represents the push-pull system in which the intramolecular charge transfer (ICT) takes place between the electron donor NH and the electron acceptor NO_2 groups, through the system of conjugated double bonds improving the high response of non-linear process [4]. However, the intermolecular charge transfer (CT) emerging from the weak hydrogen bonds parallel to the polar axis *c* in the orthorhombic BNA crystal lay in the opposite directions to the ICT and therefore competes with it [5].

In this work we present fluorescence and phosphorescence spectra of the orthorhombic BNA crystal in the 5-200 K temperature range, the spectrum of the BNA molecules dissolved in the Shpolskii matrix of *n*-heptane, and the Stokes shifts between the absorption and emission onsets. The electronic transitions parameters such as energies, oscillator strengths and dipole moments of excited states in the BNA molecule has been calculated by the semi-empirical quantum chemical methods to facilitate the interpretation of the experimental studies. These results are compared with those of BNA precursor, MNA [6]. The aim of this work is to propose the mechanism of emission behavior in the BNA crystal in terms of the structure-property relationship.

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ENHANCEMENT OF OPTICAL KERR EFFECT IN NEMATIC LIQUID CRYSTAL DUE TO INTERACTION WITH LOCALIZED SURFACE PLASMON

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We study the Optical Kerr Effect (OKE) in nematic Liquid Crystal (LC) and a mechanism of interaction of Localized Surface Plasmon (LSP) excited on gold or silver nanoparticles with LC molecules. We conduct an experiment in pump and probe configuration with probe beam coming from He-Ne laser (λ = 632.8 nm) and probe light from doubled in frequency Nd:YAG laser with λ_p = 532 nm. The sample is a LC cell in Twisted Nematic (TN) configuration with twisted angle 90^o, which is placed in cross polarizer system. We observe the signal were pump light is on or off for time long enough to LC molecules rotate and achieve the state of the lowest energy. Observations were made in function of DC voltage applied to the LC cell. Our theoretical model explains the dynamics of this process as well as the amplitude of the equilibrium state in function of applied voltage for the pure LC. Based on this model we try to explain the interaction of LC molecules with LSP which can be excited on the metal nanoparticles by pump light.

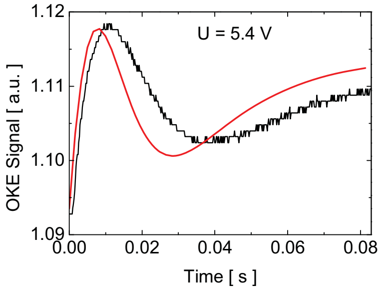

Fig. 1. Dynamic of OKE Signal measured (black line) and theoretical model (red line)

Acknowledgments: Polish Ministry of Education and Science grant no N N507 475237 and Wroclaw University of Technology.

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FLUORESCENCE POLARIZATION SINGLE COMPLEX IMAGING OF CIRCULAR LH2 ANTENNA

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Single complex fluorescence polarization spectroscopy is applied to study the peripheral light harvesting antenna (LH2) from photosynthetic purple bacterium *Rhodopseudomonas (Rps.) acidophila* at room temperature and at 77 K. The measured two-dimensional excitation-emission polarization plots are used to construct geometric representation for the absorbing (B800 or B850) and emitting (B850) rings as ellipses. Obtained shapes and orientations of the ellipses is discussed in terms of tilted LH2 complexes where emission occurs from energetically disordered B850 excitons. The angle between the principal axes of the absorbing and emitting ellipses in case of B850 excitation at 77K and at room temperature is analyzed using exciton relaxation model.

QUANTUM-CHEMICAL CALCULATIONS OF NOVEL PHOSPHORESCENT IRIDIUM COMPLEXES

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Organic light-emitting diodes (OLEDs) are one of the most promising light sources for modern electronic devices and lighting systems [1]. OLEDs are usually made of several layers of different organic materials, each layer having a specific function. Molecular complexes containing heavy metal atom, such as Pt or Ir, are regarded as one of the most promising materials for light-emitting layer of OLEDs because of their high efficiency and wavelength tunability [2,3]. Theoretical and experimental research of such compounds is therefore crucial in development of OLED devices.

Here we present results based on quantum-chemical calculations of structural and electronic properties of bis(2-phenylbenzothiazole)-iridium-acetylacetonate ($(pbt)_2Ir(acac)$) molecular complex and its derivatives. Atomic structure and excitation properties of the compounds are determined using several computational models; the results are compared between the models and to the experimental data. The calculations were performed using Gaussian03 and GAMESS-US programs.

The molecular structure of separate pbt ligand and the entire complex was optimized using density functional theory (DFT) with B3LYP functional and 6-31G(d) basis set. Absorption spectra of the resulting compounds were obtained using time dependent DFT (TD-DFT) method. Influence of the polarization continuum solvent model (PCM) to the calculation results was also tested; solvent effects were found to have an impact on excitation properties, while changes in molecule geometry were insignificant for these complexes. The optimized geometries were in good correspondence to the results of similar theoretical studies [4], and moreover, the absorption spectra agreed fairly well with the experimental data.

In addition to the ground-state structure (S_0) geometry optimization of the lowest triplet state (T_1), as well as calculations of the excited triplet states at both geometries were performed. The results indicate that the lowest-lying singlet and triplet states are both strongly linked to HOMO-LUMO electron transition between iridium atom and one of the two pbt ligands. Because of the identical ligands, the excitation spectrum in the S_0 geometry exhibits pairs of states with very similar differences in the excitation energies; however, this symmetry is broken in the T_1 geometry (Fig. 1).

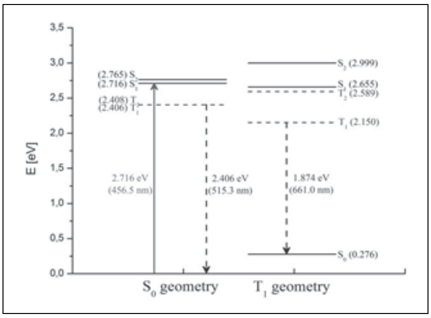

Figure 1. Lowest excited states of $(pbt)_2Ir(acac)$ complex in the S_0 and T_1 geometries

Geometry optimization and excited states calculations of the extended ligand with additional carbazole groups and the resulting Ir complex were performed using the DFT method. It is shown that wavefunction character in the lowest excited states is not affected by addition of the charge transporting groups.

Finally, the interaction between singlet and triplet energy states was explored. The interaction strength was evaluated from the splitting of energy states caused by spin-orbit coupling. Additional concern for the accuracy of computational results is determined by relatively heavy sulfur atom present in the pbt ligand. To assess the possible effect of the S atom, additional optimization was performed using model core potential approach with triple-zeta valence basis set (MCP-TZP, as implemented in GAMESS-US). Resulting geometries and absorption spectra were compared to the experiment results.

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REDUCTION OF THE GRAPHITE OXIDE TO GRAPHENE WITH LASER IRRADIATION

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Today there are many processes used to obtain graphene such as chemical vapor deposition, electrostatic force assisted exfoliation [1], pulsed laser ablation of graphite on silicon [2] etc. However, new manufacturing processes, which are reliable and simple, need to be developed for production of graphene on macro scale. Reduction of graphite oxide (GO) to graphene is one of promising ways. Contrast in the thermal conductivity of GO and graphene should be beneficial for many practical applications, especially for the circuits with efficient heat transfer. Laser irradiation can be used locally convert the graphite oxide film into graphene, and even complex micro-scale graphene patterns can be produced from GO on a substrate [3]. The aim of this work was to use laser treatment to form the thermo-conductive graphene-containing domains on the surface of thermal insulating GO films.

Picosecond laser (PL10100, 10 ps, 100 kHz, from Ekspla) and nanosecond laser (NL15100, 10 ns, 20 kHz, from Ekspla) were used in the irradiation experiments. Experimental setup included the laser, electro-optical shutter, nonlinear crystal for wavelength conversion, beam expander and galvanometer scanners with focusing objectives for both 1064 nm and 532 nm wavelengths. Graphite oxide was synthesized using a standard (Hummers – Otieman) and modified methods from a graphite precursor. Organic dyes from different classes (triphenylmethane, xanthene, diazo, anthraquinone, etc.) were used as additives. Focused laser beam was scanned over surface of GO layer on the polymer substrate using different settings of laser power and scan speed, controlling the irradiation dose. Experiments were performed in air as well as in nitrogen atmosphere.

Raman is the most versatile tool in detection of carbon allotrope forms. Measurements on laser-irradiated and untreated GO film areas were performed by using the confocal Raman spectrometer/microscope LabRam HR800 (Horiba Jobin Yvon) equipped with a He-Ne laser and a liquid nitrogen cooled CCD camera down to -132°C working temperature. Laser power at the sample was limited to 1 mW and the laser beam was focused to ~ 2 μm diameter spot on the surface. Each spectrum was recorded by accumulation of 10 scans yielding overall integration time of 100 s.

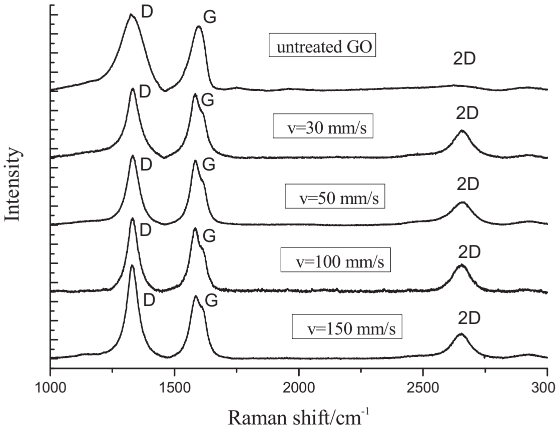

Fig. 1. Raman spectra of untreated GO film and irradiated by picosecond laser at various scanning speeds in air. Laser: mean power 100 mW, wavelength 1064 nm; GO film: thickness 800 nm, suspension – neutral, filtrated to H_2O; Substrate - MagnaNylon® (pore d=0.2 μm).

Low ratio of intensities D- to G-lines as well as high intensity of 2D line are measures of graphene phase quality. Depending on laser treatment parameters, the ratio I_D / $I_{G,}$ decreased up to 10 times. The 2D-line appeared after laser irradiation, indicating graphene phase formation. Shape of the 2D-line corresponded to formation of graphene multi-layers. Processing in nitrogen atmosphere led do reduced intensity of the D-line, but complete healing of the defects in the films was not achieved. Laser radiation facilitates reduction of graphite oxide to graphene however further route in GO film formation and laser treatment procedures are required.

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TEMPERATURE-DEPENDENT ENERGY TRANSFER AND LUMINESCENCE OF LANTHANIDE COMPLEXES

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Lanthanide complexes, due to their unique luminescence properties, are broad used as luminescent labels in various biomedical applications such as dissociation enhanced lanthanide fluorescence immunoassay (DELFIA), time-resolved microscopy and for developing organic light-emitting devices (OLEDs) in display technologies. Over the past decade there has been noticeable growth of interest in producing temperature sensitive paint (TSP) and dual luminophore pressure/temperature sensitive paint (DL-PSP) based on europium or terbium compounds. Such luminescent sensors can present results in two-dimensional (2D) and even three-dimensional (3D) aspects. They are extensively used in aerodynamical measurements.

Many works have been devoted to the investigations of the spectral and luminescence properties of lanthanide complexes. The ligand sensitized lanthanide luminescence is a complicated process involving several energy levels on ligand and on the excited levels of lanthanide ions. Quantum yield of luminescence of Ln $^{3+}$ ion strongly depends on the chemical structure, the composition of a complex and the temperature. However the mechanisms and the efficiency of temperature quenching of the luminescence quantum yield and lifetime of europium complexes are not fully understood. This makes the optimization of lanthanides complexes for temperature sensing complicated. The low value of luminescent quantum yield often limits applications of lanthanide complexes in high technology.

The absolute quantum yield and lifetime of ${}^5D_o \longrightarrow {}^7F_j$ luminescence of the Eu $^{3+}$ ion in europium complexes with fluorinated β-diketones has been measured on excitation of luminescence in the UV $S_o \longrightarrow S_1$ absorption band of the ligand within the temperature range of 77-365 K. Quantum yields of the luminescence in these complexes in PMMA films were 0,3 - 0,7 at the room temperature and it approached to unity at 77K.

Based on the analysis of the experimental dependences obtained and solution of the balance equations for stationary and nonstationary cases, we have developed a new approach to the determination of the energy levels scheme and rate constants transitions involved in the energy transfer from ligand on Eu3+ ion and subsequent f-f luminescence of ion. The rate constants of all processes of electron excitation energy conversion for 11 europium β-diketonate complexes have been determined. The role of the state with charge transfer in thermal deactivation ${}^5D_0$ and ${}^5D_1$ europium energy levels has been revealed. The investigations performed showed that the efficiency of intra-molecular energy transfer from the ligand to the ion in europium complexes with fluorinated β -diketones is close to unity, and the non-radiant degradation of the electron excitation energy is attributed first of all to the thermally induced transitions from the ${}^5D_0$ and ${}^5D_j$ levels of the ion with the participation of levels that have experienced charge transfer from ligand to Eu^{3+} with reduction of the latter to Eu^{2+}. It seems that the donor-acceptor properties of ligands are the main factors that are responsible for the quantum yields of sensitized ${}^5D_o \longrightarrow {}^7F_j$ luminescence being different from unity at room temperature.

The method presented allows to determine rate constants nonradiative transitions in large interval of its values. It is important that we can investigate fast energy relaxation in piko- and nanoscale of time with using experiment in microscale of luminescence lifetimes. Such approach may be applied for the other molecular systems that have temperature dependent luminescence.

Acknowledgementes. This work was partly supported by research project from the Polish Ministry of Science and Higher Education NN313 442737.

SECOND-ORDER PERTURBATION ANALYSIS OF DISORDERED FRENKEL EXCITONS IN CIRCULAR MOLECULAR AGGREGATES

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Inhomogeneous broadening caused by structural irregularities of surrounding molecules may severely disturb excitonic features of molecular aggregates. In analysis of these systems, analytical approach is of great use because it eases understanding of the relationship between particular experimental observables and physical parameters of the system. Previous analytical studies of excitons in the disordered circular aggregates have been mainly focused on the properties of the lowest exciton levels and limited to the first-order correction terms in perturbation series expansion [1]. However, there exists particular spectral quantities of great interest, like Davydov splitting and gap between the second and first excited energy levels, that have vanishing first-order terms [1].

In this work, we present analytical study of the above mentioned observables in diagonally disordered circular molecular aggregates. We applied second-order perturbation theory accompanied by numerical simulations. Aggregates with one and two heterogeneous molecules per unit cell were considered. It was shown that distributions of the second order corrections for any of the excitonic energy level can be expressed as a linear combination of independently distributed squared Gaussian variables. If combined, these expressions can be related to excitonic bandwidth and gap between two lowest exciton levels observed, correspondingly, by fluorescence excitation anisotropy and hole burning spectroscopy experiments. This in turn, provides new analytical estimates of the disorder and resonant coupling intensity from experimental data.

Finally, we applied obtained analytical results to the analysis of the spectroscopic data from bacterial light harvesting complexes LH2 [2, 3]. Particularly, the consistency analysis of the disorder shift and broadening of the hole burning action spectrum showed no convergence in the realistic limits of the resonance coupling and relative disorder. This provides new evidence on the limitations of the Frenkel exciton model in describing the lowest exciton state in LH2. Implications of our results to the analysis of spectroscopic data of artificial light harvesting cyclic porphyrin arrays are presented too.

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PHOSPHORESCENT BIS-CYCLOMETALLATED IRIDIUM COMPLEXES BASED ON TRIAZOLE LIGAND

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Organic light-emitting diodes (OLEDs) are currently attracting a lot of attention owing to their applications in full-color flat-panel displays and solid state lighting [1]. Among the huge variety of organic luminophores available there are phosphorescent ones, which are particularly attractive for electroluminescence applications. In contrast to fluorescent materials they can offer internal quantum efficiencies up to 100 % by forcing both singlet and triplet states to emit light [2]. This is achieved by utilizing transition metal-ligand complexes (e.g. iridium(III) complexes), which can overcome the forbidden nature of the transitions from the triplet states due to the strong spin–orbit coupling of the transition metal, giving rise to mixing of the singlet and triplet excited states.

For OLEDs to be useful in display applications, true red, green, and blue emissions of sufficient luminescent efficiencies and proper chromaticity are required. To date, there is a greater success in the research of green triplet emitters than red ones. In accordance with the energy-gap law the design and synthesis of efficient red emitters is intrinsically more difficult. Since the quenching mechanism is intrinsic, it causes the main obstacle in achieving red emitters of high efficiency. Hence, many red organic dyes currently in use do not show a good compromise between device efficiency and color purity because of the nature of red emitters.

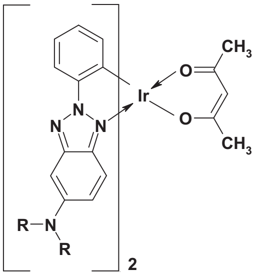

Figure 1. General structure of the investigated iridium complexes.

In the past few years a number of new red emitting iridium complexes for OLEDs have been reported. Various nitrogen-containing heterocycles such as quinolines, isoquinolines, quinazolines, and quinoxalines have been of special interest in accomplishing red phosphorescent emission. However, 1,2,3-triazoles have been virtually overlooked and only recently few examples have been published. The purpose of the present work is investigation of the red-emitting 1,2,3-triazole-based iridium complexes in order to study their emission properties.

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PHOTOPHYSICS OF ORGANIC AND HYBRID LIGHT EMITTING MATERIALS: FROM BODIPY DYES TO QUANTUM DOTS

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The development of organic and organic-inorganic hybrid light-emitting materials can be guided by photophysical measurements. Here we show two examples.

In the first, ultrafast fluorescence upconversion spectroscopy is performed on two Bodipy dye molecules, where ring rotation has been restricted in one and not in the other, Figure 1. Observing the ultrafast emission from the S_2 and S_1 states in both materials enables the rate of $S_2 \rightarrow S_1$ internal conversion to be measured. Such higher states are active in photobiology, notably with carotenoids, and could open up new possibilities for photochemistry. Rapid internal conversion from these high-energy states offers a form of protection against the deleterious effects of UV irradiation, and this has many important practical benefits. It is found that hindering the rotation of the meso-phenyl ring slows the rate of internal conversion from 50 to 90 fs.

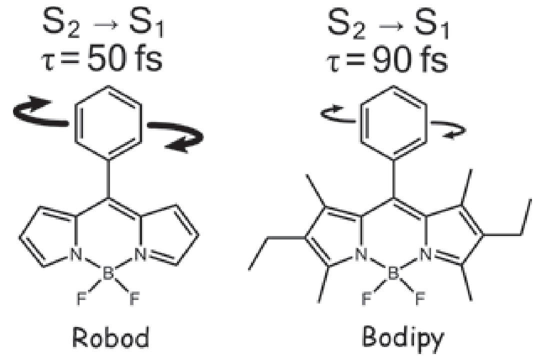

Figure 1. Chemical structures of the two Bodipy dyes investigated and schematic indication of meso-phenyl ring rotation that plays a role in the $S_2 \rightarrow S_1$ internal conversion process.

In the second system photophysical measurements are presented that examine part of a novel methodology for laser patterning and processing of polymer quantum dot blends for light emitting devices. By blending a polyfluorene host and a cadmium sulphate quantum dot precursor one can create films that are suitable for laser patterning, a process which will generate CdS quantum dots in situ in the already prepared films. Here photophysical measurements have been performed, using thermal annealing in vacuum as an analogy to laser processing, looking at the effect that the polymer host and precursor have on quantum dot formation and finding the optimal times and temperatures for thermal annealing.

NON-LINEAR MULTIMODAL OPTICAL MICROSCOPE

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Light microscopy has greatly advanced our understanding of the world on the micro-scale. Various light-matter interactions are used to investigate different physical properties of the specimen, e.g. in bright field microscopy, image contrast is based on absorbance and scattering of light. As developments in optical techniques progress, the more specific contrast mechanisms are used, the higher spatial resolution and higher sensitivity levels are achieved. In particular, the use of non-linear light-matter interactions in microscopy has emerged as a powerful research tool for biology [1]. In the past few years, there had been number of aproaches to combine multiple non-linear contrast mechanisms in one microscope [2-5].

In this work we present non-linear multimodal optical microscope based on coherent anti-Stokes Raman scattering (CARS) micro-spectrometer [6] and multimodal imaging of some biological objects (i.e. green algae, starch granules). A fundamental beam of picosecond laser operating in a cavity dumping regime (Nd:YVO_4, 1064 nm) at 1MHz repetition rate is used to pump optical parametric generator, which serves as a two-color, signal beam (850-1040 nm) and idler beam (1060-1395 nm), excitation light source. Excitation beams are directed to the standard inverted microscope (Olympus IX71) and focused on the sample with an oil-immersion objective (Olympus, Plan Apochrom., 60×, NA 1.42). This experimental setup can be used for imaging with multiple non-linear contrast mechanisms: coherent anti-Stokes Raman scattering, two-photon excitation fluorescence (TPEF), and second harmonic generation (SHG).

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SPECTROSCOPIC ANALYSIS OF POLYSILANES CONFINED IN DIFFERENT SiO_2 AND TiO_2 NANOSTRUCTURES

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Potential application of nanosize polymers in different technologies such is transport and luminescent layers in electroluminescent diodes, sensors, and photoresistors stimulates investigation of their optical and electrical properties. Recently the possibility to manipulate properties of nanosize polysilanes by incorporating them into mesoporous silica has been demonstrated. It was shown that one can control the number of embedding polymer chains, their conformation and orientation, and, thus, optical properties by simply changing diameter of nanopores. These investigations revealed new polymer conformational states with different degree of disordering, which are not present in polymer solutions and in solid films [1 – 3].

In this work four novel composite films based on photoconducting silicon-organic polymer poly(di-n-hexylsilane)-PDHS incorporated into different SiO_2 and TiO_2 nanostructures, namely in nanoporous SiO_2 and TiO_2 films, silica photonic crystals and silica gel, have been fabricated. Optical and conformational properties of the composites have been studied by using photoluminescence (FL), absorption, FL excitation spectra as well as FL decay measurements in the wide temperature range of (5-330) K. The analysis of the FL spectra of the composites shows three different polymer conformations coexisting inside a pore: gauche- and trans- conformations, and aggregates. Intensity if the aggregate fluorescence in photonic crystal and in silica gel gradually decreases by increasing temperature, while in porous SiO_2 and TiO_2 films the temperature dependences are more complex: the fluorescence intensity gradually decreases by increasing temperature below trans-gauche transition, while at higher temperatures it increases until 310 K, when aggregates are thermally destroyed (Figure 1) [3].

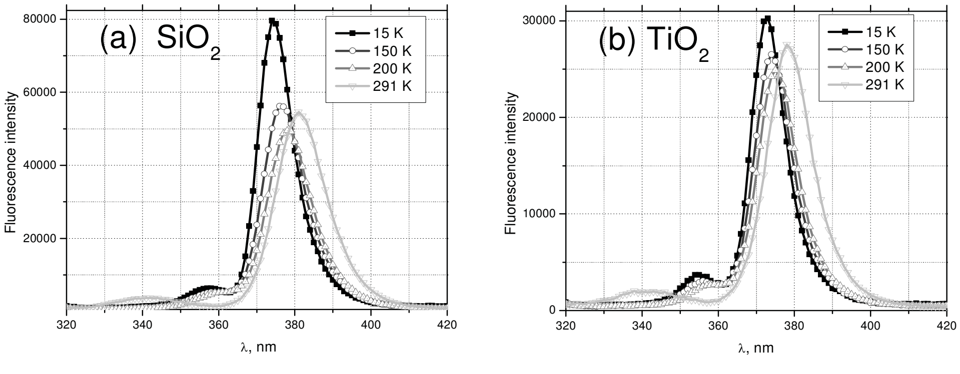

Figure 1. Temperature dependence of FL spectra of: a) PDHS/SiO_2 porous film; b) PDHS/TiO_2 porous film. λ_{ex}= 280 nm.

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EXCITATION ENERGY TRANSFER IN POROUS SILICON AND CONJUGATED POLYMER COMPOSITES

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Porous silicon (PS) has been intensively investigated during last decades due to potential applications of the material in optoelectronics. Hybrid inorganic-organic structures open new application perspectives, because of new and controllable properties. Conjugated polymers doped with semiconductor quantum dots have been demonstrated to possess interesting properties for their application for solar energy conversion. Porous silicon covered by functionally active organic layers presents an alternative way of the formation of hybrid structures. Excitation energy transfer from semiconductor quantum dots to conjugated polymers has been demonstrated in several publications [1, 2]. Attempt to address the energy transfer in PS/conjugated polymer structure has been reported in [3]. However, the processes taking place during fluorescence of these composites aren't sufficiently examined. The energy transfer processes in such composites are expected to be particularly complex because of the complex dynamics of the PS fluorescence. Both, energy transfer from PS to conjugated polymer and backward are expected, and both of them may take place is the same sample depending on the experiment conditions.

In our work we used time-resolved fluorescence measurements to investigate energy transfer in PS/conjugated polymer composites. THF solutions of m-LPPP and MEH-PPV polymers were spin-coated onto porous silicon substrate to create the composites. Figure 1 demonstrates absorption spectra of the MEH-PPV film as well as fluorescence spectra of porous silicon and MEH-PPV suggesting a possible energy transfer route from PS to the polymer. After close examination of fluorescence spectra and decay kinetics of the composites as well as their constituents, we conclude that energy transfer from PS to polymer takes place during initial several nanoseconds after the composite excitation. Observation of the energy transfer in opposite direction was impeded by the energy transfer processes taking place in porous silicon itself.

This work was partly supported by the Lithuanian Science Council Research Fellowship Award (V.P.).

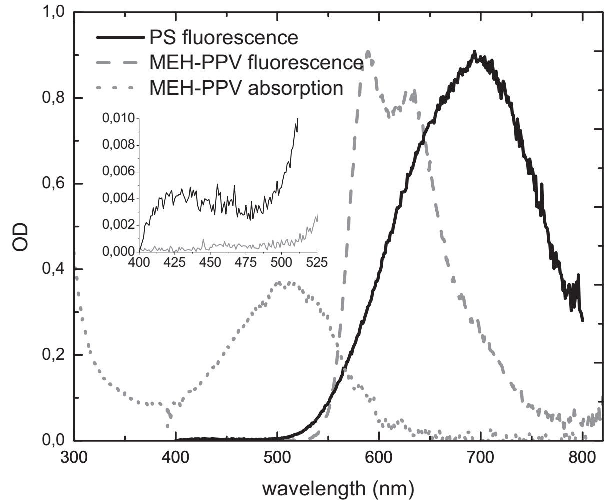

Figure 1. Absrption spectra of MEH-PPV and fluorescence spectra of MEH-PPV and PS. Inset shows a close-up view of fluorescence spectra in 400…525 nm region.

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EXCITON DYNAMICS AND RELAXATION IN A HETERODIMER

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Molecular dimer is the smallest system reflecting the main features of exciton dynamics in molecular aggregates. Moreover, such a dimer can also play a role of a quenching center in condensed phases, especially in the case when its constituents possess essentially different spectral and dynamical characteristics. Indeed, recently it has been proposed that the heterodimer composed of chlorophyll and carotenoid molecules can be a trapping center responsible for the non-photochemical quenching of excess energy in photosynthesis of green plants at high light conditions due to fast relaxation of the lowest excited state of carotenoid [1, 2] or due to the charge transfer (CT) state formation [3]. Here we present our analysis of an excitonic *hetero*dimer, having the constituent monomers asymmetric in a number of ways (site energies, reorganization energies or equivalently spectral line widths, excitation lifetimes, etc.) as opposed to a *homo*dimer (identical monomers) or in some sense even to a heterodimer with solely different site energies.

The absorption spectrum, the evolution of excitation and the excitation lifetime dependence on the energetic positions of states due to the excitonic mixing of the heterodimer are considered. The key feature of the dimer in question corresponds to an optically forbidden and extremely short-lived state of one of the monomers. Our calculations were performed using both the Redfield approach based on the perturbative scheme for the system-bath interaction and the recently developed hierarchical equations of motion (HEOM), which takes this interaction into account non-perturbatively. From this comparison we demonstrate the limits of validity of the Redfield scheme. Because of the non-perturbative nature of the HEOM we were able to treat both the coherence dephasing and population dynamics, which revealed us the presence of an effective renormalization of the resonance coupling different from the prescription of the well-known small-polaron transformation. As for the lifetimes, we found that the ones of the excitonic states (i.e. excitonically mixed) depend on the energy gap between the states in the site basis as shown in the figure and are insensitive to which state is the lower one. This result demonstrates the possible limits for the effective quenching by such heterodimer.

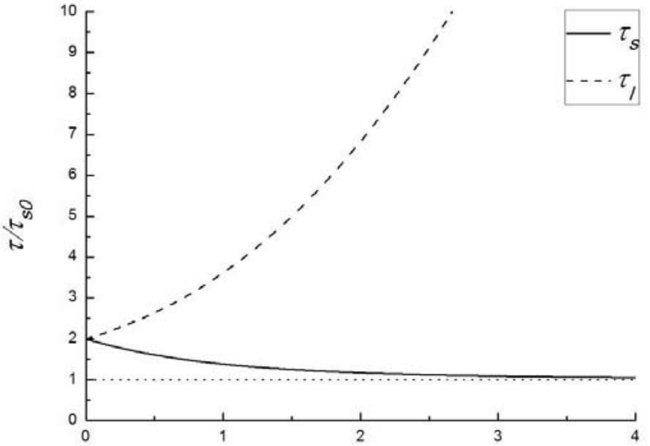

Figure. Lifetimes of the excitonic states of the heterodimer depending on the energy gap (between the short and long living original (electronic) states) ΔE normalized to the resonance interaction, J. Indices "*s*" and "*l*" denote respectively the short-lived and the long-lived states. Both lifetimes are normalized to the lifetime of the excited short-lived monomer, τ_{s0}, on the assumption that $1/\tau_{l0} \approx 0$.

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INTRAMOLECULAR VIBRATIONS AND QUANTUM COHERENCE DYNAMICS IN 2D SPECTRA SIMULATIONS OF PORPHYRIN HEXAMER

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A novel spectroscopic tool – two-dimensional (2D) optical spectroscopy – has enriched our knowledge about quantum dynamics in various systems ranging from the photosynthetic aggregates [1,2] to semiconductors [3], conjugated polymers [4] and low-dimensional systems, such as carbon nanotubes or J-aggregates [5-7]. Apart from capability of direct mapping of excitation energy transfer pathways, this method also provides very intriguing results of quantum coherence dynamics – the interplay of dephasing and decoherence. The lack of a consistent model for the bath-induced decoherence and energy transfer in molecular systems makes it hard to ravel out the causes of the phenomenon of quantum coherence oscillations. The heterogeneous dynamics of correlated and uncorrelated system-bath motion, quantum transfer and intermolecular vibrations can result in a complex coherence dynamics, observed experimentally [1,8]

In this study, quantum coherence dynamics, maintained by simulated 2D spectra, are presented for a system of porphyrin hexamer. Spectra are obtained by using the response-function theory assuming that the system is coupled to a single underdamped mode of thermal system-bath motion. The spectra evidently perceive cross-peak oscillations of vibrational nature and agree with experimental results well. It is concluded, that the origin of experimentally observed oscillations cannot be confused with any other mechanism, but intramolecular vibrations. The model for simulating low-temperature spectra is also proposed in this work.

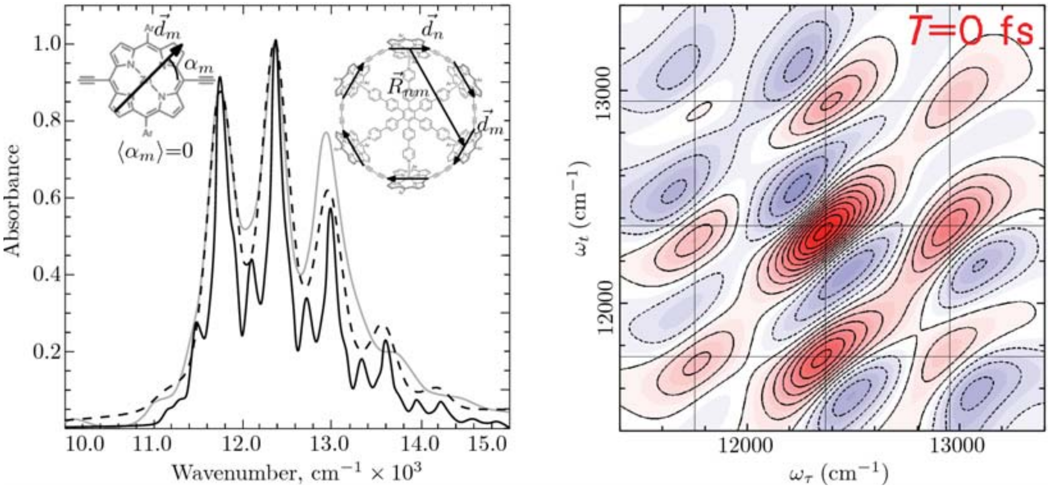

Fig. 1. Structure of a porphyrin[6] ring on a hexadentate template and configuration of dipole moments; linear absorption spectra: experiment and simulation at room temperature, simulation at 77K (grey, dashed and solid line, respectively); simulated 2D spectrum (right).

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LUMINESCENCE STUDY OF DIFFERENT PHASES OF MOLECULAR COMPOUND SALOL

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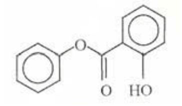
Salol, or phenyl-2-hydroxybenzoate, or phenyl salicylate ($(HO)C_6H_4CO_2C_6H_5)$) are three names for an ester with diversified applications, namely as a stabilizer for cellulosic and vinyl plastics, as an ingredient for suntan preparations, and also as an analgesic and antipyretic. In our previous study we have shown that the cold crystallization tends to form the metastable polymorphic modification. The conditions of formation of different polymorphic forms have been clearly established in our previous investigations using Raman and infrared spectroscopy [1, 2]. However, to our knowledge, a luminescence study of salol has not been performed so far. This observation motivated us to conduct the present study. The molecule of salol consists of two phenyl rings, which are connected by three single bonds through two, carbon and oxygen, atoms. The hydroxyl group is attached on one of the phenyl rings in the orto-position.



Fluorescence spectra measurements were performed by using a MPF-4 Hitachi spectrofluorimeter. The samples for the measurements were encapsulated in cylindrical glass tubes. The excitation wavelength was 363 and 340 nm.

It was established that the luminescence spectra of both polymorphic modifications of salol at 4.2 K consist of well resolved progression of three broad bands. The average spacing between each band is 1250 cm^{-1}. In general we have observed two pronounced changes between the luminescence spectra of two polymorphic modifications. The first is the shift of the emission band of the stable phase to the red by about 750 cm^{-1} relative to the metastable phase. The second is the broadening of the emission band of the stable phase as compared to the band in the metastable phase. The spectrum of the stable phase has a full width at half-maximum (fwhm) amplitude of 3500 cm^{-1}. The spectrum of the metastable phase has a fwhm = 2500 cm^{-1}. Also the spectra of both modifications are sensitive to the changes in excitation wavelength, and the vibronic structure on the luminescence bands of both modifications is smearing with increasing temperature.

. Raman and IR spectroscopy was used as an aid for assigning the vibronic structure present in the emission. It was established that the progression interval corresponds to the $\nu(C - OH)$ stretching vibrations, which are strongly influence by the intermolecular hydrogen-bonding interactions. The presence of an OH group in the 2-position on one ring asymmetrizes the molecule, localizing the electronic excitation to the OH-substituted ring.

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APPLIANCE OF SMECTIC PHASE OF PHOTOCHROMIC LIQUID CRYSTALS FOR HOLOGRAPHIC GRATING RECORDING

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Liquid crystal phase of azobenzene liquid crystals or its mixtures can be changed by light causing molecular reorientation (order order transition) or by isotropisation of the molecules distribution (order disorder transition) [1]. Our previous studies have shown [2], that diffraction gratings can be inscribed holographically in the nematic phase of pure low molecular azobenzene derivates, but growth of photoinduced isotropic domains can cause disappearance of the grating.

Not much information in literature can be found about holographic recording in low molecular smectic materials.

In this work thermotropic liquid crystals from a group of 4-hexyl-4’-alkoxyazobenzenes is characterized with regard to materials’ diffraction response during holographic grating recording. The materials exhibit smectic phases at temperatures from 40 to 81 C. Sandwich-like samples with thickness of few μm were filled with studied materials and used in further investigations.

For the measurements Degenerate Two Wave Mixing setup, equipped with temperature stabilizing system is used. Diffraction gratings are recorded by cw Ar^+ laser ($\lambda = 514$ nm). The influence of temperature, light intensity and grating period on the diffraction response during holographic recording in the samples is checked.

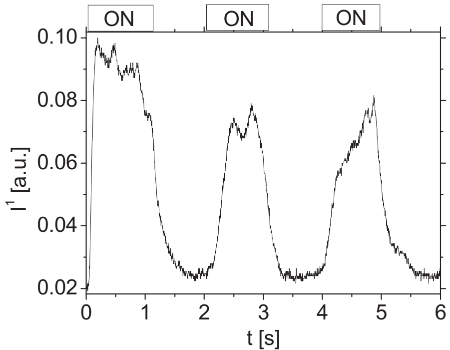

Fig. Diffraction efficiency evolution during cyclic recording and erasure of grating in material 6-O12.

As opposed to our previous studies of holographic recording within nematic phase, it is possible to use studied materials for record a diffraction grating within their smectic phase which remain at non-zero signal level after tens of minutes. Moreover full erasure and re-writing of the gratings can be done in studied materials (Fig.).

Results of the measurements of diffraction grating recording in studied materials will be presented. Influence of the recording parameters on the diffraction response will be discussed. It is a possibility of usage this type of materials in construction of reversible optical switches.

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DIRECT OBSERVATION OF THE *n*,π*-TYPE EXCITED SINGLET AND TRIPLET STATES OF *N*-TRIPHENYLMETHYLSALICYLIDENEIMINE MOLECULE

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N-triphenylmethylsalicylideneimine (MS1) belongs to the group of Schiff bases with medium-strong intramolecular H-bond. Photo-induced rearrangement of MS1 as a whole opens possibility of creation photochromic isomer with broken H-bond [1].

It is well known, that a necessary requirement for understanding the photochemistry is knowledge of the energy levels sequence of the reactant molecule and the pathways of these levels changing during the photoreactions. Particularly, in case of Schiff bases with chelate ring, among several well defined stable molecular conformations, essential importance has a configuration with strongly twisted geometry, related to excited singlet state of the *n*,π*-type [2].

Because of that reason knowing the energy of the $^1(n,\pi^*)$ state is crucial both in the analysis of the proton transfer processes in the excited state and in molecular photochromism. However, there is no experimental data on the $^{1,3}n,\pi^*$-type excited states in case of the Schiff bases. Moreover, those molecules do not exhibit phosphorescence, as a rule.

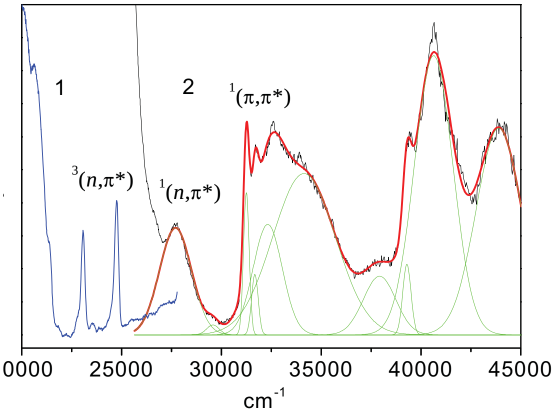

Figure 1.
The emission and the excitation emission spectra of MS1 in isooctan, at 77 K.
On the left: (1) long wavelength part of the phosphorescence spectra (E_{exc}= 31250 cm^{-1}).
On the right: (2) phosphorescence excitation spectra monitored at 0,0 transition. Envelope of the nonlinear fit of the spectrum is also shown. Relative energy gap $\Delta E[^1(n,\pi^*)\ \ ^1(\pi,\pi^*)] = 3470$ cm^{-1}, and singlet triplet splitting $\Delta E\ [^1(n,\pi^*)\ \ ^3(\pi,\pi^*)] \approx 3000$ cm^{-1}.

In this work, we present low-temperature spectral features of (MS1) in nonpolar solvent relevant to the mentioned above excited singlet and triplet states, observed directly. In discussion, the results of the MS1 luminescence investigations in polar environment at RT by means of time-correlated fluorescence and femtosecond transient absorption in polar protic solutions are also taken into account [3].

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TERAHERZ PROBING OF CNT / EPOXY COMPOSITES

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This communication presents the study of spectral features of nanocarbon based epoxy resin composites in the terahertz frequencies (0.2-3 THz, 3-18THz) where the search of new operational materials and components is of particular importance for various promising applications. The series of close-to-percolation threshold carbon nanotubes (CNT) samples, both multi-walled and single-walled, with 0.5 wt.% of nanocarbon were prepared using epoxy resin Epikote 828 by Hexion Company, different types of fillers, listed below, and our own made curing agent called A1 (it is a modified TEPA). The types of fillers used, were:

- *commercial Multi-Wall CNTs (MWNTs), Purity: 95%+, Diameter: 20–40 nm and Length : 0.5 – 200 μm;*
- *Commercial Single-Wall CNTs (SWNTs), Purity: 90%+, Average Diameter: 1.5nm and Length : 10 - 20 μm.*

A high THz attenuation ability is demonstrated in the range 0.2-3 THz by the CNT-based samples, especially by SWNT. The transmission at 1 THz through the sample containing 0.5 wt.% of SWNT inclusions is 12 times less then through pure resin, and 3 times less in the case of MWNT incorporation.

In the far-infrared frequency range (from 3 to 18 THz) a small reflection of THz signal were observed (up to 5%) for all types of nanocarbon inclusions. The maximal reflection is demonstrated by the net epoxy resin, which denotes a strong screening effect of the given matrix.

A theoretical interpretation of the observed THz spectrum is given, within the framework of nanoelectromagnetics [1], utilizing the theory of antenna-like behavior of isolated carbon nanotubes in the THz range predicted in Ref. [2].

Acknowledgements

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DICHOTOMOUS EXCITON MODEL IN SPECTRAL SIMULATIONS OF LIGHT-HARVESTING COMPLEXES

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Photosynthetic aggregates in natural environment “operate” at ambient temperature ranging in very narrow temperature region: in plants roughly from ~0 C (273 K) to 40 C (313 K). In this temperature range the properties of photosynthetic aggregates must be conserved, what is confirmed by the spectroscopic measurements [1]. Here a simple model of an electronic system, coupled to a harmonic bath with a specific bath spectral density can be used. However absorption experiments at much lower temperatures (down to 4 K) for a light harvesting complex 2 (LH2) from species of photosynthetic bacteria, *Rhodobacter sphaeroides* and *Rhodoblastus acidophilus* show that the spectral bandwidths increase with temperature, while peak positions move in opposite directions: the B800 band to the red side and the B850 band to the violet side of the spectrum. This temperature dependence is not smooth and show switching behavior at around 50-150 K, which cannot be described by the simple model.

In this work a simulation of the temperature dependence of absorption spectra of LH2 complexes was performed in a temperature range of 4 K to 300 K. The homogeneous part of the absorption spectra was calculated using the modified Redfield theory based on the exciton model [2,3]. The inhomogeneous properties of the exciton model (the diagonal disorder) were extended as follows.

The diagonal disorder was assumed to be of two-state switching (dichotomous) type, previously introduced to describe a single molecule spectroscopy [4]. The model assumes that the bacteriochlorophyl (Bchl) molecules constituting an LH2 ring can be in one of the two conformational states, each having different ground state energy and a different electronic transition energy. Ratio of occupations of these conformational states satisfies the Boltzmann distribution, thus effectively making this disorder model temperature-dependent.

Numerical analysis has been performed for the model parameters, the ground state energies and the transition energies searching for an optimum fit with experimental data. Various system-bath coupling parameters have been analyzed, different spectral densities were applied to conformational states of Bchl molecules as well. The optimum fit parameters were found to describe the experimental data reasonably well in the entire temperature range.

Having the set of optimal parameters, we have calculated the two-dimensional spectroscopy signals at different temperatures and compare them with the experiments of Zigmantas et al [5].

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SPECTROSCOPIC PROPERTIES OF CARBAZOLE-FLUORENE-BENZOTIADIAZOLE COMPOUNDS

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Design and syntheses of molecular derivatives possessing desired optical, electrical, thermal and chemical properties is one of the main directions of the development of molecular optoelectronics. Relatively simple molecules possessing a single functional group often can not meet all the requirements. Consequently incorporation of different organic functional groups in molecular structure responsible for some particular molecule properties and leading to novel characteristics plays a key role in molecular design. Due to unique physical properties carbazole (C), fluorene (F) and benzotiadiazole (B) moieties are preferable over a remarkable variety of functional groups.

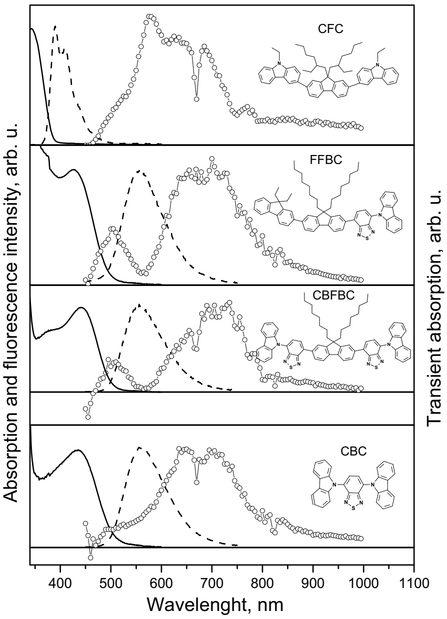

Figure 1. Absorption (solid line), fluorescence (dach line) and difference absorption spectra of all investigated compounds in dilute THF solution.

This report presents spectroscopic properties of novel organic multifunctional compounds named as CFC, FFBC, CBFBC and CBC, under names of connected functional groups. Fluorescence and the long wavelength absorption properties of these molecules are determined by the intramolecular charge transfer states related to the electron transfer between different functional moieties. The investigated molecules have large, more than 60%, florescence quantum yields in solutions, which drop several times in solid films. Importantly, that the fluorescence decay times decrease in solids much less significantly than the quantum yields. By using fluorescence, femtosecond transient absorption and quantum chemical calculations we investigated processes responsible for the drop of the fluorescence efficiency is solids. In addition to the migration controlled exciton quenching, conformational changes of the molecules play an important role in relaxation processes. Conformational relaxation taking place in solutions is suppressed in close-packed structures. Two fluorescence bands observed in nonpolar solutions and only one long wavelength band present in polar solutions indicate that molecules posses two excited states strongly coupled to environment. Transient absorption investigations and quantum chemistry calculations suggest that the dipole moment of the radiative transition increases after relaxation of excited molecules to the polar low energy excited states due to conformational reorganizations of excited molecules.

Acknowledgements

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CHARACTERIZATION OF POSITIVE CHARGE BEARING MERCAPTOHEXYLPYRIDINIUM SAM AT GOLD ELECTRODE

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Self-assembled monolayers (SAMs) from organethiol molecules adsorbed on noble metals are widely used to construct surfaces with desirable properties. Often is important to establish a stable positive charge on the surface capable to attract anions from the solution phase. Such surfaces may be used as sensor platforms, in development of catalytical processes, and environmental studies [1]. Organethiol molecules terminated by amino group are often used to design positively charged groups at interface. However, the amino functional group in surface-bound monolayers retains protonated only at certain conditions because of deprotonation in more alkaline solutions and interaction with the surface through the amino group. One way to overcome these problems is formation of SAMs from organethiol molecules bearing pyridinium functional group. In order to create and control the function of positively charged surface-bound functionalities, understanding of structure of adsorbed species at the molecular level is required. Surface-enhanced Raman spectroscopy is able to provide rich structural information on the bonding and orientation of particular molecular groups at the metal/solution interface [2]. In this work structure of SAM of 1-(6-mercaptohexyl)pyridinium (MHP) chloride adsorbed at Au electrode surface was characterized by SERS and linear sweep voltammetry methods. Quantum chemical calculations were performed to ensure the assignments of vibrational modes.

For interpretation of experimental data the geometry of Au_3-MHP complex was optimized and vibrational frequencies were calculated. Based on dependence of parameters of SERS bands on temperature and adsorption time in MHP solution the marker bands of MHP structure have been evaluated. In particular, it was demonstrated that the hydrocarbon chain stretching C–C vibration near 1082 cm^{-1} sensitively probes the gauche/trans isomerization at the interface. At shot immersion times in adsorption solution soft C–H stretching mode at 2830 cm^{-1} was detected indicating direct contact of hydrocarbon chain methylene groups with the metal surface [3]. Potential dependent studied have shown drastic changes in relative intensities of the SERS bands (Fig. 1); relative intensity of ring ν_{8a} mode near 1634 cm^{-1} was found to increase comparing with totally symmetric ring mode ν_{1a} at 1029 cm^{-1}. Based on analysis of marker bands and intensity-potential dependence at different excitation wavelengths it was concluded that potential-induced reorientation of MHP with respect to electrode surface take place. In addition, the enhancement due to the metal-molecule charge transfer (CT) resonance [4] was found to operate in the studied system.

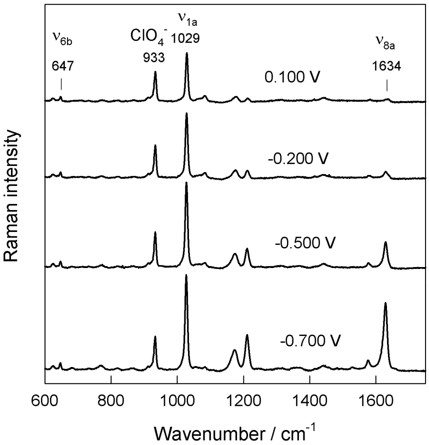

Figure 1. SERS spectra of adsorbed MHP on Au electrode in 0.1 M $NaClO_4$ solution at different potentials (vs. Ag/AgCl electrode). Excitation wavelength is 785 nm (30 mW). 933-cm^{-1} band is due to attracted ClO_4^- ions at interface.

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CONTROL OF THE OPTICAL PROPERTIES OF PYRROLOPYRIMIDINE DERIVATIVES BY POLAR GROUPS

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Pyrrolo[2,3-*d*]pyrimidine compounds are known to possess antibacterial, antiviral, antifungal and antitumor properties, and therefore are attractive for medical applications. Oligoarylenes bearing the pyrrolo[2,3-*d*]pyrimidine core demonstrate good π-conjugation accompanied by fairly high emission efficiency. Due to their structural similarity to two of the four DNA bases such compounds were shown to be ideally suited for DNA probing. To employ the pyrrolopyrimidines in fluorescent biosensors it is extremely important to be able to control their photophysical properties, which can be remarkably altered by attaching polar groups.

In this work a series of novel oligoarylenes with pyrrolo[2,3-*d*]pyrimidine core has been synthesized and their photophysical properties under the influence of various polar groups have been investigated. The properties of the compounds in the diluted and condensed states were evaluated by utilizing absorption and fluorescence spectroscopy, and by estimating excited state decay times and fluorescence quantum yields. The experimental results were supported by density functional theory (DFT) calculations.

The pyrrolopyrimidine derivative bearing two phenyl side-groups (compound **1a** in Fig. 1) expressed fluorescence quantum yield of 42% in dilute solution, which was dramatically reduced to 3.6% by introducing electron-withdrawing *tert*-butoxycarbonyl (*t*-BuOCO) group (compound **1b**). The reduction in the quantum yield was followed by fluorescence blue shift and significant shortening of the fluorescence decay time. The changes in fluorescence properties were elucidated by DFT calculations indicating a key role of the polar *t*-BuOCO fragment in the twisting of the phenyl rotor. This fragment was found to inhibit planarization of the phenyl rotor initially forming 30° angle with regard to the pyrrolopyrimidine core, whereas the absence of the *t*-BuOCO fragment allowed for complete planarization of the rotor resulting in an enhanced π-conjugation, increased emission efficiency and decay time. The results in solutions were confirmed by the measurements of the compounds in a rigid polymer matrix with the suppressed twisting of the rotors. The extension of π-conjugation by incorporating additional carbazole outer groups (compounds **2a** and **2b** in Fig. 1) resulted in an enhanced fluorescence quantum yield up to 67%. DFT calculations implied essential role of the carbazoles considerably affecting molecular charge redistribution upon excitation and also indicated that molecular planarization is unlikely and that it is unaffected by attachment of the *t*-BuOCO fragment.

An impact of other polar groups like cyanophenyl and methoxyphenyl was found to be important for tailoring the optical properties of pyrrolo[2,3-*d*]pyrimidines and is being discussed in this work.

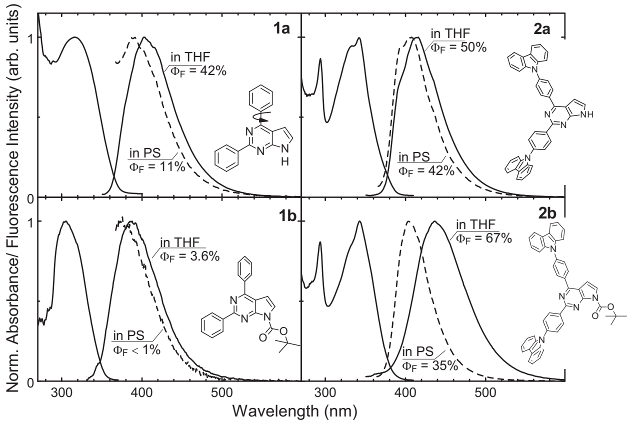

Figure 1. Normalized absorption and fluorescence spectra of pyrrolo[2,3-*d*]pyrimidines **1a,b** and **2a,b** in dilute THF solution (solid line) and polystyrene matrix (dashed line).

NANO-, BIO-SYSTEMS

MULTIFUNCTIONAL NANOPARTICLES FOR TWO-PHOTON INDUCED PHOTODYNAMIC THERAPY

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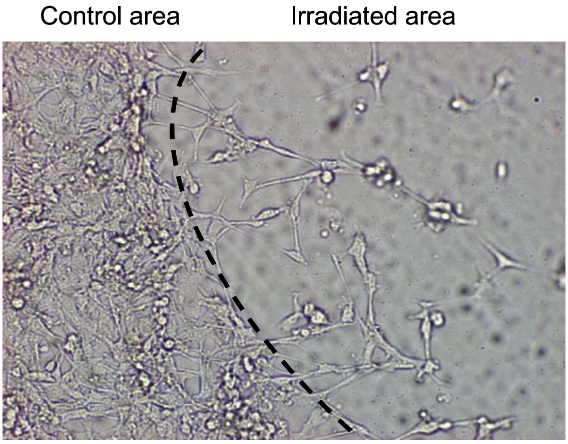
The use of a two-photon excitation offers new perspectives for photodynamic therapy (PDT) of cancer, especially for the treatment of small solid tumors. Actually, the nonlinear dependence of multiphoton absorption on laser intensity leads to very high spatial selectivity, allowing for enhancement of the selectivity of the treatment, and the near infrared light used for the irradiation allows for the treatment of tumors at increased penetration depth.

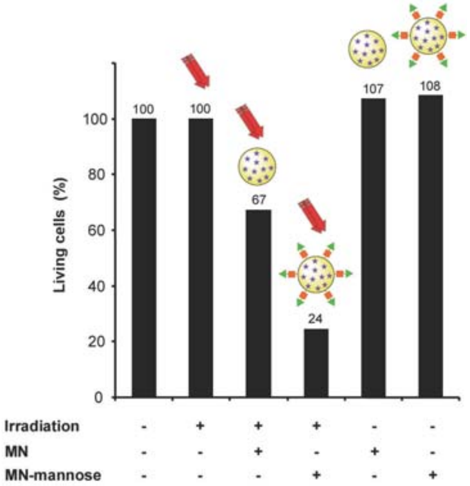
We have developed new organic two-photon photosensitizers [1], combining large two-photon absorption cross-sections in the biological spectral window (σ_2 = 1200-1500 GM), a full transparency in this spectral range, and exhibiting suitable photosensitization efficiency (Φ_Δ = 0.2-0.3) together with significant fluorescence (Φ_F = 0.5-0.6) useful for *in vivo* monitoring.

In order to combine the selectivity of the activation of the two-photon sensitizers with a high affinity for cancer cells, photosensitizers were covalently incorporated within mesoporous silica nanoparticles, the surface of which was post-functionalized with mannose moieties (allowing efficient targeting of lectins over-expressed by cancer cells) [2].

While being non-toxic under day-light illumination, these multifunctional nanoparticles were found to be extremely active in inducing cancer cell death upon short two-photon excitation, as shown by two-photon excited PDT experiments, *in vitro* on human breast and colon cancer cell lines, and *in vivo* on athymic mice bearing tumor xenografts.



Microscope image of human breast cancer cells (MDA-MB-231) incubated for 24 h with multifunctional nanoparticles (MN) and then submitted to two-photon irradiation at 760 nm for 3 sec. Cytotoxicity occurred in the irradiated area only.



Human breast cancer cells (MDA-MB-231) incubated for 4h with multifunctional nanoparticles (20 μg / mL), submitted to two-photon irradiation at 760 nm for 3 sec.

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SERS CHARACTERIZATION OF DECAPEPTIDE NEUROMEDIN B INTERACTION WITH SILVER, GOLD, AND COPPER ELECTRODES

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A subject of fundamental importance in biocatalysis, bioelectrochemistry, construction of biosensors, and biomaterials biocompatibility analysis is the understanding of a bonding phenomenon of peptides to a metal surface [1]. Neuromedin B (NMB) is a bombesin-related peptide composed of ten amino acid residues (H-Gly-Asn-Leu-Trp-Ala-Thr-Gly-His-Phe-Met-NH_2). Small peptides from bombesin family perform important functions in central nervous system and peripheral tissues, including regulation of exocrine and endocrine secretions, cell growth, blood pressure, and glucose level [2]. Recently, it was demonstrated the participation of NMB in the progression of cancer diseases [3]. Analysis of bonding this peptide to metals and its recognition on a picomolar level require a technique, which must be molecular specific and highly sensitive. Surface-enhanced Raman spectroscopy (SERS) fulfill these criteria allowing to elucidate molecular structure of adsorbed species at submonolayer level [4]. In this work we used SERS, electrochemistry, and Generalized Two Dimensional Correlation Analysis methods to define NMB adsorption states on the Ag, Au, and Cu electrode surfaces at different applied electrode potentials.

The orientation of NMB and the adsorption mechanism were determined based on the analysis of relative enhancement, broadening, and shift in wavenumber of particular bands depending on the nature of the electrode and the potential applied. Adsorbed NMB showed bands due to vibrations of the moieties that are in contact or close proximity to the electrode surface, including the Phe and Trp rings, the sulfur atom of Met, the –CCN- and –C=O units of Asn, and His residue. Based on downshift of frequency and broadening of the F12 band (near 1003 cm^{-1}) of Phe, and appearance of soft C-H stretching mode near 2820 cm^{-1} [5] it is demonstrated that the aromatic ring and methylene groups of the amino acid side chains interact or are in contact with Ag electrode surface at sufficiently negative electrode potential. Potential-difference spectrum analysis revealed binding of imidazole ring of His residue to Cu surface at relatively positive studied potentials (Fig 1.).

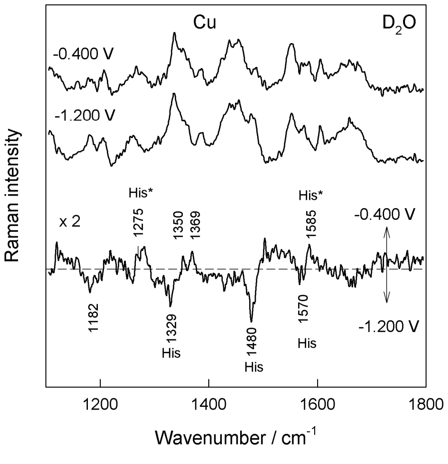

Figure 1. SERS spectra of adsorbed NMB on Cu electrode in 1100-1800 cm^{-1} spectral region at -0.400 and -1.200 V electrode potentials in 0.1 M Na_2SO_4 solution containing 0.01 M phosphate buffer (pH 7.0) and 10^{-5} M NMB in D_2O solvent. Difference spectrum is also shown. His and His* denote the free and bonded to Cu surface His residue bands, respectively. Spectra are normalized according to the F12 band of Phe at 1003 cm^{-1}.

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SENSORIC AND BIOCATALYTIC PROPERTIES OF IMMOBILIZED PHENOLOXIDASES

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The manipulation of nanostructured materials in conjunction with biological molecules has led to the development of a new class of hybrid modified electrodes in which both enhancement of charge transport and biological activity preservation may be obtained. These scientific developments have benefited from experimental techniques capable of manipulating of nanomaterials and biopolymers, enzymes, DNA fragments, or the other biological molecules [1].

In enzymatic devices, efforts have been concentrated on the control over enzyme activity, which is highly dependent on the interface between the nanocomposite and the enzyme. Such control has led to immobilization techniques suitable for anchoring the enzyme close to electrode with preservation of biological activity. In the electrochemical devices, where preservation of the enzyme activity at the nanocomposite/enzyme interface is the key for designing efficient electrodes, charge transfer between enzyme and electrode should be fast and reversible. This charge transfer may be also optimized with some mediating particles being used in conjunction with the biological molecules at the electrode surface .

Several methods for modification of electrodes with protein particles were reported i.e.: layer-by-layer technique, electrodeposition and Langmuir-Blodgett (LB) technique.

Another common method for enzyme immobilization is electrolytic deposition. This method has been extensively used to create immobilized enzyme electrodes with conducting polymers. The forms a monolayer by electrostatical, adsorbing enzyme to a charged surface of polymer.

Continuing systematic investigation in fabrication of protein – conducting material sensitive layers [2], we have reported here the results of research directed into the properties of laccase from *Cerrena unicolor* and tyrosinase from *Agaricus bisporus* integrated to thin films (electropolymer layers). The immobilized phenoloxidases proved to be an excellent ,bioanalytical tool for monitoring phenolic pollutants and as an element of a biofuel cells. Furthermore, the sensor sensitization can be achieved by interlacing to ordered film conducting amphiphiles according to the successful previous experience [3]. Conducting polymers admixed into the film is supposed to be a good mediator element in phenolic oxidases sensor. The interlaced polymer is expected to facilitate the electron transfer as well enhancing the sensor sensitivity.

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INFLUENCE OF THE INTERFACE ON THE SOLID SURFACE COATINGS FORMED BY THE FIBRIL-LIKE ASSEMBLIES OF ALPHA-SYNUCLEIN

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Intentional combination of supramolecular and nanostructured solid arrangements on the surfaces of electronic systems offers highly promising opportunities in creating unique technologies of multicomponent and multifunctional assemblies acceptable for detection of external influences, transfer of signals and a response generation. Advances in the technology of the hybrid materials are still hindered by a lack of detailed understanding about adsorption of supramolecules and multimolecular arrangements (e.g. fibrils) on the solid surfaces. Large biomolecular objects do not simply attach to or detach from the surfaces but are involved in complex phenomena such as re-arrangement, cooperative effects, surface aggregation and so on. There is a huge interest in clearing various aspects of these phenomena. In this work, we studied the solid surface coatings self-arranged from the colloidal solutions containing the fibril-like assemblies of alpha-synuclein (α-syn).

The samples with thin biomolecular films were prepared by a deposition of α-syn fibrils from the colloidal solutions on various solid substrates, namely, mica, Si, CaF_2, KBr. The solutions typically contained the fibrilized α-syn protein (approx. 10–30 mg/mL). The concentration of fibrils was reduced by diluting the initial solution with 100 mM glycine-HCl solution with NaN_3 (0.01%), if necessary. The fixed volume of the solution (from 1 μL to 6 μL) was casted on the clean surface of solid substrates. After the incubation at room temperature in the clean air for 18 h, the samples were washed by distilled water and dried at 30 ºC in an oven with the clean air flow for 2–3 h.

The morphology of the fibrils was studied in the diluted samples prepared on the atomically flat mica surfaces. The samples were investigated by the modes of Scanning Probe Microscopy (SPM) implemented in the Dimension 3100/Nanoscope IVa. Separated fibrils were visualized in these samples (Fig. 1). The fibrils typically were from 300 nm up to 3 μm in length and about 4.2 nm in height. Mechanical properties of the films were investigated by measuring the force-distance curves with a sharp silicon tip (SNL type).

Thinner (200–400 nm) and thicker (700–800 nm) coatings with α-syn fibrils were prepared for spectroscopic studies. These samples were also studied by the SPM. The optical response of hybrid samples was studied in the photon energy range 1–5.5 eV by spectroscopic ellipsometry technique making use of photometric ellipsometer. The ellipsometric data were analyzed by pseudodielectric function approximation (for α-syn/CaF_2) and by multi-layer model (for α-syn/Si). The observed spectra corresponded to those indicated for the secondary and tertiary structure of proteins.

FTIR studies have been carried out by means of a Nicolet 8700 FT-IR spectrometer. Vibration circular dichroism (VCD) spectra were measured in the region 1300–1700 cm^{-1} by using a standard FT-IR Spectrometer VERTEX 70 with PMA 50 module. The results have shown that the fine structure of FTIR spectra depended on the properties of the interface between the film and the substrate and also on the thickness of the thin films. It was also found that the spectral position of components of VCD spectra measured on thick α-syn/CaF_2 film, in which the presence of fibrils were indicated by SPM, corresponded to FTIR spectrum of thin film of on CaF_2 substrate.

The results of experiments were explained by a model of interface formation. It was proposed that the positive charge on the surface of ionic salts substrates interacted electrostatically with the negatively-charged acidic C-terminal of α-syn leading to the formation of ionic bonds. The positively-charged N-terminal of α-syn possessing the α-helix structure is responsible for VCD effect observed in hybrid α-syn/CaF_2 samples. It should be noted that the fine structure of FTIR spectra for α-syn deposited on Si substrate was similar to that for thick films on CaF_2.

Summarizing it can be emphasized that the thin films of α-syn on solid substrates are stable formations, in contrast to α-syn solutions. The structure and physical properties of the hybrid formations depend strongly on the origin of the substrate due to both the individual changes on the surfaces in the liquid surrounding and the specific interfaces produced by the interactions between the solids and the α-syn fibrils.

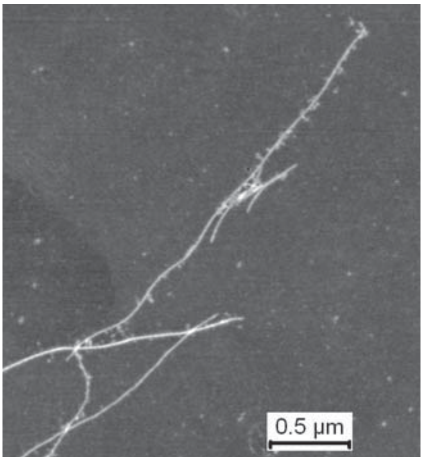

Fig.1. Topography of α-syn fibrils film on mica surface.

MECHANISMS OF PROTON TRANSLOCATION AND CATALYTIC REACTION IN NITRIC OXIDE REDUCTASE: COMPUTATIONAL STUDY

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Under anaerobic conditions some bacteria can use nitrate instead of oxygen in a process called denitrification. A membrane protein nitric oxide reductase (NOR) catalyzes a key step of the denitrification cycle. This enzyme belongs to the superfamily of O2-reducing heme-copper oxidases and is assumed to be the evolutionary ancestor of the proton pump cytochrome c oxidase. In order to get complete understanding of the NOR functioning, one needs to explain the details of the proton transfer mechanism and catalytic reaction at the active site, and the first crystal structures of NOR (cNOR type from *Ps. aerug.* [1] and qNOR type from *G. stearoth.* [2]) provide such opportunity.

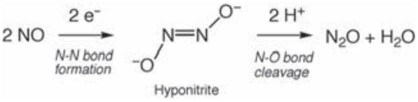
We will present results of the first computational studies of NOR [2-3].

1) Proton transfer mechanism

We have performed simulations of the explicit proton translocation processes by the EVB method [4], and obtained free-energy profiles along different pathways. Among important findings are new proton pathways, which were not predicted from the X-ray structure and could be identified only by means of computer simulations. Simulations also revealed that, despite a high structural similarity between cNOR and qNOR, they utilize strikingly different proton uptake mechanisms.

2) Enzymatic reaction

We have utilized quantum chemistry and QM/MM approaches to describe nitric oxide reduction mechanism at the enzyme's active site. A minimal model for quantum calculations consisted of the binuclear reaction center (Fe of the heme b_3 and Fe_B, a non-heme iron) and its first-shell ligands. We have obtained optimized geometries within the active-site complex and evaluated activation barriers for different intermediate steps. More advanced QM/MM simulations allowed us: (i) to obtain a realistic picture of the catalytic cycle, (ii) to explore important conformational changes in the active site, and (iii) to estimate the effect of the protein environment on catalysis.



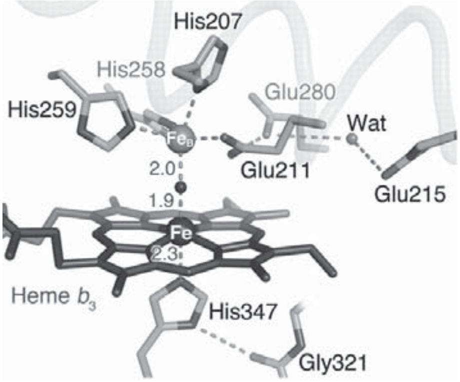


Figure 1. Structure of the active site of cNOR.

Our results provide insights into electronic properties of NOR and into evolution of proton transfer mechanisms in respiratory enzymes.

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SYNERGISTIC CYTOTOXICITY OF VITAMINS C AND K_3 COMPLEX DUE TO EFFICIENT INTERMOLECULAR TRANSFER OF ELECTRONS

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Malignant glioma is the most common primary tumour of the central nervous system and is still an incurable. It usually causes death within two years after conventional therapies [1]. The development of more potent and less toxic compounds represents one of the major goals to overwhelm the poor outcome of patients with glioblastoma. Amongst different alimentary factors, vitamin C and vitamin K_3 (menadione, 2-methyl-1,4-naphthoquinone) have also been considered as possible antitumor agents [2], however, none studies on glioma has been carried out to date. The aim of this work was to study the cytotoxicity of vitamins C and K_3 and their mixture on rat glioma C6 cells *in vitro* and the plausible mechanism of the synergism of their anticancer action.

The cytotoxicity of vitamins C and K_3 alone as well as their mixture was estimated from the reduction of the cell viability. Cell viability was determined by means of a colony-forming assay [3]. Vitamin K_3 killed 50% of cells at the concentration of 7 μM. Treatment of cells by both vitamins at the ratio of 100:1 (VC:VK_3) greatly enhanced their cytotoxicity towards rat glioma C6 cell line. The concentration of vitamin K_3 required to kill 50% of cells was reduced from 7.0 to 1.4 μM, that is, 5 times (Fig. 1A).

It is assumed, that the synergistic anticancer effect of the ascorbate/menadione combination is likely explained by the redox-cycling that occurs between these compounds – vitamin C significantly increases the rate and product yield of the K_3 redox reaction [2]. However, the detailed theoretical analysis of this system has not been done yet. Therefore, the theoretical quantum-chemical analysis of the dynamic electron transfer processes within the complexes containing various forms of vitamins C (*L*-ascorbate, two forms) and K_3 (menadione, one form) has been carried out.

Optimization of the ground state complex geometry was provided by means of *GAUSSIAN03* package using HF/6-311G and HF/6-311G(2df.2pd) basis. Simulation of the intermolecular electron transfer (IET) was done using NUVOLA package [4], in the framework of molecular orbitals (MO) expressed as linear combination of atomic orbitals (AO). Rate of IET *k* was calculated using Fermi Golden rule:

$$k = \frac{2\pi}{\hbar}\left\langle \alpha \middle| \hat{H} \middle| \beta \right\rangle^2 \delta(E_\alpha - E_\beta) \tag{1}$$

Results of simulations allow us to create the model of reaction pathway. Various possibilities have been analyzed and discussed. Optimized structure of the complex is presented in Fig. 1B.

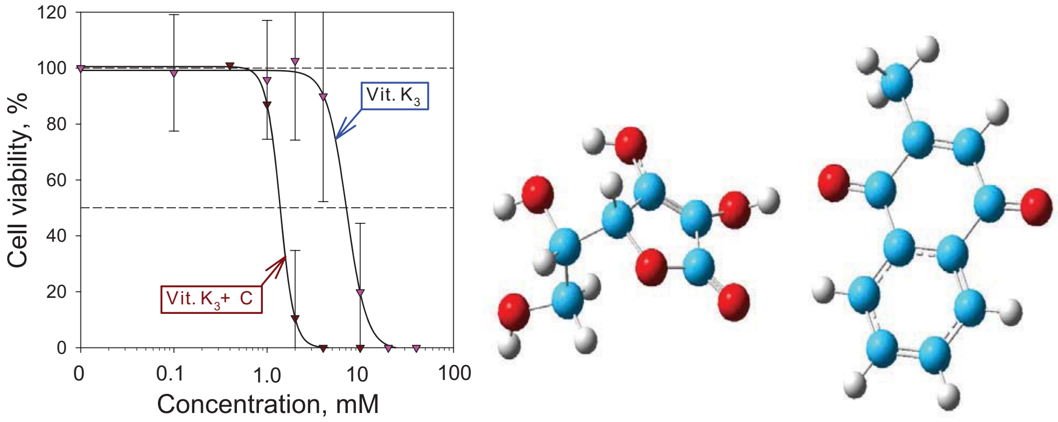

Fig. 1. **(A)** Dependences of the viability of rat glioma C6 cells on the concentration of vitamin K_3 alone and its mixture with vitamin C at the ratio of 1:100. **(B)** Optimized structure of the vitamins C and K_3 complex (carbon atoms are colored in blue, oxygen – red, hydrogen – white).

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LINEAR AND NONLINEAR OPTICAL PROPERTIES OF DNA/RHODAMINE-SILICA THIN FILMS

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The double-helix structure of deoxyribonucleic acid (DNA) exhibits interesting optical and electronic properties that are could be utilized for photonics and electronics applications. The system based on biological molecules[1] often shows superior properties, as compared to conventional organic or inorganic materials. The main goal of this work was the investigation of the linear and nonlinear optical properties of DNA/Rhodamine(Rh)-silica thin films, as they are promising systems for applications including optical waveguides. The films were characterized by UV-Vis spectroscopy, while the and Second- and Third Harmonic Generation Maker fringes techniques have been employed for the determination of the nonlinear optical parameters, as the latter can provide information about the electronic contribution to the nonlinearity[2]. The DNA/Rh-silica thin films were directly synthesized by microemulsion assisted sol–gel dip-coating on glass substrates. The structural characterizations of DNA/Rh-silica materials were done by transmittance and diffuse reflectance UV–VIS measurements. The Second harmonic generation (SHG) and Third harmonic generation (THG) measurements were performed employing a diode pumped passively mode-locked Nd:YVO4 laser working at 1064 nm with 30 ps pulse duration and 10 Hz repetition rate. The samples with DNA showed better transmittance and fluorescence efficiency. The nonlinear optical response was studied versus the concentration of Rh and DNA. The results obtained by NLO will be discussed and compared to reference materials.

Acknowledgement

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EFFECT OF NANOSIZE METAL OVERLAYER ON C_{60} THIN FILM OPTICAL PARAMETERS NEAR FUNDAMENTAL ABSORPTION EDGE

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The perspectives of using C_{60} thin films in optical and electronic devices require the knowledge of the dependence of their optical parameters on the heterostructures composition (substrate and overlayer), conditions of their manufacturing operation or modified treatments. The optical absorption band gap of C_{60} films was shown to depend [1] on their degree of crystallinity that in turn can be dependent both on the deposition conditions and on the internal mechanical stresses [2] in heterostructures.

In this work, we investigate the effect of nanosize metal overlayer, both evaporated on C_{60} films (Bi, In) and attached as nanoparticles of Ag [3] or Au [4], on the optical parameters of C_{60} films near the fundamental absorption edge. The values of direct band gap (E_g), the optical gap (E_o) in the framework of Tauc model and the Urbach tail parameter (Eu) were determined from the absorption coefficient (α) spectra plotted in coordinates $(\alpha h\nu)2$, $(\alpha h\nu)1/2$, $\ln\alpha$ vs $h\nu$, respectively. The C_{60} films of thicknesses from 100 to 500 nm were deposited on Si or SiO_2/Si substrates by vacuum thermal evaporation without heating substrates. The C_{60} film thickness value and spectra of its effective optical parameters (refractive index *n* and extinction coefficient *k*, used for the calculation of α) were determined from the reflectance spectra, measured in the wavelengths range of λ=400-1100 nm at variable angles of incidence of p- and s-polarized light.

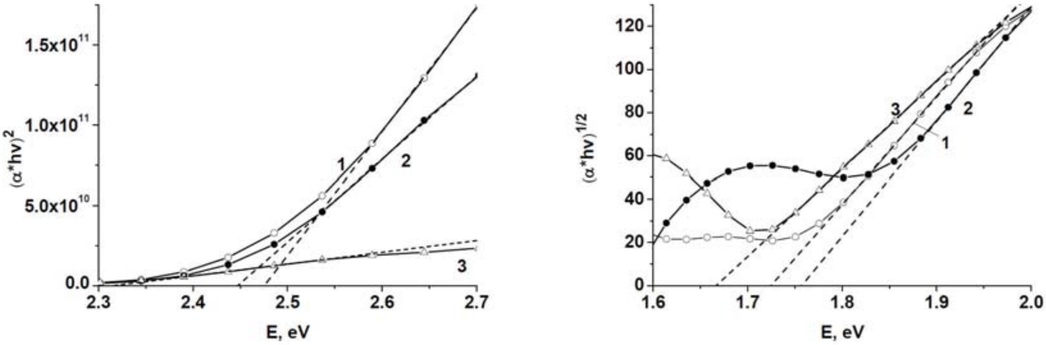

Figure 1. Spectra of the light absorption coefficients α in coordinates $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ vs $h\nu$ for C_{60}-Bi films with the thicknesses, nm: 499 (1), 283 (2) and 242 (3).

The decrease of the near-edge optical absorption parameters of C_{60} films, deposited on thermally oxidized Si substrate, was observed in the case of nanosize (≤1 nm) metal overlayer. Specifically, E_g=2.32±0.02 eV was obtained for C_{60} layer thickness of ~240 nm (Bi) or ~260 nm (In) with respect to E_g=2.44±0.03 eV for the films with greater ratios of C_{60} to metal layer thicknesses. Simultaneous decrease of E_o from (1.75±0.04) eV to 1.67 eV was observed for C_{60}-Bi film. For C_{60}/Si structures with C_{60} films, modified with 1.8-diaminooctane or 1.8-dithioloctane, with thickness of ~100nm, the decrease of all optical parameters (E_g, E_o, E_u) was found after deposition of Ag or Au nanoparticles, respectively.

Thus, the found effect of nanosize metal overlayer on optical parameters of C_{60} thin films near the fundamental absorption edge testifies diminishing the structural disorder in C_{60} films, apparently caused by internal mechanical stressed in heterostructure.

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FORMATION OF AU-NANOPARTICLES IN LC PPI DENDRIMERS

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Poly(propylene imine) (PPI) dendrimers of various generations (G1-G5) conjugated with liquid crystalline (LC) entities have shown a potential to generate different size Au nanoparticles. Synthesis of different generation (G1-G5) dendrimers was described in [1]. The complexes of Au nanoparticles with dendrimers were prepared by using a standard method [2]. Both solution and thin films of the present hybrid systems were investigated. The localized surface plasmon resonance (LSPR) band [3] of Au nanoparticles has been observed by optical absorption in the visible spectral region from 520 to 550 nm. A red shift of LSPR band maximum was observed with increasing the particle size. The size and size distribution of gold nanoparticles in different PPI dendrimer generations were directly determined from TEM measurements. Therefore, passing from higher to lower dendrimer generations, the size of Au nanoparticles could be varied from 5 to 75 nm, respectively. TEM studies (Fig. 1) confirmed that the size and size distribution of Au-nanoparticles depended on the dendrimer generation indicating different formation mechanism controlled via the interaction with PPI core and/or the LC entities on the dendrimer surface [4].

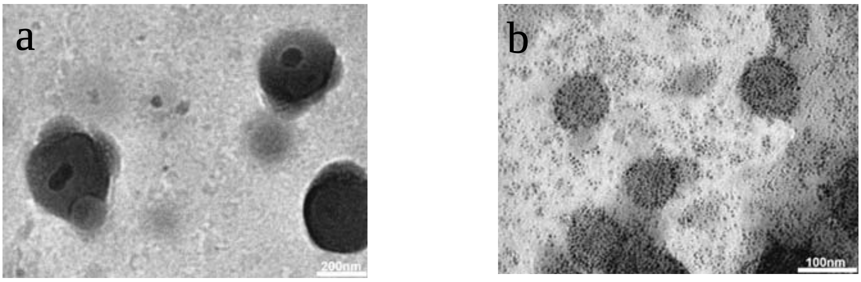

Figure 1. TEM micrographs of two generations G3 (a) and G5 (b) of poly(propylene imine) dendrimers with gold nanoparticles.

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STUDY OF BOVINE LEUKEMIA VIRUS ANTIGEN GROWTH KINETICS BY TOTAL INTERNAL REFLECTION ELLIPSOMETRY

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Proper-immobilization of antibody on solid-liquid interfaces plays an important role in the development of immunosensors [1]. Total internal reflection ellipsometry (TIRE) [2] gives new possibilities to obtain the antibody binging rates by investigation of ellipsometric parameters ($\Psi(t)$ and $\Delta(t)$) changes in time. Usually, the analysis of antibody layer grow kinetics is performed using modeling based on Langmuir equation assuming that refractive index or thickness of the layer is constant. These assumptions require additional evidence which can be obtained from analysis of Ψ and Δ diagrams [3].

In this work TIRE was used for study of Bovine leukemia virus antigen gp51 (BLV) grow kinetics on biological recognition layers made from intact- and fragmented-antibodies. Two differently prepared biological recognition layers formed on gold substrate were studied: first layer was based on intact-antibodies (intact-Ab), second layer was based on chemically fragmented specific antibodies (frag-Ab), which were obtained by reduction of intact-Ab.

In order to make the sample “Au$_1$” the frag-Ab (0.44 mg/ml) was dissolved in the PBS (pH 7.4) and injected into the cell with fixed Bk7 glass substrate plated by thin Au layer. After that the antibody solution was injected. This solution was prepared by mixing of 0.1 M 2-mercaptoethanol solution and 0.01 M PBS (pH 7.4). The mixture was incubated at 37ºC temperature for 90 minutes. The 2-mercaptoethanol reduces disulfide bridges in the hinge region of the antibody molecule which holds two heavy chains together and from one immunoglobulin molecule (H-L)$_2$ two reduced antibody fragments (H-L) were formed. The sample “Au$_2$” was prepared in the following way: self-assembled monolayer of 11-mercaptoundecanoic acid molecules was formed on the surface of Au deposited over the Bk7 glass substrate. For covalent immobilization of intact-antibodies, activation of the self assembled monolayer (SAM) using a mixture of 0.1 M of EDC and NHS in water was performed. During this procedure functionally active NHS esters were obtained by the reaction of MUA carboxyl groups with a mixture of EDC and NHS.

Analyte detection was performed by the injection of bovine leukemia virus antigen *gp*51 solution (c = 0.5 mg/ml). Due to immobilized antibody interaction with antigen *gp*51 and formation of corresponding complex changes in refractive index of protein-based layer were registered. These changes were evaluated as an influence of additionally formed “antigen layer”. Antibody-antigen interaction kinetics was measured from changes of ellipsometric parameters Ψ and Δ *vs.* time at fixed wavelength λ=670nm. The results were analyzed using the association and dissociation process described by Langmuir equation assuming that: i) biosensor surface contains two types of association centers (traps), ii) first type consist of traps with low association binding force, iii) the second type consist of traps with high association binding force. Typical for first type was that antigen molecular can be trapped or dissociated from the traps. In case of second type traps the antigen molecular can be only trapped and cannot left the trap.

In order to calculate the kinetic parameters of association ($k_a \cdot c$) and dissociation (k_d), here c is volume density of antigen in buffer solution, the relation between ellipsometric parameter Ψ and Δ was obtained using effective media approach, assuming that refractive index of antigen monolayer is directly proportional to Ψ and Δ value. It was obtained that in case of intact-Ab monolayer the $k_{a1} \cdot c$ and k_{d1} of first type of traps were 1.26×10^{-3} s^{-1} and 7.8×10^{-2} s^{-1} respectively. For second type of the traps of this monolayer the $k_{a2} \cdot c$ was 3.7×10^{-4}. In case of frag-Ab these parameters were $k_{a1} \cdot c = 5 \times 10^{-4}$ s^{-1}, $k_{d1} = 2 \times 10^{-2}$ s^{-1} and $k_{a2} \cdot c = 8 \times 10^{-5}$ s^{-1} respectively. Additionally the Δ *vs.* Ψ diagrams was used in order to estimate the validity of the model.

It was concluded that TIRE enables to resolve differences in nanostructures of intact-Ab and frag-Ab layers and analytical sensitivity of the Δ parameter of TIRE is 3 times better in case of frag-Ab in comparison to the intact-Ab. Analysis of Δ *vs.* Ψ diagrams gives more information about kinetic processes of proteins in comparison with conventional surface plasmon resonance biosensors.

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p-PHENYLENEDIACETONITRILE NANOPARTICLES WITH FLUORESCENCE TURN-ON

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Low dimensionality accompanied with the fascinating optical, electronic, chemical and mechanical properties, different from those of isolated molecules or bulk material, enabled organic nanoparticles to penetrate the application areas of photovoltaics, light-emitting devices, field-effect transistors, biological and fluorescent labels, photocatalysis, bio- and chemo-sensors [1]. Fluorescent organic nanoparticles (FONs), are particularly attractive for OLED, labeling and sensing applications due to their high brightness and long-term stability. Formation of FONs involves a certain type of molecules exhibiting an unusual fluorescence turn-on in the aggregated form, so called aggregation-induced emission (AIE) phenomenon. The fluorescence turn-on in the aggregated phase is very unusual, since commonly, intermolecular coupling enhances nonradiative deactivation resulting in severe emission quenching. However, driven by the specific molecular packing along with the restricted intramolecular torsional motions, AIE enhancement of several orders in magnitude is possible [2].

In this work, formation of novel *p*-phenylenediacetonitrile-based FONs (see Figure 1) in aqueous solution by reprecipitation method is presented.

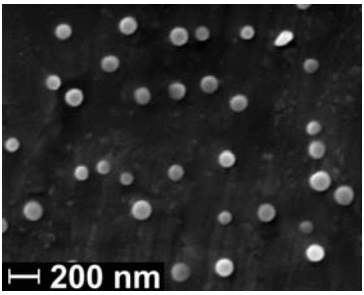

Figure 1. Field emission scanning electron microscopy image of the *p*-phenylenediacetonitrile-based FONs casted on aluminum substrate.

Nitrile groups have been intentionally introduced into the backbone of phenylenediacetonitrile compounds to induce twisted molecular conformations in the isolated state by the groups induced steric hindrance [3,4]. Moreover, incorporation of nitrile groups efficiently suppressed concentration quenching of emission in the compounds [4]. For the formation of FONs the derivatives were designed to have identical *p*-phenylenediacetonitrile-based core yet different end-groups. Very different in size and polarity, phenyl and hexyl-carbazolyl end-groups allowed evaluating influence of their bulkiness/polarity on the formation of FONs and on their properties. Optical and morphological properties of the FONs, tunability of their sizes and relation with their constituting molecular structures were thoroughly evaluated by utilizing dynamic light scattering and a number of microscopy and spectroscopy techniques including scanning electron microscopy, confocal fluorescence microscopy, absorption and fluorescence spectroscopy, fluorescence lifetime and fluorescence quantum efficiency evaluation techniques. Finally, the application of the phenylenediacetonitrile FONs for sensing of organic vapors via fluorescence “on/off” switching was demonstrated.

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STUDY OF VIBRATIONAL RELAXATION AND SOLVATATION IN ACETONITRILE DISSOLVED IN IONIC AND ORGANIC LIQUIDS USING VIBRATIONAL AND 2D CORRELATION SPECTROSCOPY

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Acetonitrile molecules were mixed with ionic liquid (Ethyl-dimethyl-propylammonium bis (trifluoromethylsulfonyl) imide and others) at the rate of 1 to 5, and the different IR spectra when changing the temperature were observed. From the IR spectra the different spectral parameters were calculated and compared to those in the publications.

Only one of the spectral acetonitrile bands was observed (ν_{2253}), due to the insufficient concentration of AN in the ionic liquid, because of that, the ν_{920} band was not visible (Fig. 1.). The other band, ν_{2249}, which corresponds to CN vibrations of acetonitrile molecule, was observed, and examined using theoretical calculations from different publications [1, 2], and later on – using an innovative method – 2D correlation spectroscopy. This method showed that the acetonitrile band ν_{2249} was composed of three peaks.

The variation of half-widths, relaxations times and integral intensities depending on temperature was examined. Relaxation times at higher temperatures have decreased. The results imply that the acetonitrile molecule release its energy faster when in ionic liquid.

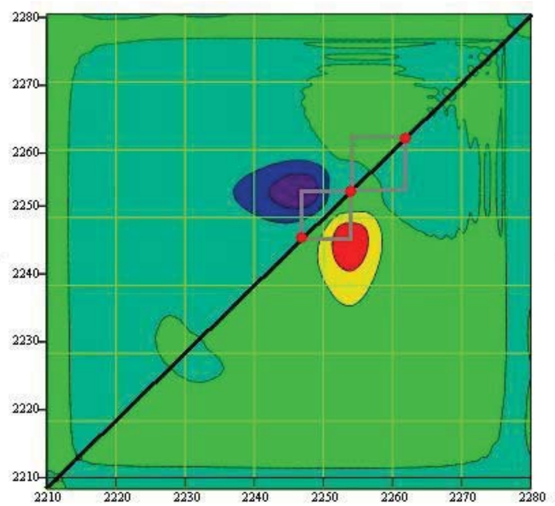

Fig. 1. Two dimensional FTIR asynchronous spectrum of Acetonitrile/Ethyl-dimethyl-propylammonium bis (trifluoromethylsulfonyl) imide solution in the region of v_{2253} band.

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ULTRAFAST DYNAMICS OF PHOTOCHROMIC SWITCHES BASED ON OXAZINE RING OPENING

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Synthesized over two decades ago [1], and re-introduced into scientific community recently[2, 3], photochromic compounds based on oxazine ring opening are attractive because of their high switching speeds and good stability and possibility of modifying their colouring properties via the introduction of additional side groups around the active centre of the molecule.

In this study, we present investigations of the ultrafast dynamics of a series of indolo-benzoxazine photochromic switches. Despite the fact that their different chemical structures result in different spectra of the ring-open form, their picosecond kinetics exhibit remarkable similarities. Immediately after the excitation, induced absorption is formed covering almost entire visible and near-UV range. Within 10 ps, the signal diminishes and thereafter increases again forming the final spectrum that subsequently decays back to the ground state (see Fig. 1). In cases of some compounds, initial spectrum strongly resembles the final one, with an intermediate low-absorbing state. The dynamics of model compounds (constituent parts of the photoswitch molecule) is also presented, trying to attribute specific spectrotemporal changes to the separate parts of the compound. The spectral change due to photoexcitation is compared with chemical opening of oxazine ring using strong base or acid.

We try to tackle several issues of this peculiar dynamics:

- When exactly is the excited state lost in the photoinduced transformation of the molecule?
- Why is there strong resemblance between the initial and final photoinduced spectrum?
- Why is the chemically opened molecular forms different from the ones formed by the photoexcitation?
- What governs the switching speeds and spectral properties of different compounds?

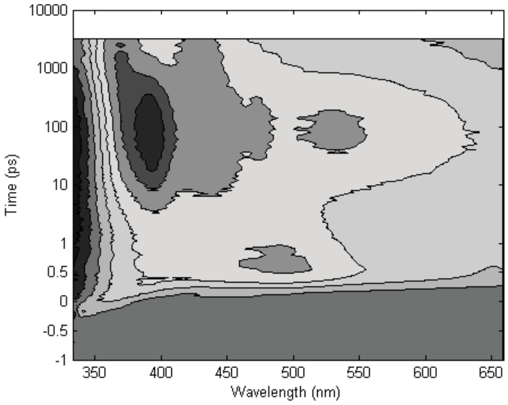

Figure 1. Femtosecond pump-probe data measured on the standard indolo-benzoxazine photoswitch [4].

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THE PHOTOCHROMISM OF BENZOINDOLO-BENZOXAZINES

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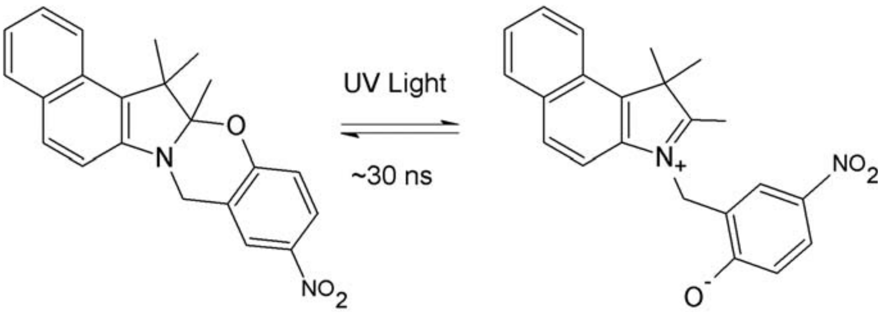
A recently discovered class of indolo-benzoxazine (IB) photochromic compounds is attractive due to their fast switching times and excellent fatigue resistance [1]. Furthermore, many structural modifications of the basic IB compound retain these features [2, 3] thereby enabling a functional engineering approach (design of compounds with desired absorption, fluorescence properties or featuring special sensitivity to the environment) on a molecular scale. However, little is still known about the photophysics of the IB photochromic reaction and the governing mechanisms of the various photochromic parameters. This knowledge is required as a guidance for more efficient and productive molecular engineering work.

In this study, we present a spectroscopic investigation of five new IB compounds in the nanosecond domain. The selected compounds differ only slightly one from the other and from the basic and, therefore, reference IB compound [1, 4], allowing us observe the relative spectrotemporal differences caused by the incremental addition of benzene-derived groups to the reference IB compound. To characterize these differences we performed flash-photolysis experiments on these compounds dissolved in acetonitrile and methanol and recorded steady-state spectra of organic acid/base-induced forms of the molecules. Interestingly, one particular modification (the substitution of the indole fragment with benzoindole) has a much more profound effect on the photo- and solvatochromic action of the resulting compound, while other similar modifications alter the recorded dynamics only slightly. Furthermore, the benzoindole substituted compounds featured transient spectra, which could not be decomposed to a superposition of the chemically induced form spectra, in contrast to a broad range of other IB derivatives [2, 3]. These observations suggest a non-equal role of the constituent molecular fragments to the photochromic properties of the entire molecule.



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DEVICES

POLYMER ELECTROPHOSPHORESCENT COMPOSITES FOR DEVICES WITH WHITE LIGHT EMISSION

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The polymer phosphorescence composites are the most promising candidates for application in the light emitting diodes (LEDs) [1] and recently they are also used in new type devices like organic light emitting field effect transistors (OLEFETs) [2]. For preparation of the polymer electrophosphorescent composites the blend concept of a low-molecular weight phosphorescent emitter with a proper polymer matrice is usually applied. Transfer of excited state energy thus plays an important role in the operation of such devices. Singlet and triplet excitons can be first generated by electron-hole recombination in the polymer host and then transfer their energy to the dopant. The triplet state of the phosphorescent emitter may be also formed by charge recombination at the guest molecule. In both cases, the singlet and the triplet energy levels of the host have to be well above the triplet state of the guest emitter to be efficient and prevent back transfer. Among phosphorescent dyes, iridium complexes are extensively used in electrophosphorescent devices due to their relatively short triplet lifetimes and high quantum efficiency of light emission [3]. The devices with emission layer obtained by using the guest-host systems based on polymer with large HOMO-LUMO separation allow getting selective emission from visible light range as well as white light [1,4].

In this study the composites based on polymer matrice-poly(N-vinylcarbazole) (PVK) with 40 wt. % content of 2-(4-tert-butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole (PBD) were used as the emissive layers in polymer light emitting diodes (PLEDs) for the white light emission. The iridium (III) bis(2-(2’-benzothienyl)pyridinatoN,$C^{3'}$) (acetyl-acetonate) (Btp$_2$Ir(acac)) and iridium (III) bis(2-(4,6-difluorephenyl)pyridinato-N,$C^{2'}$) (FIrpic) have been used as a phosphorescent dopants with a total content of 3 wt. % which were homogeneously dispersed in PVK/PBD matrice. Excitation energy of the matrice is transferred to Btp$_2$Ir(acac) and FIrpic which act as an efficient radiative recombination centres, giving respectively red and bluish green light emission. Analysis of photoluminescence spectra indicates the possibility of the obtaining white light emission from the investigated composites through optimizing the relative rate of Btp$_2$Ir(acac) and FIrpic.

The electroluminescence spectra (EL) of the prepared PLEDs confirm that the relative fractions of dopants influence on the colour of emitted light. The CIE 1931 colour coordinates (0.35, 0.38) for the relative weight rate between Btp$_2$Ir(acac) and FIrpic at the level of 1:4 correspond to "warm" white light. The unequal contribution of emission bands in the EL spectra corresponding to dopants is associated mainly with the presence of competing trapping states located at dopant molecules. The Btp$_2$Ir(acac) introduces a deeper traps into PVK/PBD matrice for holes than FIrpic [1,5].

Acknowledgements
This work was partially supported by grants N N507 399939 of Polish Ministry of Science and Higher Education and NoE *FlexNet* UE ICT 247745 (7FP).

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ELECTRONIC AND THERMAL PROPERTIES OF LOW BAND-GAP COPOLYMERS OF TRIARYLAMINE AND NAPHTALENEDIIMIDE

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Derivatives of naphtalenediimide and perylenediimide are studied as n-type organic semiconductors, mostly as acceptors in bulk-heterojunction solar cells [1] and active layers of n-channel organic field-effect transistors [2]. For some applications it seems desirable to obtain a semiconducting material that is capable of transporting both electrons and holes efficiently (ambipolar charge transport) [3].

For this end, we prepared three novel compounds, that is, two polymers: poly(AZ-NI)-I and poly(AZ-NI)-II and one model compound: AZ-NI, consisting of electron-donating triarylamine and electron-accepting naphthalene diimide moieties connected by eletron-rich imine linkages . The materials were obtained via condensation of a naphtalenediimide-containing diamine and 4-formyltriphenylamine, 4,4’-diformyltriphenylamine and 4,4’,4”-triformyltriphenylamine, respectively. The structures of the compounds have been confirmed by IR and ^{1}H-NMR as well as elemental analysis. Optical properties of the AZ-NIs in solution and as blends with PMMA were studied by UV-Vis and photoluminescence spectroscopy. The UV-Vis absorption spectra consisted of overlapping naphtalenediimide and triarylamine absorption bands and no solvatochromism was observed. Upon excitation, the model compound AZ-NI emitted green light, whereas poly(AZ-NI)-I and poly(AZ-NI)-II emitted blue light. There was no overlap between the emission and absorption spectra and the calculated Stokes shifts were quite large, suggesting that the excited-state conformations are significantly different than that of the ground states.

Electrochemical properties of the compounds were investigated by means of cyclic voltammetry, differential pulse voltammetry and UV-Vis spectroelectrochemistry. The reduction profiles of the three materials were very similar and typical of naphtalenediimides, while the oxidation onset of the polymers was significantly lower than that of the monomeric AZ-NI. Preliminary current-voltage measurements were carried out on devices having the following architecture: ITO/organic layer/Al, where the organic layer was AZ-NI, poly(AZ-NI)-I or poly(AZ-NI)-II, respectively. The current values and turn-on voltages were found to depend strongly on the kind of the organic layer, but in each case the turn-on voltage was significantly lower than 1 V.

Additionally, thermal properties of the compounds were studied using TGA. The onset of thermal decomposition of the polymers was as high as 350°C. Thermal degradation kinetics was analyzed using of Coats-Redfen equation.

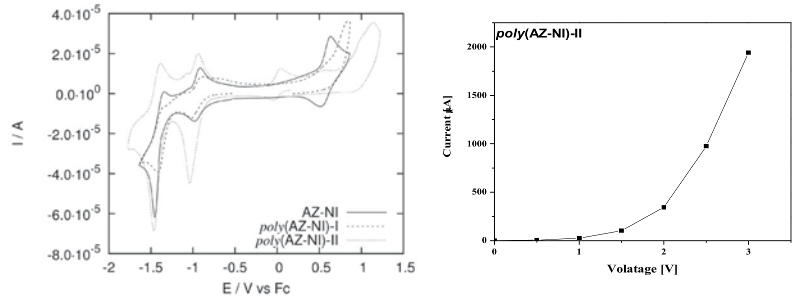

Figure 1. Cyclic voltammograms of thin films of the studied materials (left) and I-V curve of the device ITO/*poly*(AZ-NI)-II/Al .

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ULTRAFAST HOLE TRANSFER DYNAMICS IN POLYMER:FULLERENE BLENDS

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Current state-of-the-art organic photovoltaic devices are based on polymer:fullerene bulk heterojunctions [1]. Absorption of sunlight in conventional polymer:[60]PCBM blends occurs primarily by the polymer with a subsequent electron transfer to the fullerene. However, with the recent introduction of [70]PCBM fullerene the role of the absorption by the fullerene itself also became substantial. The creation of an exciton on the PCBM molecule is followed by its dissociation into potentially useful charges through the so-called hole-transfer (HT) process. Despite their obvious fundamental importance and practical interest to solar cell design, HT dynamics have received surprisingly little attention so far [2].

We investigate the ultrafast hole transfer from [70]PCBM to different polymers in polymer: [70]PCBM blends through visible pump – IR probe spectroscopy using selective [70]PCBM excitation, while probing the presence of charges through detection of the the low-energy polymer polaron band at 3 □m. Tuning the fullerene concentration allows us to vary the fullerene contribution to the overall absorption efficiency, and address the morphology issue.

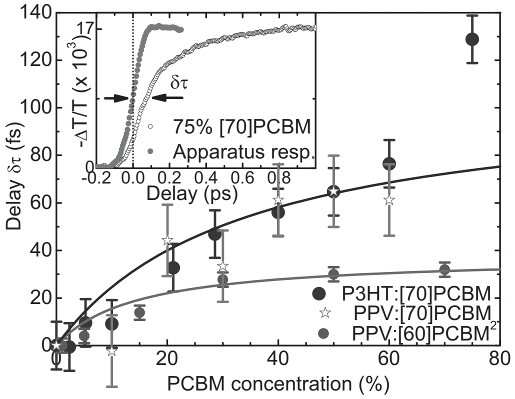

Figure 1. Hole transfer delay as a function of PCBM content in different polymer-fullerene blends. The inset shows an example of the photoinduced absorption transient from which the delay is inferred.

We found that in the P3HT:[70]PCBM blends, the hole transfer time is noticeably longer than in MDMO-PPV:[60]PCBM blends (Fig.1). Also, in all blends the charge generation efficiency at the ultrafast time scale sharply decreases with the increase of fullerene concentration. which indicates a limited exciton diffusion length in the fullerene domain.

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CHARGE TRANSFER FROM CONTACTS TO POLYMER/FULLERENE BLEND IN P3HT:PCBM DEVICES

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We report dark CELIV measurements on P3HT:PCBM solar cell devices with differing metals as contact materials. Extraction of charges without any light excitation indicates a significant amount of charges being transferred from the metal contacts into the polymer/fullerene blend.

We have observed dark extraction of charges on the order of 10^{16} cm^{-3} in P3HT:PCBM solar cell devices. In order to clarify the origin of these charges we have performed dark CELIV (double pulse CELIV) on electron-dominated and hole-dominated devices. The same contact material has been used as both top and bottom contact in order to minimize the built in field. A dark CELIV measurement of a P3HT:PCBM device with aluminum as both bottom and top contact is shown in figure 1.

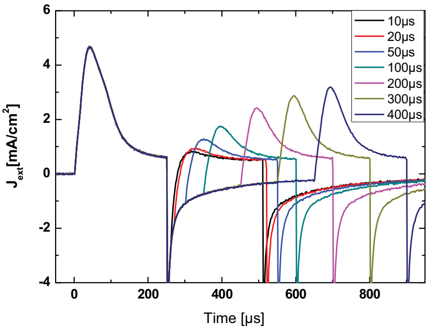

Figure 1. Dark CELIV measurement of a P3HT:PCBM device with aluminum contacts.

It can be seen that the regeneration of charges in the device corresponds with a current backflow into the device. We interpret this as a charge transfer from the contacts to the active layer due to Fermi level alignment in accordance with the Integer Charge Transfer model [1]. Our results indicate that charge transfer occurs both from gold contacts to P3HT and from aluminum contacts to PCBM.

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EFFECT OF SUBSTITUTES TO PHTHALOCYANINE MOLECULES ON THE PROPERTIES OF THEIR FILMS AND HETEROSTRUCTURES

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In spite of significant achievements in the increasing of efficiency of organic solar cells (OSC), nowadays, the synthesis and technology for new dyes have been intensively developed, since the technology of OSC fabrication on the basis of soluble C60 derivatives is expensive.

Therefore the aim of this paper is development of the basis for fabrication technology of cheep organic heterostructures on the basis of phthalocyanine derivatives, the study of their optical and photovoltaic properties and estimation the possibility of usage of these structures for OSC fabrication.

Optical and photovoltaic properties of three phthalocyanine derivatives: ZnPc(Sulfonamide)$_{1\text{-}2}$ (ZPS), ZnPc(NH$_2$)$_4$ (ZPN), H$_2$Pc(NH$_2$)$_4$, (HPN) and their heterostructures with organic semiconductors films: N, N`-dimethyl perylene-tetracarboxylic acid diimide (MPP), pentacene (Pn), and lead phthalocyanine (PbPc) have been studied. ZPS films were deposited from their solution in chloroform, ZPN films from their solution in dimethylformamide (DMFA) and H$_2$Pc(NH$_2$)$_4$ from aqua solution with NaOH by means of sprinkling and/or spin coating. Organic semiconductor films were deposited by vacuum evaporation at the substrate temperature 370K. These heterostructures were deposited on the glass substrates with and without transparent conductive ITO layer.

It was established that bonding of sulfonamide groups (tails) to phthalocyanine molecules does not effect almost the absorption spectra (AS) in chloroform solution, i.e. AS ZPS are typical for organic dyes with weak intermolecular interaction (for example ZnPc and their derivatives with tert-Butyl substitutes) but significantly increases ZnPc solubility in volatile organic solvents. This allowed to obtain the uniform films by deposition from the solution. On the contrary the NH$_2$ groups bonding does not lead to the increasing of solubility in organic solvents. AS of its solution and films show additional absorption in the long wave range relative to AS of ZPS and broader bands. This can be explained by the fact that (NH$_2$)$_4$ bonding significantly increases the aggregates creation (coagulation efficiency) and this leads to colloidal solution formation even at the small concentration of these dyes. Compared to the intermolecular interaction in ZPS an additional interaction between molecules appears in aggregates and this is the reason of bands broadening.

In addition sulfonamide groups bonding to ZnPc molecules influences a little the efficiency of charge carriers photogeneration in ZPS films. The bonding of (NH$_2$)$_4$ groups to ZnPc and H$_2$Pc molecules decreases the photovoltaic sensitivity more then one order of magnitude (in 50 times in the range of high absorption) compared to ZPS films. As a consequence the photovoltaic sensitivity of the films of these phthalocyanine derivatives decreases in the line ZPS→ZPN→HPN (at the illumination of the free surface of studied films as well as their interface with ITO).

A significant potential barrier arises on the interface between evaporated in vacuum organic semiconductors films and deposited earlier films of studied phthalocyanine derivatives during heterostructures preparation. This leads to the significant increasing of the photovoltaic photosensitivity of these heterostructures compared to the films of phthalocyanine derivatives as a result of the increasing of photogenerated charge carrier separation efficiency in the built in electric field of this barrier.

The highest photovoltaic sensitivity was observed in the heterostructures made of pentacene films but the widest spectral range of the photosensitivity in the structures with the films of lead phthalocyanine, which is probably more important for the solar cells.

The authors are thankful to prof. S. Nespurek for purified phthalocyanine derivatives and useful advices.

EFFICIENT BILAYER ELECTRODES FOR PHOTOSENSITIVE ORGANIC HETEROSTRUCTURE AND SOLAR CELLS

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At the present time the processes on the intrerface between photovoltaically active layer and electrodes are studied not enough though they substantially influence the stability, series resistance, excitons and charge carriers recombination rate, and therefore on the efficiency of organic solar cells. It is difficult to obtain simultaneously good adhesion, stability, low recombination rate and desired potential barrier height with using anode and cathode made only from the same material. Thus, ITO electrodes have a good adhesion to glass and quarts substrates, they are stable but on the interface between photosensitive organic semiconductors (OS) and the electrode the significant concentration of uncontrollable impurities is formed which work as the traps for excitons and charge carriers. On the other hand the frequently used layers of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) complex (PEDOT:PSS) and CuI have bad adhesion to glass substrates but good adhesion to layers of ITO. Based on the zone diagrams of OS one can expect the formation of good barrier contacts with n-type OS and good Ohmic contacts with p-type OS. Therefore, the aim of the paper is searching the ways of using bilayer electrodes for the photosensitivity increase of their heterostructures with photosensitive organic semiconductors.

The possibility of increasing the photosensitivity of organic heterostructures by using the bilayer transparent electrodes of ITO both with organic conducting polymer PEDOT:PSS and CuI has been verified experimentally. Photosensitive *n*-type OS – N,N`-dimethyl-3,4,9,10-perylenetetracarboxylic acid diimide (MPP) was chosen as a component of these heterostructures.

It has been established that the usage of ITO/PEDOT:PSS bilayer electrodes leads to the increasing of photovoltaic sensitivity of these heterostructures by 2-3 orders and by 1-2 orders when using CuI. Comparison of the spectral dependencies of the structures with and without intermediate layer of PEDOT:PSS shows that the reasons are decreasing excitons and charge carriers recombination and increasing the potential barrier heights on the interface between MPP and layers of PEDOT:PSS and CuI. In addition, the photovoltaic sensitivity increases stronger in the case of the charge transfer (CT) excitons excitation than in the case of Frenkel excitons that can be caused by more effective CT excitons separation (opposite to Frenkel excitons) in the built-in electric field near to the PEDOT:PSS/MPP interface.

Preliminary study of another structures shows that increasing the photovoltaic sensitivity is observed also in the structures of ITO/PEDOT:PSS/Pentacene and ITO/polyaniline:PSS/MPP. The value of the increase depends on the material of the intermediate layer and OS.

Thus, the usage of bilayer transparent in the visible spectral range electrodes (ITO/PEDOT:PSS and ITO/CuI) allows to optimize not only the homogeneity and electrodes work function but also to increase the photovoltaic sensitivity of their heterostructures with the organic semiconductors as a result of excitons recombination decreasing on the interface and changes of the potential barrier height. The largest increase of the photovoltage has been observed in ITO/ PEDOT:PSS /MPP structures during CT excitons excitation.

KINETIC STUDIES OF PHOTOSWITCHABLE GATE INSULATOR IN OFETS

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Bistable photochromic systems have become of key interest for application in organic electronics, particularly in organic field effect transistors (OFETs) [1,2]. A possible realization of a light-driven OFET consists in a photochromic material admixed to the OFET gate insulator. Fabrication of such structures has already been reported [3-5]. The reversible light-driven switching of source-drain current in such devices has been attributed to altering the electric permittivity of the dielectric layer due to changes of dipole moment of photochromic molecules dissolved in the bulk of the layer. Furthermore, dipoles present on the semiconductor-insulator interface can additionally affect the performance of the switch [3,5]. A confirmation of the mechanisms put forward above would come from a direct comparison of the optical absorption, electric permittivity and current-voltage characteristics and the temporal behavior of these parameters during exposition to light triggering the photochromic reaction.

In the present communication we report on kinetic studies of OFETs in which photochromic spiropyran (SP) was added to the gate insulator (PMMA). An n-type perylene derivative (P13) was used as the semiconductor. The reference sample (capacitor) for dielectric measurements was an OFET structure without P13 (Figure 1).

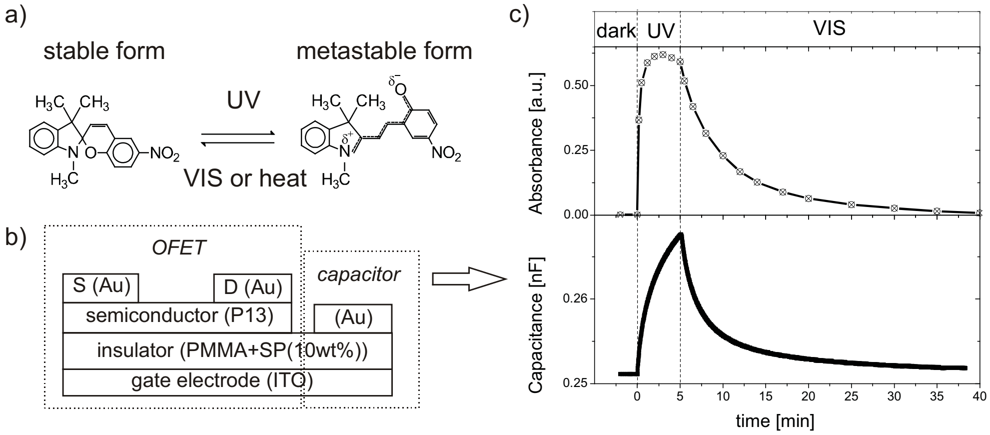

Fig. 1 (a) The photochromic reaction of SP; (b) A scheme of OFET and the capacitor formed between gate and source (S) and drain (D) electrodes without P13. (c) Temporal evolution of absorption at 580 nm and of capacitance, measured in a PMMA+SP(10wt%) layer under UV and visible (VIS) illumination.

The rates of absorption and capacitance changes, under UV and visible light, were evaluated. At short illumination times (< 150s), the respective rate constants are similar thus indicating that the capacitance changes are related to the photochromic process. A longer illumination, however, results in a slow decay of the absorption, while capacitance of the structure continues to rise. Processes responsible for such temporal dependencies will be discussed in the contribution.

Acknowledgements: This work was supported by the European Commission through the Human Potential Programme (Marie-Curie RTN BIMORE, Grant No. MRTN-CT-2006-035859) and by the Wrocław University of Technology.

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ELECTRICAL PROPERTIES OF P3HT:CDSE NANOCOMPOSITE

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Recently, a large number of reports has been dedicated to development of hybrid materials made of nanoparticles (NPs) embedded into a matrix, commonly a polymeric one [1]. Such nanocomposites have been extensively studied due to their unique optoelectronic and photonic features. The admixture of nanoparticles to polymer and formation of nanocomposite affects charge carrier transport in different ways. For example, enhanced charge carrier mobility was measured by the time-of-flight method in polymer:quantum dots (QDs) systems [2] and in organic field effect transistors (OFETs) in nanotetrapods:polymer systems [3]. Embedding quantum dots in OFET's insulator layer changes the relative electric permittivity of the dielectric influencing the source-drain current and the charge carrier mobility [4]. On the other hand, a decrease of charge carriers mobility was observed in studies of OFETs. The quantum dots added to the layer between the dielectric and the organic semiconductor acted as trapping centers of charge carriers [5]. The effect of trapping could be used in development of optoelectrical memories and switches [6]. In other studies no influence of nanoparticels on electrical properties of hybrid material was elucidated [7]. As a summary of the above studies the following conclusions could be made. The mechanism of charge carrier transport in polymer:nanoparticles systems is still not completely understood and complementary studies of the influence of nanoparticles on charge carrier transport in semiconductive polymers are required.

In this work we present the synthesis of CdSe quantum dots and studies of electrical properties of a system built from poly(3-hexylthiophene) (P3HT) containing CdSe nanoparticles embedded in the polymer matrix. Output and transfer current voltage characteristics of organic field effect transistors with spin coated active layer were analyzed. Different compositions of P3HT and CdSe quantum dots were used and the influence of CdSe concentration in P3HT on the charge carrier mobility, the On/Off ratio, the threshold voltage and subthreshold swing are described. Addition of CdSe into polymer matrix decreases the field effect charge carrier mobility and the threshold voltage. The observed effect indicates that QDs act as trapping centers being originated from structural and energetical disorder in the polymer matrix.

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ELECTRODES FOR GAOHPC:PCBM/P3HT:PCBM BULK HETEROJUNCTION SOLAR CELL.

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Organic photovoltaic devices have attracted attention and are a promising effective alternative for conver-ting solar energy into electrical energy. The bulk heterojunction approach appears to be one of the most promising concepts of creating efficient, low cost and easily producible organic solar cells. For this purpose one of the best materials is regioregular poly-3-hexylthiophene (P3HT), which is widely used as a donor molecule and a hole transporter, with soluble fullerene derivative (PCBM) as acceptor and electron transporter. The main drawback of this highly efficient blend is its limited spectral range, covering only 350-650 nm spectral interval[1]. So the main aim of the present work was to extend the spectral range of the cell up to 850 nm by adding second bulk heterojunction layer of complementary absorption spectrum to P3HT:PCBM layer. It was recently shown that combining or stacking multiple materials of complementary absorption profiles can improve characteristics of organic PV devices without the need for an intercellular connection layer [2]. Therefore hydroxygallium phthalocyanine (GaOHPc) and PCBM blend was used as additional layer because GaOHPc has strong and wide intermolecular charge transfer (CT) absorption band around 830-850nm [3]. Thus novel organic bi-layer bulk heterojunction system (GaOHPc:PCBM/P3HT:PCBM) has been built by spin coating technique having high charge carrier photogeneration efficiency in 350 – 850 nm spectral range. ITO glass was covered by 30nm thick PEDOT:PSS (Clevios 1000) layer followed by GaOHPc:PCBM blend. This bulk heterojunction layer was covered by P3HT:PCBM blend from the solution in chlorbenzene or dichlorobenzene. As top electrode In or Al or Sm electrodes were evaporated in vacuum 10^{-6} – 10^{-5}mbar. When In electrode were used a 0,5 – 0,7 thick BaF_2 layer was inserted between electrode and an organic layer. Short circuit photocurrent external quantum efficiency (EQE) spectral dependences, luxampere and voltampere dependences were measured in vacuum 10^{-6} mbar. The samples were illuminated using grating monochromator by chopper modulated monochromatic light through the ITO electrode in the 350 – 1000 nm spectral region with intensity 10^{9} – 10^{16} phot/(cm^{2}*s). Light modulation period was chosen as 6 s long and intensity was controlled with Si photodiode. Electrode material and sample thermal annealing in vacuum influence on short circuit photocurrent EQE values, open circuit voltages (Voc) and fill factors has been investigated. The smallest Voc values were obtained for samples with In top electrode and its value was only 0,25V for low light intensity at 10^{12} phot/(cm^{2}*s) and 0,35V for high intensities at 10^{15} (phot/cm^{2}*s). After inserting thin BaF_2 layer Voc value increased to Voc=0,48V. The samples with top Al electrode exhibited higher Voc values ~0,7 - 0,8V, but very low fill factors. The highest Voc values were obtained for samples with Sm electrode, where these values exceeded 1 Volt. It was found that thermal annealing in vacuum at 100C increases EQE values more than 2 – 3 times, and these values reach more than 45% at P3HT absorption band (520 nm) and 25% at GaOHPc band (850 nm) for low light intensities (10^{12} phot/(cm^{2}*s)) for samples with top BaF_2/In electrodes. At higher light intensities EQE values diminish probably due to low hole polaron mobilities in GaOHPc:PCBM layer.

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ORGANIC FIELD EFFECT TRANSISTORS FABRICATED BY PLOTTER PRINTING AND SPRAY DEPOSITION OF MATERIALS

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Organic electronic devices have received extensive attention because of their potential application in flexible electronics, large-area displays, radio-frequency identification tags, sensors, etc. The crucial advantage of organic electronics rests in a prospect of low cost manufacturing of electronic circuits achievable by deposition of electronic components from solution by, e.g., ink-jet printing and spray coating.

A common challenge in most printing techniques is the limitation in feature size. The linewidth of 20-100 µm is achievable with standard ink-jet printers. One may achieve a further decrease of the size of printed features at the price, however, of a dramatic increase of the cost of fabrication [1]. A way of overcoming this obstacle is the technique of plotter printing, enabling one to draw very smooth lines and thus to achieve short (ca. 5 µm) channel lengths between source and drain electrodes. On the other hand, this method is not contactless, thus limiting the choice of materials for substrates [2]. Spray deposition of semiconductor/dielectric/metallic layers building an electronic device is less sensitive to solution properties (e.g. viscosity) in comparison to ink-jet printing and, contrary to the spin coating technique, allows for a successive deposition of several layers using the same solvent.

The aim of the present study is to test the performance of novel organic field effect transistors (FETs) fabricated by plotter printing of electrodes and spray deposition of the semiconductor. Poly(3-hexylthiophene) (P3HT) and Si/SiO$_2$ substrates were used as organic semiconductor and gate electrode with insulator, respectively. The source-drain electrodes of FETs were printed using a PEDOT:PSS aqueous solution, with a piezoelectric-assisted microplotter (SONOPLOT).

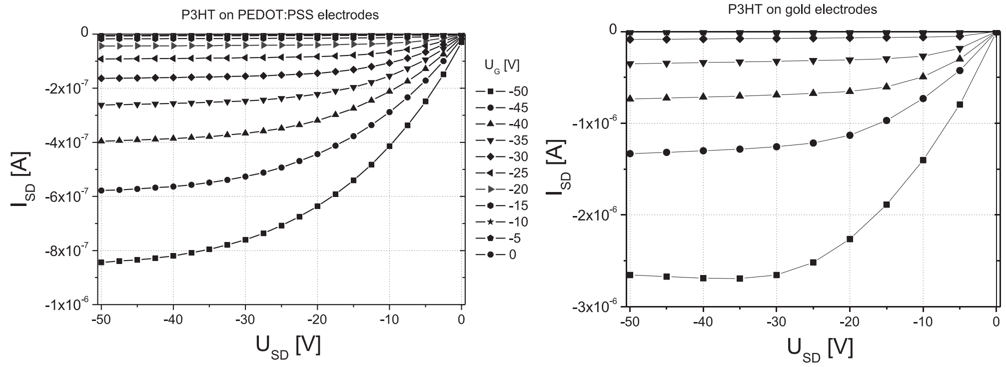

Figure 1. Comparison of output characteristics of FETs with plotted PEDOT:PSS electrodes and evaporated gold electrodes. The channel lengths were ca. 150 µm and 10 µm for PEDOT:PSS and gold, respectively.

The characteristics of FETs with printed electrodes were compared with those of FETs with photolitograpically deposited gold electrodes. The mobilities of charge carriers in both types of devices were of the same order (10^{-3} cm^2/Vs). The threshold voltages in FETs with printed PEDOT:PSS electrodes were significantly lower than those in the devices with gold electrodes (-10 V compared to –25 V), evidencing good prospects of the new technique for practical application.

Acknowledgements

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LIGHT-HARVESTING AND PHOTO-REGULATION IN MOLECULAR SYSTEMS BASED ON A HEXAPHENYLBENZENE FRAMEWORK

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Realizing the promise of solar energy requires new technologies to convert solar energy to electrical and chemical energy inexpensively, efficiently, and safely [1]. The molecules to be discussed exemplify several of the current themes in artificial photosynthesis research. It is clear that it is now possible to create in the laboratory artificial reaction centers that convert light energy into electrochemical potential via photoinduced electron transfer [2]. The charge-separated states can be formed with quantum yields of essentially unity, can store a significant fraction of the photon energy, and have lifetimes that are long enough to consider using the stored energy to make electricity or drive redox catalysts. It is also possible to enhance the function of these reaction centers by addition of multichromophoric antenna arrays [3-4] that extend the range of wavelengths that the reaction centers can use effectively. Finally, photoregulatory function can also be incorporated [5-6], and may ultimately be necessary to prevent photodamage to these organic systems. The unusual triode tube or transistor-like photoregulatory ability to modulate intense, shorter-wavelength fluorescence with longer-wavelength light is demonstrated in one of the presented molecular systems as well [7].

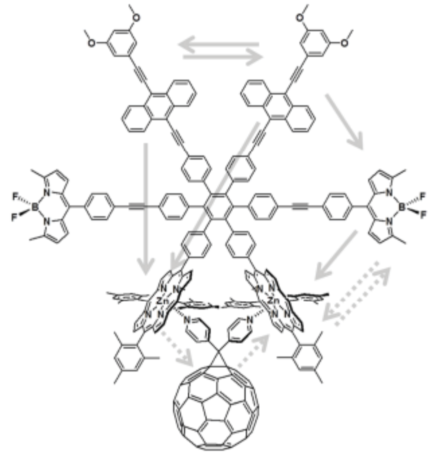

Figure 1. Light-harvesting heptad showing singlet excitation energy (solid arrows) and electron (dotted arrows) transfer pathways.

We have chosen examples based on a single organic framework – hexaphenylbenzene – as an organizing unit for the various chromophores, donors and acceptors. Hexaphenylbenzene (Figure 1) is a useful choice because it has points of attachment for a large number of peripheral substituents on the six phenyl rings surrounding the central benzene ring, is constrained to a rigid conformation in which the six peripheral rings are nearly perpendicular to the central ring, and can be readily synthesized with a number of well-defined substitution patterns.

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ELECTRIC CURRENT FLOW THROUGH ORGANIC HETEROJUNCTION IN THE PRESENCE OF IMAGE FORCE

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Organic junctions are used in rectifying and electroluminescent diodes, photovoltaic cells, transistors and others. Electrical conduction is an important property of organic junctions for operation of many organic electronic devices. Electric current flow through an organic junction depends on the HOMO and LUMO levels and work functions of the employed electrodes [1]. Image interactions, occurring at the interface between two organic layers, can also strongly affect the electric current flowing through the junction, since they bend HOMO and LUMO levels.

Image forces depend on the relation between dielectric constants of materials of the junction (ε_1 and ε_2). According to papers [2, 3] the change of potential energy of a charge carrier in the first layer, resulting from the image force created close to the interface, may be expressed as follows:

$$E_{i1/2}(x) = \mp \frac{e^2}{16\pi\varepsilon_1\varepsilon_0}\,\frac{\varepsilon_2-\varepsilon_1}{\varepsilon_2+\varepsilon_1}\,\frac{1}{|x|},$$

where x is a distance of the charge carrier from the interface between dielectrics, $\varepsilon_{1,2}$ are the relative permittivities and indexes 1, 2 correspond to first and second layer. With respect to values of ε_1 and ε_2, we can distinguish three different types of junctions of two organic materials: a-type: $\varepsilon_1 = \varepsilon_2$, b-type: $\varepsilon_1 > \varepsilon_2$ and c-type: $\varepsilon_1 < \varepsilon_2$ (fig. 1).

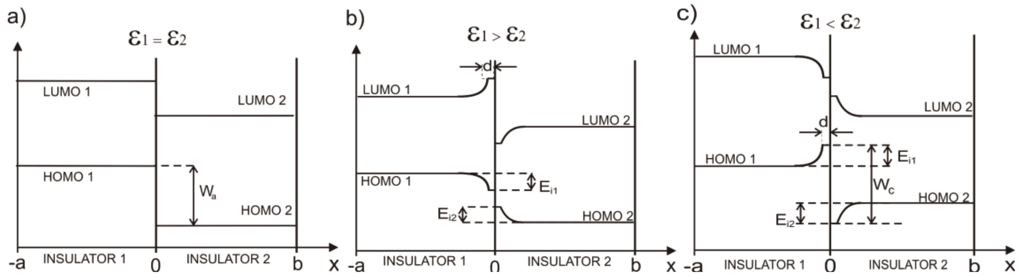

Figure 1. Energy level diagrams of the heterojunction of two different organic insulators, where a and b are the thicknesses of organic layers. a) - image forces can be neglected ($\varepsilon_1 = \varepsilon_2$); b) – energy levels bending due to the image force for $\varepsilon_1 > \varepsilon_2$; c) - energy levels bending due to the image force for $\varepsilon_1 < \varepsilon_2$.

In case of the a-type junction, image force doesn't occur, whereas in the cases b and c potential energy of a charge carrier at the junction can be either increased or lowered due to image potential. It means that this carrier can be repelled or attracted by the interface.

We have analysed the significance of dielectric constants of materials forming the junction for its electrical properties. We have calculated the change of the height of potential barrier at the junction due to image interaction and the ratio of current density obtained regarding image potential and current density obtained when image forces were neglected.

Selected experimental results for junctions composed of layers with big differences of dielectric constants will be presented.

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STUDY OF ELECTROCHEMICAL REDUCTION OF NO_2 WITH POROUS CARBON ELECTRODE IN ROOM TEMPERATURE IONIC LIQUIDS

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Nitrogen dioxide (NO_2) is widely used in chemical industries and it is also a major air pollutant, mostly due to combustion of fossil fuels with use of air for oxidation. As a strong oxidant, NO_2 is toxic for living organisms including humans, and thus the legislations of most countries have established threshold values 40-200 $\mu g.m^{-3}$ [1] for environment and 10-20 $mg.m^{-3}$ for short exposures on a workplace.

This creates strong need for a sensitive and reliable detectors for NO_2. Most of the common detectors now on market are based on electrochemical reduction of NO_2 at an indicator electrode with H_2SO_4 as a supporting electrolyte [2]. The aqueous solution of H_2SO_4 maintains equilibrium concentration with the water vapor pressure, thus the cell performance depends on the relative humidity, leading sometimes to malfunction of the cell in extremes.

It is known that NO_2 can be detected electrochemically in room temperature ionic liquid (RTIL) [3]. We show how hydrophobic electrolytes such as some RTILs can be utilized to overcome the humidity influence. We found that the chemical composition of RTIL was important for observation of the redox reaction of carbon electrode with nitrogen dioxide in extreme humidity conditions.

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TRANSPORT PHENOMENA

RESONANCE ENERGY TRANSFER IN CHARGE-TRANSFER DYES: THE ROLE OF DARK STATES IN AN ESSENTIAL-STATE PICTURE

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Resonance Energy Transfer (RET) involves the transfer of a virtual photon from an excited molecule, the energy donor, to a different molecule, the energy acceptor. The growing interest in this phenomenon is related to the possibility to exploit RET in the hot fields of organic light emitting diodes, photovoltaics and artificial light harvesting.

In the late forties, Förster developed a very efficient approach, based on the dipolar approximation, to relate the RET rate to experimentally accessible quantities, namely the intensity of emission and absorption of the energy donor and acceptor, respectively [1]. The Förster theory was successfully applied to several systems that satisfy the requirements of the dipolar approximation, i.e. systems where the distances between chromophores are larger than their dimensions. According to the Förster model, only one-photon allowed states (i.e. “bright” states) can take an active part in RET.

In this contribution, we address the role of dark states (i.e. of states with vanishing transition dipole moment from the ground state) in RET processes involving charge-transfer (CT) dyes. CT dyes are constituted by electron donor and electron acceptor groups linked through π-conjugated bridges, and their low-energy physics is governed by CT resonances. This class of chromophores is interesting for several applications, ranging from nonlinear optics to molecular electronics. CT chromophores are fairly large molecules and the presence of dark states in multibranched CT chromophores makes these systems particularly interesting to investigate the limitations of Förster theory.

CT dyes are accurately described by essential-state models [2], i.e. by accounting for a minimal set of electronic states, corresponding to the resonating structures of the chromophores. Essential-state models have already been exploited to describe linear and nonlinear optical properties of dipolar and multipolar CT chromophores, leading to a deep insight of complex and interesting phenomena, such as bistability or symmetry breaking. Moreover, essential-state models account quite naturally for electrostatic interactions, allowing the investigation of multichromophoric systems [3] and aggregates [4]. Here we adopt the same approach to evaluate interaction energies relevant to RET processes [5]. Our results demonstrate that dark states can take an active role in RET, with interaction energies that, depending on the relative orientation of the chromophores, can be even larger that those relevant to bright states for intermolecular distances in the 4-10 Å range. Essential-state models, whose predictions are *quantitatively* confirmed by TDDFT results, provide a physical explanation of the origin and relevance of dark states in RET processes and allow to relate RET interaction energies towards bright and dark states to the supramolecular symmetry of the RET-pair, offering reliable design strategies to optimize RET-interactions.

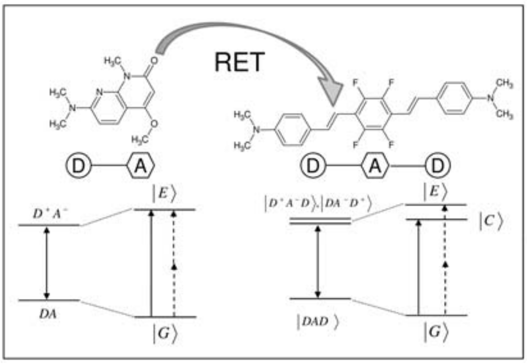

Figure 1. Molecular structures and schematic description of essential-state models for polar (left) and quadrupolar (right) CT dyes.

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IMPACT OF THE GAUSSIAN DISTRIBUTION OF TRAPPING STATES ON THERMALLY STIMULATED CURRENT SPECTRA IN MDMO-PPV

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Carrier trapping was investigated in [poly-(2-methoxyl, 5-(3,77dimethyloctyloxy)] para phenylenevinylene (MDMO-PPV) by the thermally stimulated current spectroscopy depending on the excitation wavelength and applied electrical field. Excitation below and above the band-gap by the light passed through the long-pass colour filters with cut-off energies ranging from 1.77 eV up to 3.1 eV was used to assure selective excitation of the defect states. The thermally stimulated current spectra had demonstrated distinctive differences depending on the excitation energy and applied voltage. The numerical modelling of the experimental curves revealed that the full TSC is a superposition of several peaks resulting from the Gaussian site-energy distribution of the localized states. Two traps with the Gaussian distribution of the states having the effective mean activation energies of about 0.22 eV and 0.40 eV were prevailing. The standard deviations of the distributions were evaluated to be 70-100 meV. The trap filling and charge generation processes were shown to be dependent on the excitation wavelength and applied electric field. By changing excitation spectral range the thermal activation energy values varied due to different filling of distributed in energy scale energy states. The increasing electric field used to reduce carrier activation energy because of the lowering potential barrier heights. The results are direct indication by the photo-thermo-electrical methods of the distributed in energy trapping states.

OPTICAL AND ELECTRICAL PROPERTIES OF NEW DIKETO-PYRROLO-PYRROLES FOR ORGANIC ELECTRONICS

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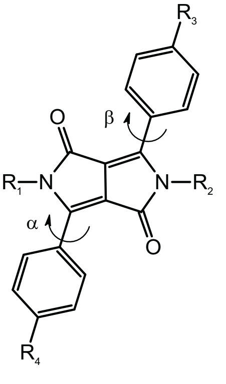
Derivatives of 3,6-diphenyl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione, commonly referred to as DPPs, constitute recent industrially important class of high-performance pigments [1]. They are endowed with brilliant shades (ranging from yellow-orange to red-violet) and exhibit exceptional chemical, heat, light, and weather fastness. It has been shown that DPP units introduced into various materials e.g. polymers, dendrimers, polymer-surfactant complexes, and oligomers results in deeply coloured, highly photoluminescent and electroluminescent materials. In order to tune the DPPs properties, we modified the basic structure by introduction of electron donating and/or withdrawing groups. Furthermore, solubilising groups were attached to enable solution based depostition techniques, see Figure 1.

Introduction of electron-donating groups increased the molar absorption coefficient (ε) and was accompanied with strong bathochromic shift. This behaviour implies that charge separation occurs via electron delocalization leading to creation of permanent dipole moment. Blurring of vibration structure in absorption spectra of mono substituted derrivatives imply interaction with polar dimethylsulfoxide and shows polar character of the mono substituted DPPs. Introduction of the *N*-alkylation led to the decrease of the ε and hypsochromic shift and loss of vibrational structure. We proposed the same mechanism as for the *N*-alkylated only derivatives [2]: the *N*-alkylation causes rotation of the phenyls (see the angles α and β in Figure 1) and consequently breaks the molecule symmetry. This causes decrease of the effective conjugation and increases the polarity.

To test the derivatives performance in electronic devices, thin films were prepared by spin-coating and by vacuum evaporation. The key impact on the morphology of thin layers was found to be based on the *N*-substitution of central DPP unit by alkyl side chains. The main role plays the type of substitution: the unsymmetrical or symmetrical. The symmetrically substituted derivatives form planar large crystallites, whereas the asymmetrically substituted derivatives form highly rough fiber crystallites. On the basis of the findings described above symmetrically substituted derivatives resulted as suitable for electrical characterization. The prepared organic diode like devices from the phenyl di-piperidino substituted *N,N*-alkylated DPP (strucute VIII) showed reasonable electroluminiscence signal (the turn-on voltage for this diode was ~3V). The derivative III showed increased current flow under illumination by white light, indicating charge carrier photogeneration. Charge carrier mobilities were determined using organic field effect transitors. The obtained values were in the range 10^{-7} to 10^{-6} $cm^2s^{-1}V^{-1}$.



	R_1	R_2	R_3	R_4
I	H	H	H	H
II	C_4H_9	H	H	H
III	C_4H_9	C_4H_9	H	H
IV	H	H	$N\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$	H
V	H	H	$N\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$	$N\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$
VI	H	H		
VII	C_4H_9	H		
VIII	C_4H_9	C_4H_9		
IX	C_4H_9	H	Cl	Cl
X	C_4H_9	C_4H_9	Cl	Cl

Figure 1. The basic structure of 3,6-diphenyl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4 dione, also known as DPP (structure I) and the prepared derrivatives.

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ON SMALL SIGNAL CAPACITANCE SPECTRA OF ORGANIC PLANAR SYSTEMS

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An energy diagram (ED) of materials forming an organic device provides essential information about levels transporting charge carriers and about possible barriers at interfaces. Ordinarily, electrical characteristics of organic devices are analyzed with reference to their ED. On the other hand as electric current flows through an organic system various processes can take place at interfaces and sometimes it is hardly to assume their occurrence referring only to ED. For instance, Au with its work function equal to 5.1 eV could be treated as an ohmic contact for copper phthalocyanine (CuPc), since its ionization energy is also 5.1 eV. However, ultraviolet photoemission spectroscopy of Au/CuPc interface [1] as well as our research on Au/CuPc/Au system performed with the use of small signal technique [2,3] did not confirm this assumption. Analysis of small signal capacitance spectra (SSCS) led us to the conclusion that electric current in Au/CuPc/Au system is limited by emission of charge carriers from electrodes and not by space charge in the bulk of CuPc.

In general, analysis of SSCS can provide essential information, about charge-carrier transport through organic devices, which is not easy to get from other measurements. The main advantage of small signal technique is the fact that it is applied directly to the device which is in focus of interest. We should merely keep in mind that in contradiction to inorganic semiconductor systems the presence of depletion region is unnecessary to obtain interesting SSCS.

This presentation will deal with SSCS of selected planar systems with single organic layer, with organic-organic or organic-inorganic bilayer. The subject of our analysis will be small signal spectra of complex capacitance obtained at different values of bias. We will limit ourselves to general conclusions about charge carrier transport through the systems without ad hoc assumptions, for instance, about the presence of depletion region at any interfaces. Relationships between SSCS and direct current voltage curves will be discussed.

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PHOTOVOLTAIC PROPERTIES OF CdTe/PERYLENE DYE THIN FILM HETEROJUNCTION

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Results of researches on photovoltaic effect in the system based on cadmium telluride/N-N'-dimethylperylene-3,4,9,10-dicarboximide (CdTe/MePTCDI) heterojunction will be presented. It is an example of a hybrid organic-inorganic heterojunction. The systems with such type of heterojunction have recently attracted a great deal of attention due to their likely application in solar cells [1,2]. Cadmium-telluride is a good absorber of sunlight and it is used in inorganic thin-layer photovoltaic cells [3]. MePTCDI is an organic dye with strong light absorption within the 400 600 nm range and relatively high electron mobility.

Investigations have been performed on two types of systems thermally evaporated in vacuum, namely on ITO/CdTe/MePTCDI/BCP/Ag and on Au/CdTe/MePTCDI/Al. The BCP (bathocuproine) layer acts as a carrier blocking layer and prevents the organic material from damage during Ag deposition.

Measurements of dark current and photocurrent-voltage curves as well as of spectral and light-intensity dependences of short-circuit current and open-circuit voltage have been performed. In the dark a current-rectification effect was observed: the rectification ration yielded 10÷150. The illumination of the system resulted in photovoltaic effect caused by carrier generation in CdTe layer and exciton dissociation at the CdTe/MePTCDI interface. The results obtained will be compared with the results carried out on the system with F_{16}ZnPc layer [4].

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ELECTRICAL CONDUCTIVITY AND OPTICAL TRANSMITTANCE OF SINGLE-WALL CARBON NANOTUBES FILMS

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Due to their unique electrical and optical properties carbon nanotubes arrays are known as promising materials for a numerous applications in opto- and nanoelectronics. Processing of nanotubes on macroscopic scale and investigation of their synergetic properties is a most important task for realistic application of these materials. Both electrical and optical properties of carbon nanotubes arrays depend not only on the chirality and diameter but on the length of individual nanotubes as well.

We report here results of experimental investigations of conductivity and optical transmittance in far infrared range of carbon nanotubes films fabricated from short single-wall carbon nanotubes (SWCNTs) with length and diameter of individual tubes of 2-5 µm and 1.2-1.5 nm, respectively. The samples were prepared by spraying of the *N,N*-dimethylformamide-SWCNTs suspension onto a clean silicon or polycrystalline Al_2O_3 substrates for further testing of optical transmittance and electrical conductivity, respectively. The substrates were heated during spraying to rapidly evaporate the *N,N*-dimethylformamide at temperature 180 ^{0}C. Homogeneous SWCNTs dispersions were prepared by sonication in *N,N*-dimethylformamide of bundled single-wall carbon nanotubes produced by arc-discharge method.

In order to determine charge transport mechanisms, temperature dependencies of the resistance $R(T)$ were measured in the temperature range 2-300 K in close-cycled refrigerator Cryogenics. We used different models (variable range hopping (VRH), weak localization (WL), and fluctuation induced tunneling) for approximation of experimental results as far as different charge transport mechanisms can be observed in the arrays of nanotubes [1]. We found that in high temperature range $R(T)$ dependencies follows WL behavior. At the temperatures below 15 K VRH and fluctuation induced tunneling are supposed to coexist in SWCNT films.

In order to study optical density of SWCNT film, Bruker IFS-66 instrument was used for the registration of Fourier transmittance infrared (FTIR) spectra. The spectra has broad peak with center at wave length of about 50 µm. This peak is supposed to be due to finite length effect in CNT [2].

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PHOTOGENERATION OF FREE CHARGE CARRIERS IN Π-CONJUGATED POLYMERS WITH BULKY SIDE GROUPS

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We have studied the photogeneration of free charge carriers in Poly{1-[4-(trimethylsilyl)phenyl]-2-phenylacetylene}, PDPA (cf. Fig. 1). In such a system an exciton formed upon photon absorption diffuses along a π-conjugated chain until it is self-trapped in a place where two chains approach (meet) each other in space. Then, it is assumed that the exciton transformation to the initial charge transfer (CT) state proceeds as an electron transfer from one chain to the overlapping (or approaching) side groups, where it is self-trapped. The mobile hole can move in the applied external electric field provided that the attractive Coulomb potential is overpowered. Experimental data of photogeneration efficiency (open circles on the left side of Fig. 1.) could not be explained neither by 3-D nor 1-D Onsager models. Instead, we have modified the model of Arkhipov, Emelianova and Baessler (AEB) [1] and it proved out to be successful. The AEB model assumes, first, that the hole oscillates harmonically around the minimum of its total potential and, for the second, it thermally dissociates over a potential energy barrier, where the activation energy equals to the difference between the maximum of the potential energy and the minimum of the harmonic oscillator. The model itself is a compromise between the quantum nature of a delocalized hole dynamics and a the thermally activated hole dissociation. Our model modification included two additional key assumptions: First, the permittivity effectively changes with the electric field. Indeed, experimental data could be explained for high fields with relative permittivity $\varepsilon_r \sim 4$ (solid line in left Fig. 1). For medium electric fields the permittivity achieved values $\varepsilon_r \sim 2.5$ (dashed line) and for small values of electric field the permittivity dropped to values $\varepsilon_r \sim 1.5$ (dotted line). For increasing values of applied electric field the travelling distance of the hole in the 1-D chain statistically also increases. For the latter quantity relatively large the permittivity increases due to the high 1-D screening of delocalized orbitals. On the other hand, for small travelling distance the permittivity rather approaches its microscopic value partly modified by the presence of phenyl groups. This property is very responsible for the fact that the experimental values of photogeneration efficiency didn't saturate at low fields ~ 10^5 V/m, as it is usually observed for nonlinear organic materials, but they continuously decrease with decreasing electric field. Moreover, such a behaviour was experimentally verified for various thicknesses of PDPA samples, so the effect cannot be explained by the space charge distribution.

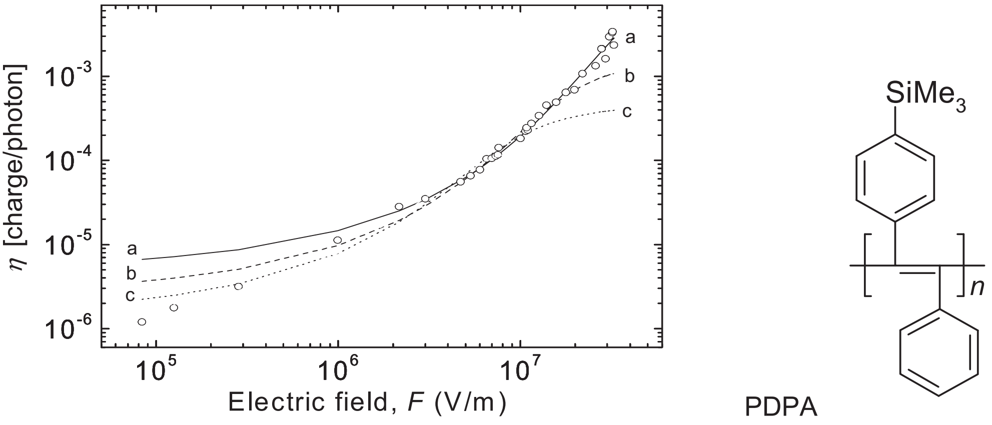

Figure 1. Efficiency of photogenerated free charge carriers in PDPA vs. electric field. Experimental data are denoted by open cirles. Theoretical curves by a) solid line (relative permittivity $\varepsilon_r = 3.8$), b) dashed line ($\varepsilon_r = 2.5$) c) dotted line ($\varepsilon_r = 1.5$) 2.5

Acknowledgement: This work was supported by the projects COST OC 10007 (Czech MEYS), MEB05010 (Czech MEYS and Polish MSHE) and P205/10/2280 (Czech Science Foundation).

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UNUSUAL FEATURES OF CHARGE CARRIER TRAPS ENERGY SPECTRA IN SILICON ORGANIC POLYMERS

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Silicon organic polymers are of considerable research interest because of their unusual optical and electrical properties and because they may serve as a possible model for the charge carrier transport in disordered photoconductors. It is commonly accepted that the charge carrier transport in these polymers is controlled by charge hopping through intrinsic states derived from domain-like segments of the silicon chains. The low-temperature thermally stimulated luminescence (TSL) method is directly related to the detrapping processes providing thus an adequate function of the distribution of trapped charge carriers.

In the present work, the peculiarities of charge carrier traps energy spectra in silicon organic polymers are studied by the enhanced fractional TSL. This technique has allowed obtaining a large number of fractional curves and thus considerably increasing the energy resolution of the method. Moreover, correction of the real TSL signal was performed for each fraction as the existence of the essential dependence of the background glow on temperature has been proven. The results were compared with the data obtained by traditional TSL [1].

The study has revealed for the first time that:

1. Discrete dependence of the activation energy of the traps on temperature is observed in the films of the silicon organic polymers which distinctly differ from the results of earlier studies for which linear dependence of the activation energy on temperature was typical [1].
2. Integral TSL curves have considerable width exceeding by much the width of the calculated elementary curves. This is due not to the continuity of the energy spectrum for traps but rather to the dispersion of the frequency factor determined by the level of transparency of the barriers between potential wells, first of which corresponds to the state of a polaron localized on a trap and the second is formed by temperature fluctuations. It is shown that for the traps of the same depth the frequency factors may differ as much as by four orders of magnitude.
3. The values of the activation energy correlate with the frequencies of the fully symmetrical Ag- modes (0.0463 and 0.0334 eV) of the silicon chain in the Raman spectrum, which confirms the hypothesis that the traps for holes in silicon organic polymers are the segments of the backbone chain confined by the conformational defects. Obtained results are evidence of the direct manifestation of the polaron nature of the traps in the studied polymers.

The validity of the interpretation of the TSL spectra in terms of the energetic relaxation of photogenerated charge carriers within a manifold of the states of Gaussian distributions is yet being discussed.

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POLING OF EO POLYMERS - CORONA DISCHARGE PROCESS OPTIMIZATION.

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An increasing interest has been devoted to new nonlinear optical (NLO) active organic materials due to their low cost, easy processability and potential applications as organic optical components. Such materials must possess large second-order nonlinear coefficients which can be obtained by electric field poling. For maximal possible NLO efficiency one must achieve the highest polar order in the system maintaining the chromophore structure, concentration and thin film optical properties. One of the most popular poling techniques at the moment is poling with corona discharge. For polymer poling purposes the corona triode device seems very attractive due to the fact that one can have good estimation of poling field, low probability of electrical breakdown in the sample, etc. We have built a computer controlled corona triode device which allows us to capture current-voltage characteristics of the system as well as perform EO polymer poling at constant grid potential or sample current. The poling efficiency can depend on multiple parameters as shown previously [1-3]. To optimize these parameters one has to develop a reproducible corona poling process. It can be done by means of cutting out uncertainties in surface charging ionic flux generation by corona needle – control grid system. Upon to our experience there are two important things to be done. First of all - an ambient air in corona chamber should be replaced with nitrogen by a constant, very slow flow of gas through the system. In case of air the humidity alternates along with the environment conditions and therefore causes uncertainty in corona generated ionic composition and conductivity. Moreover, corona discharge in air creates large amount of ozone, which is highly reactive and in some cases could destroy NLO active chromophores in polymer. The second thing to be done in order to obtain constant ion flux on the grid (by number and speed of charged particles) is to keep constant corona needle to control grid potential. At these circumstances the grid to sample gap behaves almost ohmic and in the case of nitrogen gas filed system the gap resistance is not dependent on temperature. As a result, poling field over sample film can be estimated from grid potential and sample current measurements over large range of poling temperatures.

After fulfilling above mentioned conditions the poling efficiency can be optimized by altering poling temperature and control grid – sample system parameters, for instance – grid to sample distance and potential. In order to demonstrate difficulty of such optimization, results of corona poling of host – guest polymer films of PMMA with DMABI (10%wt) chromophore will be presented. The NLO coefficients were determined by Maker fringe technique. Desirable sample parameters after poling, such as high polar order (necessary condition NLO efficiency) and low light scattering, can be quite contradicting and therefore certain equilibrium of poling conditions should be found. As an example (see Figure 1), we can demonstrate that large sample currents (in order to achieve high poling potential) can cause formation of light scattering structures in poled area of sample.

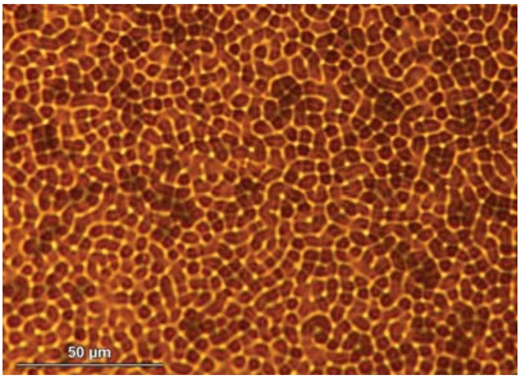

Figure 1. Optical microscope image of light scattering structures in the corona poled sample

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STUDIES OF CHARGE CARRIER TRANSPORT IN THIN FILMS OF BAY SUBSTITUTED PERYLENE BISIMIDES

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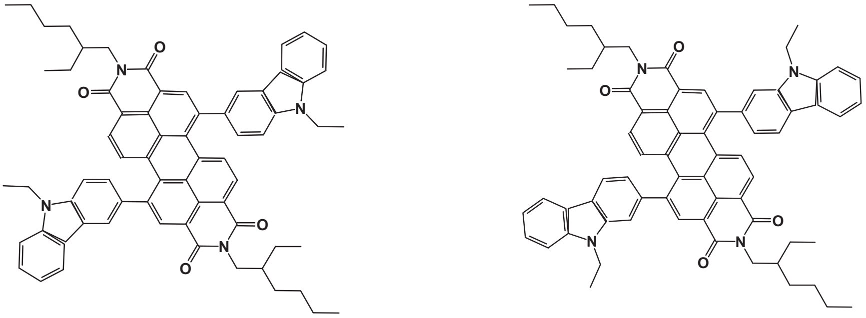
Perylene bisimide derivatives are well-known organic semiconductors. They widely employed in organic electronics and optoelectronics [1]. Extensive study of charge carrier transport has significant importance in these applications. Since perylene bisimides are proven electron-transporting materials whereas derivatives of carbazole are appealing hole-transporting molecules, it is interesting to examine the electrical-transport properties of covalently linked derivatives of these two moieties [1, 2].

In this work, we have studied electrical properties of two bay carbazolyl substituted perylene bisimide derivatives (see Figure 1) with different electrodes. "Sandwich" type samples consisting of perylene derivatives 1 or 2 as an active layer sandwiched between different metals as top contacts and gold as bottom contact were prepared. The electrodes (Au, Pd, Al, and Cu) were chosen in order to inject electrons or holes into the thin films. It is known that Au, Pd, Cu electrodes can inject holes into the organic layer, however Al can inject electrons. Values of threshold energies E_{th} from spectral dependences of photoconductivity were obtained. The work functions of metal layers and surface potential of thin film of perylene derivatives were obtained by Kelvin probe technique. The organic film thickness was of the order of 1 μm. It allows applying space charge limited current method [3]. The thermal dependencies of electrical conductivity were investigated in space charge limited current regime [4]. The dependence of activation energy E_a on voltage allows characterizing energetical structure of local trapping states in thin film. Charge carrier mobility is determined by charge extraction in a linearly increasing voltage method [5].



Compoud 1

Compound 2

Figure 1. Molecular structure

The values of oxidation and reduction potentials were measured by voltammperomety and the values of U_{redox} were obtained. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels were calculated by RHF *ab initio* calculations. Calculated energy gap values are comparable with the experimentally determined ones.

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NOOLANDI-HONG VERSUS ONSAGER MODELLING OF CHARGE PHOTOGENERATION IN ORGANIC SOLIDS

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Absorption of light in organic solids leads to creation of excited states (excitons) which may dissociate to form free charge carriers. Taking into account a large coulombic interaction radius ($r_C > 10$ nm) in these low mobility materials the charge photogeneration is commonly assumed to proceed through an intermediate stage of bound electron-hole pairs (geminate e-h pairs). The classical treatment of e-h separation process by Onsager [1,2] and Noolandi-Hong [3], based on solving the Smoluchowski equation, refers to the diffusion motion of an e-h pair in the continuous medium in the presence of combined mutual and applied electric field.

In this paper we have studied the electric field dependence of the escape probability (Ω) for various radial distribution functions (Dirac delta, Gaussian, exponential) of the e-h pairs in the framework of Noolandi-Hong (NH) model. In the NH model the final geminate recombination step proceeds on a sphere of finite radius (a) with a finite velocity (κ). We show that the commonly used Onsager theory based on his paper [1] (Onsager 1938) is a special case of a more general NH treatment for $a \to 0$ and $\kappa \to \infty$. In turn the earlier Onsager theory [2] (Onsager 1934) can be derived from the Onsager 1938 model if radial distribution function of initial e-h pairs approaches Dirac delta function, $\delta(r-r_0)$, and $r_0 \to 0$.

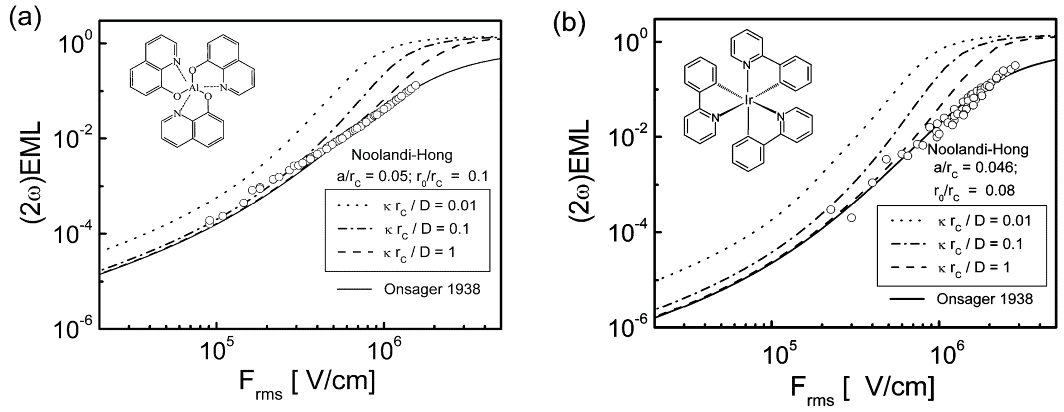

Figure 1. A comparison of the EML experimental data (circles) with theoretical curves based on the NH model with Dirac delta radii distribution for three different values of capture velocity κ. The EML data for vacuum evaporated layers of Alq$_3$ (a) and Ir(ppy)$_3$ (b) are taken from refs. [4] and [5], respectively.

We compared theoretical results with the experimental data taken from electromodulation of photoluminescence (EML) for two archetypical organic photoconductors, Alq$_3$ and Ir(ppy)$_3$, commonly used as emitters in organic LEDs (Fig. 1). In EML experiments electric field-induced increase in charge separation translates into photoluminescence (PL) quenching measured usually by modulation technique at the second harmonic (2ω) of fundamental frequency (ω) of applied electric field, $F_0 \sin(\omega t)$. The relevant quantity is (2ω)EML signal defined as $I_{2\omega}/I_{0\omega}$ where $I_{n\omega}$ stands for n-Fourier component ($n = 0, 2$) of PL intensity. From analysis of our results we infer the lower limit of surface recombination velocity, $\kappa = 1$ cm/s, in vacuum evaporated layers of Alq$_3$ and Ir(ppy)$_3$ which agrees well with an evaluation of that quantity in amorphous solids made in ref. [6].

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THE CONTACTS AND LAYER MORPHOLOGY INFLUENCE ON SHORT CIRCUIT CURRENT IN ORGANIC MATERIALS

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Organic semiconductors are successful group of materials for optoelectronic applications due to their advantages, such as fabrication at low temperature, flexibility and low cost [1]. Therefore they already have been employed in a variety of thin film devices such as photovoltaic and light emitting diodes [2]. The ability to control the way that charges and excitations move in organic materials is of great importance for the operation and efficiency of these devices. Particularly, their performance mainly depends on the diffusion of excitons and their decay processes [3] among which there is dissociation of excitons at metal/organic material interface leading to charge carrier injection.

The aim of this work is to examine the role of metallic contacts and trapping sites in the short circuit current generation via excitonic processes in organic materials. Particularly, the single organic layer with a non-uniform density of trapping sites provided with two metal electrodes with different exciton decay efficiency will be considered.

It has been shown previously for single pentacene layer provided with different metallic electrodes, that the energy of triplet excitons is not always sufficient to overcome the energy barrier at metal/pentacene interface and to cause efficient charge carrier injection into pentacene layer [4]. On the other hand, the induced local states in the layer directly influence the movement of excitons. Recently, it has been shown that the presence of traps limits the exciton diffusion in conjugated polymers [5].

In our model, we consider a device consisting of a single organic layer of a thickness d provided with two metal electrodes. We assume that a large number of excitons are created in the organic layer under illumination and subsequently they diffuse out of the illuminated region. Such process can be described by the following kinetic equation:

$$\frac{dT(x)}{dx} = G + D\frac{d^2T(x)}{dx^2} - (\beta + \beta_{HG})T(x), \tag{1}$$

where T(x) is the number of excitons per unit volume, G is the rate of photogeneration of excitons, β is the excitons decay rate from the excited states to the ground states, β_{HG} is the rate of excitons being trapped and D is diffusion coefficient. Furthermore, we assume that excitons captured by trapping sites can't escape and no longer participate in diffusive motion.

The short circuit current generated in the system due to excitons is given by :

$$j = j_1 - j_2 = \eta_1 eT(0) - \eta_2 eT(d), \tag{2}$$

where η_1 and η_2 describe the exciton decay efficiency at the metal/organic layer interfaces and T(0) and T(d) are the excitons concentration at the interface with front and back electrodes, respectively. Solving the equation (1) with different energetic distribution of traps in organic layer enables us to determine the concentration of excitons in the sample. Thus the expression represented the short circuit current can be derived directly from equation (2). From the basic analysis of the problem follows that the short circuit current will reach its maximum value when the device will be illuminated from the side of organic layer consisting of low trapping sites concentration and provided with metallic electrode with high value of the exciton decay efficiency.

The obtained, based on theoretical analysis, analytical expressions describing the short circuit current will be particularly discussed and the results of numerical study will be presented.

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THEORETICAL INVESTIGATIONS OF CHARGE TRANSPORT PROPERTIES IN OLIGOTHIOPHENES

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Theoretical prediction of the charge transporting properties of organic materials is still significant challenge for computational chemistry. There are several theoretical models such as tight binding model [1,2] and Marcus theory [1,3] which can predict charge carrier mobility in organic solids [4,5]. Usually, in real organic material more than one formalism is needed for its proper description or charge transport depending on the timescale of the investigated process. The lack of the one unified theory describing charge carrier drift in organic materials is not only reason of difficulties in this area of science. Very often there is a large problem in calculation of some key parameters determining charge transport such as: charge transfer integrals, site energies and reorganization energy.

The thiophene based materials are very promising for use in organic electronics. The high charge carrier mobility and possibility of easy and low cost film deposition make poly(3-alcilothiophenes) one of the most important conductive polymers. Also liquid crystals based on oligothiophenes has large potential in the field of organic electronics. Its unique properties related with self-organization and self-repairing makes thiophene based liquid crystals one of the most intensively studied materials for organic electronics.

In this work we present results of our calculations of charge transporting properties such as charge transfer integrals and site energies of model oligothiophenes. Some geometrical parameters determining position of oligothiophene molecules in dimers was spanned to determine relation between charge transfer integral and dimer structure. The oligomers with different lengths was investigated. Presented results are an initial step of the charge carrier mobility calculations in oligothiophene liquid crystalline column. It is also starting point of modeling of charge carrier mobility in amorphous polythiophene films.

Figure 1. Side and top view projection of the highest occupied molecular orbital (HOMO) of the pentathiophene molecule.

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EXCITATION ENERGY TRANSFER AND QUENCHING IN THE PHOTOSYNTHETIC MAJOR LIGHT-HARVESTING COMPLEXES

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The life evolved on Earth strongly depends on the light harvesting taking place by photosynthetic organisms. The photosynthetic apparatus in general consists of the light-harvesting antenna and reaction centers. In green plants the light-induced water splitting reaction is fulfilled by photosystem II, which is also responsible for the regulation ability and system adaptation to the different level of the light conditions. Because of the existence of the rapid excitation energy density control in photosystem II, termed as the non-photochemical quenching (NPQ), plant photosynthesis can function efficiently under very different light conditions up to very high intensities. This regulatory process occurs in the light-harvesting complexes, LHCII, with involvement of carotenoid molecules, as shown by recent studies using the time-resolved spectroscopy [1, 2]. It is commonly agreed that the increasing intensity of the sunlight causes some configurational changes within the LHCII which lead to the generation of additional excitation trapping centers (probably related to the carotinoid molecules) converting the excess excitation energy to heat. However, despite recent extensive studies in this field and several suggested models, a common consensus about the origin of the NPQ-traps has not been achieved so far.

Since experimentally observable excitation decay kinetics in the LHCII aggregates under NPQ conditions are mostly bi-exponential, there are two principle ways to qualitatively describe such results [3]. In the *'migration-limited'* case the excitation slowly migrates through the antenna until it reaches the NPQ-trap, and then quickly relaxes (the so-called slow/fast (SF) regime). In the converse *'trap-limited'* regime the excitation lifetime is dominated by the trapping in the NPQ-center, whereas the migration can be assumed to be relatively fast (the so-called fast/slow (FS) regime).

In order to determine the key parameters defining the excitation kinetics and thus to get an insight into the origin of the NPQ, the excitation energy transfer and quenching in LHCII aggregates was considered in terms of a coarse-grained model [4], in which only the transfer of excitons between separate pigment–protein subunits is treated explicitly, with all intra-monomer kinetics 'integrated out' of the calculation (Fig. 1).

As follows from the calculations, this model can be well-fitted to the experimental kinetics assuming different values for the excitation hopping rate between different LHCII monomers. However, certain problems are encountered while assuming FS regime: the LHCII aggregate should be rather small, and excitation will be mainly localized on the NPQ-trap. Moreover, if considering NPQ excitation dynamics at higher excitation conditions when singlet–singlet annihilation starts to dominate, in the FS regime the excitation kinetics of the aggregate are almost insensitive to the initial excitation density. Conversely, the excitation kinetics in the SF regime display strong sensitivity to the changes in excitation density. Since the experimentally observed kinetics reveal a similar dependence, it can be concluded that the SF regime is a more appropriate description for the physical origin of the NPQ-trap: the excitation dynamics is mainly determined by the excitation migration within antenna, whereas the relaxation in the NPQ-center takes just several ps. Such conclusion is also supported by the calculations according to another approach considering the excitation diffusion in the continuum medium with randomly distributed static traps.

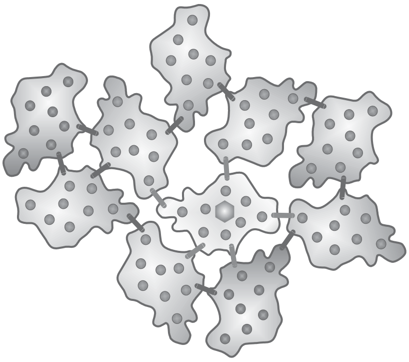

Figure 1. Coarse-grained model for the LHCII aggregate with a NPQ-trap in one of LHCII monomers (represented by hexagon; circles stand for Chl molecules; thick bars depict possible excitation transfer paths between different LHCII monomers). While modelling, only excitation transfer between different LHCII is taken into account whereas their internal structure is neglected.

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ON THE TRUE MEANING OF THE FLAT PLATEAUS ON THE TIME-OF-FLIGHT CURVES IN MOLECULARLY DOPED POLYMERS

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Flat plateaus on the time-of-flight (TOF) curves feature regularly in the studies of the carrier transport in molecularly doped polymers (MDPs). Technically, this observation facilitates the determination of the transit time and the mobility itself. However, the true physical meaning of the plateau still remains controversial. It is not a true quasiequilibrium as the Einstein relation between the mobility μ and the diffusivity D grossly fails [1]. An accepted point of view is that of only partial equilibrium with μ getting constant while D increasing in time. The Gaussian disorder model (GDM) of Bässler serves to explain this sort of the TOF current behavior (see [2]).

We consistently argued that such an approach suffers from one fundamental drawback. Existing Monte-Carlo simulations of the GDM show that as the slope of the plateau ($\beta = -d\log j / d\log t$) becomes smaller and smaller approaching zero, the slope of the post transit current decay gets larger and larger ($\beta >> 1.0$). This qualitative prediction of theory contradicts experimental data. Even for flat plateaus, the post transit current slope may be as low as 2.0-2.5 [3].

In this situation, we performed numerical calculations of the TOF transients featuring ideally flat plateaus using multiple trapping (MT) model with a Gaussian trap distribution. The GDM and MT are thought to be equivalent at low fields for proper model parameters obtained by the standard GDM approach [4, 5]. Numerical calculations show that for the total disorder σ in MDPs exceeding 0.085 eV the plateaus should have $\beta \geq 0.15$ at room temperature compared to experimental values $\leq$ 0.01 (Figure 1). Thus, to reconcile theory with experiment one needs introducing some extraneous mechanism as in [6] (two-layer MT model for universal current transients in MDPs).

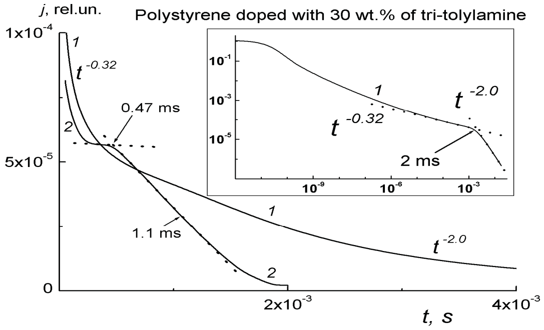

Figure 1. Computed (*1*) and experimental (*2*) TOF transients in linear and logarithmic (inset) scale. The experimental curve features flat plateau while the computed one lacks it. Note that $t_{1/2}$ (1.1 ms) is close to the transit time on the inset. Curve *2* is taken from [5] (see Fig. 1c). Both curves refer to 205 K, the electric field was 64 V/μm and the sample thickness was 10 μm.

It should be remembered that both the GDM and MT models fail to describe the Poole-Frenkel (PF) type of the mobility field dependence. In this context, the dipolar glass model [7] deserves special attention as it seems to predict flat plateaus for $\sigma \sim$ 0.13 eV with post transit current slopes about 2.2 at room temperature [8] while explaining PF effect. But this model does not allow MT computations and requires Monte-Carlo simulations (unlike the GDM it deals with the Gaussian spatially correlated energy distribution of hopping centers).

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TRANSIENT CURRENTS ACROSS POLYMER THIN FILMS CONSISTING OF SINGLE, DUAL AND TRIPLE LAYERS

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Poly(diphenylenephthalide) (PDP) is known to exhibit ambipolar conductivity and related unique properties [1,2]. In particularly, a discrete interface between two successive layers of PDP has abnormal high longitudinal conductivity while the bulk layers remain in dielectric state [3].

In this work, an influence of the interface between the PDP layers on the electron transport in the normal to the film plane direction was investigated. The study was carried out with specimens of the structure shown in Fig. 1 by the use of a conventional time-of-flight (TOF) technique in small signal regime [2]. The polymer films consisted of single through triple layers. The first layer was deposited by spin coating a solution of PDP in cyclohexanone onto ITO glass substrate and the second one – onto the top surface of the first one and so on. The polymer/polymer interface was discrete because no intermixing between the layers at such interfaces was detected [3]. A charge generating layer (CGL - Se, CuPc) was 0.2 μm in thickness.

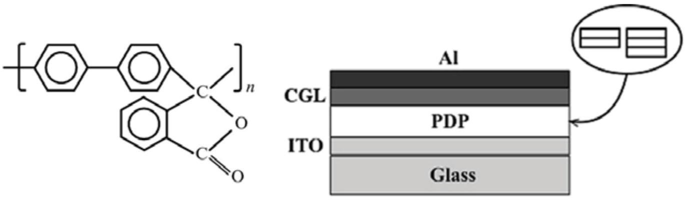

Figure 1. PDP structure (left) and cells for the TOF measurements (right).

All the TOF transients of the electron transport showed dispersive characteristic. In the log current vs log time plot, the intersection of the asymptotes of the two linear regimes was considered as a transit time t_T of electrons. The time t_T was equal to 5 ms, 4.5 ms and 3 ms in a 2.4 μm thick single-layer sample, 5.4 μm thick dual-layer sample and 7.5 μm thick triple-layers sample, respectively, at electric field of 1.6×10^5 V/cm.

It is well known from experimental evidences and theoretical models that transit time increases with the thickness of polymer single layer films [4, 5]. This appears to be not the case for the PDP films incorporating discrete interfaces between successive layers. We suggest a qualitative mechanism to describe the experimental finding. The PDP/PDP interface can be considered as a reservoir of electron-hole pairs which can dissociate easily. The assumption is based on the experimental data on anomalous high conductivity and charge mobility along the PDP/PDP interface [3] and the nature of the PDP polymer [1, 6]. In the TOF experiment, for instance in the case of a dual layer sample, as soon as a sheet of electrons is injected from CGL into the PDP layer a similar sheet of electrons is injected from the PDP/PDP interface into the second PDP layer and move toward the counter electrode. Holes can either remain at the PDP/PDP interface or drift toward the first sheet of electrons. Such behavior of the charge carriers in the dual-layer sample gives TOF transients similar to those in a single-layer sample provided the layers are equal in thickness.

In summary, it is established experimentally that electron transient currents across the PDP film consisting of a few PDP layers is significantly influenced by the interface between the layers, a possible mechanism of the influence is discussed.

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INFLUENCE OF ENERGETIC AND SPATIAL DISORDER ON THE YIELD OF GEMINATE-PAIR DISSOCIATION – A MONTE CARLO STUDY

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It is commonly accepted that the carrier photogeneration efficiency in organic solids at low light intensities is governed by the geminate carrier recombination, i.e. the recombination of a charge carrier with its parent carrier of opposite charge. In particular, the geminate recombination is considered to be essential process limiting the efficiency of organic solar cells. The classical treatment of geminate carrier recombination in continuous medium was developed by Onsager [1] and Noolandi and Hong [2]. However, in organic solids the estimated initial distances r_0 of electron-hole (e-h) pairs are only few times larger than the intermolecular distances and the atomic structure of the solid has to be taken into account. The calculation of the yield of e-h pair dissociation is then possible by the Monte Carlo method. Such studies were performed both for homogenous solids, e.g. [3 – 4], and organic heterojunctions, e.g. [5 – 6], the majority of them concerned either ordered systems or systems with energetic Gaussian disorder.

In this report we present the results of Monte Carlo calculations of the carrier dissociation yield η dependence on the external electric field strength F and the sample temperature T. As in previous papers, the calculation method consisted of simulation of carrier hopping motion on regular cubic lattice of constant a. The simulation steps are repeated until either carrier recombination or carrier collection on absorbing lattice boundary take place. Apart from Gaussian energetic disorder, the exponential one as well as spatial disorder of the solid have been considered. It is shown that the mentioned cases can be distinguished experimentally on the basis of different temperature dependencies of the free carrier yield. The exemplary results, concerning the case of exponential distribution of localized states, $N(E) \propto \exp(-E/kT_C)$ (with E – the energy variable, k – the Boltzmann constant and T_C – the characteristic temperature, determining the degree of disorder), are given in figure 1. The influence of the recombination rate and the recombination distance on the dependence of free carrier yield on electric field has also been investigated.

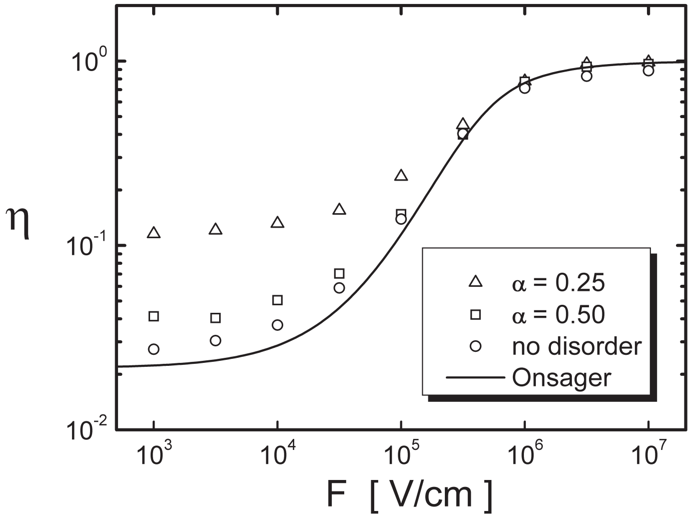

Figure 1. Electric field dependence of the e-h pair dissociation yield in lattice with no disorder (circles) and with energetic exponential disorder, characterized by the parameter $\alpha = T/T_C$ (squares and triangles). For comparison, the η *vs F* dependence, calculated from the Onsager theory [1], is also shown (solid line). Other calculation parameters are: $a = 6\cdot10^{-8}$ cm, $r_0 = 4.157\cdot10^{-7}$ cm, $T = 300$ K, dielectric constant $\varepsilon_r = 3.5$.

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PHOTOELECTRICAL PROPERTIES OF THIN FILMS OF DMABI DERIVATIVES

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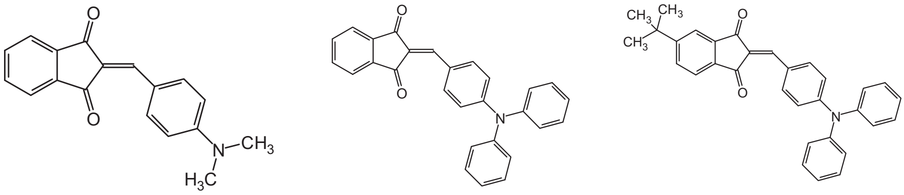
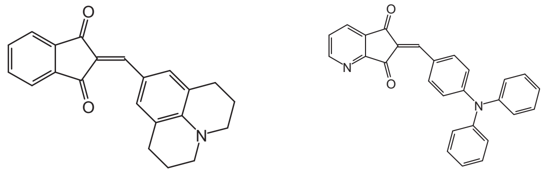
Among organic semiconductors, group of indandiones with their electrical properties, thermal and chemical stability are good candidates for use in design of novel molecular electronic devices and organic photovoltaics. To achieve higher efficiency, it is necessary to study photoelectrical properties of organic compounds in thin films. The spectral dependence of photoconductivity and the value of the quantum efficiency are important data to characterize novel materials. Better results in efficiency of the solar cells are expected when the spectral dependence of the photoconductivity is close to the Sun spectrum. Besides fundamental part of design effective solar cells is knowledge of energetic characteristics of a material. Photoelectrical properties, particularly the spectral dependence of quantum efficiency of photoconductivity and optical absorption spectra, characterize adiabatic and optical energy gaps of organic molecules in thin film. The energy gap directly affects such important electronic processes as charge carrier generation and transport.

The aim of the work is studying of the influence of molecular structure on photoelectrical properties and the energy gap values of polar indandione type molecules in thin vacuum evaporated films. Dimetilaminobenzylidene-1,3-indandione (DMABI) is known as good photoconductive material [1]. In this work four novel DMABI derivatives are chosen. In three of these derivatives the N,N-dimethyl amino electron donor part of the DMABI molecule are substituted by N,N-diphenyl amino group. In one of the derivatives carbon atom is substituted with nitrogen atom in the electron acceptor part of the molecule (N-DMABI-dPh). As fourth compound we have chosen DMABI-JU.



DMABI DMABI-dPh tBu-DMABI-dPh



DMABI-Ju N-DMABI-dPh

Fig.1. DMABI molecule and its derivatives

We have investigated photoconductivity quantum efficiency and its spectral dependence of all these DMABI derivatives. Values of the threshold energy E_{th} from spectral dependence of quantum efficiency of photoconductivity are obtained. These results are good agreement with the results following from optical and voltamperometric experiments. The quantum efficiency of photoconductivity of DMABI and its derivatives are of the order 10^{-3} el./phot. The threshold value of photoconductivity of DMABI derivatives reduces from 1,95eV for DMABI thin films to 1,75eV for DMABI-JU thin films.

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SPECTRAL DEPENDENCES OF PHOTOCURRENT IN POLYTHIOPHENE DOPED WITH SILVER NANOPARTICLES

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In last few years a lot of attention has been given to organic photovoltaic devices. Polymer solar cells have a great potential to become cheap renewable energy sources. There are several different concepts of how to improve the efficiency of organic solar cells in order to make it economically viable. Recent studies shows significant enhancement of photoconversion efficiency through addition of metal nanoparticles (MNPs) to the active polymer layer [1], but the mechanisms of the enhancement are not fully clear yet.

In a previous work we showed that the photocurrent in poly(3-hexylthiophene) (P3HT) films can be significantly increased by addition of copper nanoparticles [2]. Copper nanoparticles appeared, however, to be unstable over extended time and easily oxidized. Therefore we chose more stable silver particles for further examination of MNPs photocurrent enhancement. We investigated impact of doping with silver nanoparticles on optical and electrical properties of P3HT, which is commonly used as the donor material in photovoltaic devices. We obtained colloidal solution of Ag nanoparticles in chloroform by a simple one-step synthesis which is a modification of a method described by Seo *et al.* [3]. Characterization of optical properties of polymer with nanoparticles in solution and film was performed. For more detailed examination of influence of MNPs on photocurrent in polymer thin layer, spectrally dependent measurements of the photocurrent-voltage characteristics were conducted. Figure 1 is an example plot showing how the photocurrent measured for P3HT film doped with Ag nanoparticles correlates with the absorption spectrum. The results obtained so far appear to indicate that the enhancement of the photocurrent by the MNPs results from increase in the exciton diissociation rate rather than from enhanced light harvesting.

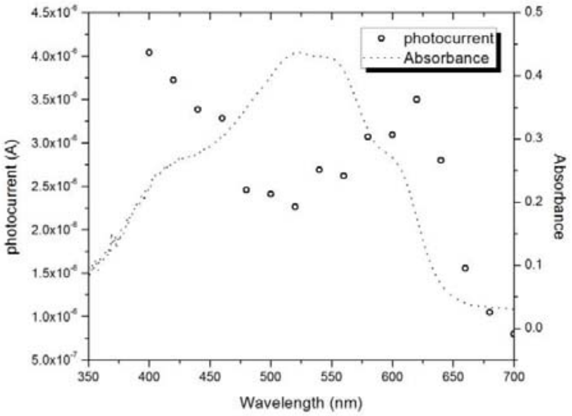

Figure 1. Photocurrent of P3HT film doped with Ag NPs and absorbance spectrum of prepared film. Photocurrent was measured under illumination with xenon lamp light passed through monochromator, with 5V bias applied.

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CHARGE CARRIER PHOTOGENERATION AND RECOMBINATION IN POLYMER/FULLERENE BULK HETEROJUNCTION FILMS

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Photogeneration and recombination of charge pairs and free charge carriers in poly-3 (hexylthiophene) (P3HT) and [6,6]-Phenyl C61 butyric acid methyl ester (PCBM) bulk heterojunction has been studied at different PCBM concentrations by means of fluorescence spectroscopy, time-of-flight (ToF) and extraction of photogenerated charge carriers by a linearly increasing voltage (photo CELIV) techniques. Quenching of P3HT fluorescence by PCBM, has been used for the evaluation of the exciton dissociation efficiency. The quantum efficiency of free carrier generation has been evaluated from ToF current transients at different electric fields. The free charge carrier recombination properties have been estimated from photo-CELIV current transients at different delay times between laser ant voltage pulses. Obtained results shows better carrier photogeneration quantum efficiency, and lower geminate recombination rate in samples with higher PCBM concentration.

HIGH MOBILITY HOLE TRANSPORTING DIPHENYLETHENYL SUBSTITUTED TRIPHENYLAMINES

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Electronic and optoelectronic devices using organic materials as active elements, for example, organic light-emitting diodes (OLED), organic photovoltaic devices (OPV), organic field-effect transistors (OFET), organic photorefractive devices, and so forth, have received a great deal of attention from the standpoint of potential technological applications as well as fundamental science[1-3]. All the devices described above involve charge transport as an essential operation process and hence, require charge-transporting materials. Therefore, development of high-performance, charge-transporting materials is a key issue for the fabrication of high-performance devices.

Realization of organic electronics potential for simple processing requires the ability to form devices by solution deposition methods, preferably using simple, inexpensive, easily purified materials.

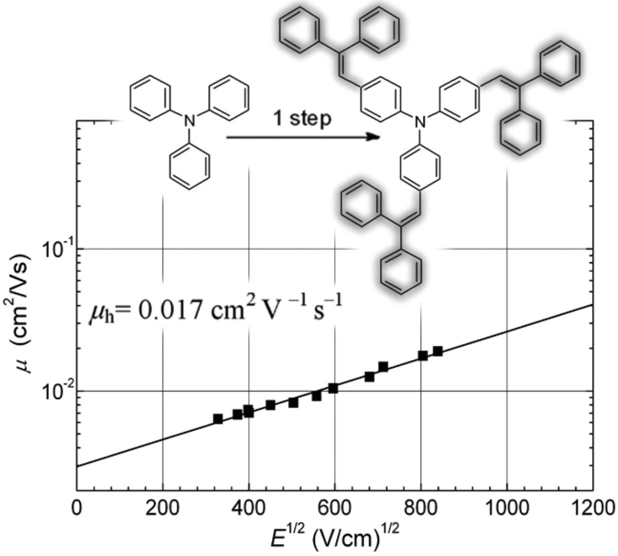

Figure 1. Mobility of the investigated star-shaped charge transporting material.

Herein we present the star-shaped charge transporting materials with a triphenylamine core and varying number of diphenylethenyl sidearms. These hole transporting organic semiconductors are obtained in one step synthesis procedure from commercially available and relatively inexpensive starting materials. Tris(4-(2,2-diphenylethenyl)phenyl)amine is an especially promising candidate because it can be handled in air, requires no high temperature annealing steps, can be solution deposited, possesses comparatively high mobility (up to 0.017 cm^2 V^{-1} s^{-1}), and could be synthesized in one step from commercially available and cheap triphenylamine.

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PHYSICOCHEMICAL PROPERTIES OF A NEW PHOTOCHROMIC LIQUID CRYSTAL

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Charge transport and the solid state photochromic properties in an interesting new compound exhibiting AIEE (Aggregation Induced Enhancement of Emission) [1] were investigated.

Basic thermal analysis (DSC) experiments showed the liquid crystal behavior, which was further examined by Polarized Optical Microscopy (POM) measurements, which proved the existence of a *Smectic C* phase. Since the compound possesses a delocalized system of π electrons, its charge transport properties were checked by the Time-of-Flight method *vs.* temperature (Fig.1). In the liquid crystal state at 140°C the transient photocurrent curves show clearly two shoulders corresponding to a fast and a slow mobility. These transit times, associate to the electronic and ionic mobilities, and are typical for this kind of mesophase and are of the order of 10^{-4} and 10^{-6} cm^2/V·s for the holes and for the ions, respectively.

As we observed a slow evolution of TOF curves and organic film aspect during the electrical measurements and more particulary during the charge photogeneration (UV ns pulsed laser), we conducted the studies of the kinetics of absorption spectra in solution and in the solid state in order to have a better understanding of the compound photochromic properties. It can be noticed that such behavior is rather exceptional, because the photochromism and fluorescence can be considered two competing mechanisms of the deactivation of excitations.

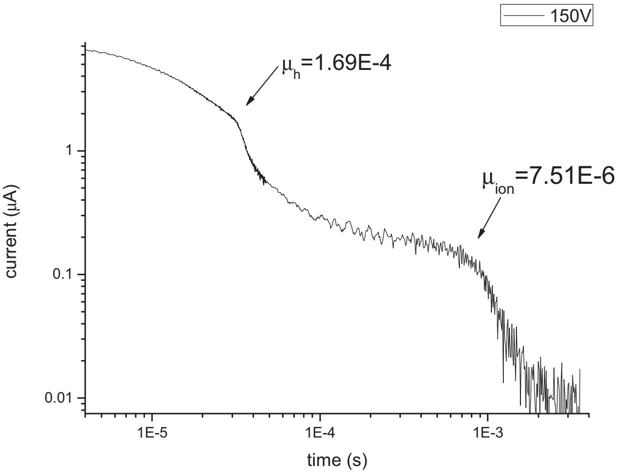

Figure 1. A transient photocurrent curve obtained for the bias of 150 V applied to the cell containing the liquid crystalline sample.

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FROM ALLYLBITHIOPHENE TO NEW CONDUCTING POLYTHIOPHENES CONTAINING ISOXAZOLE MOIETIES

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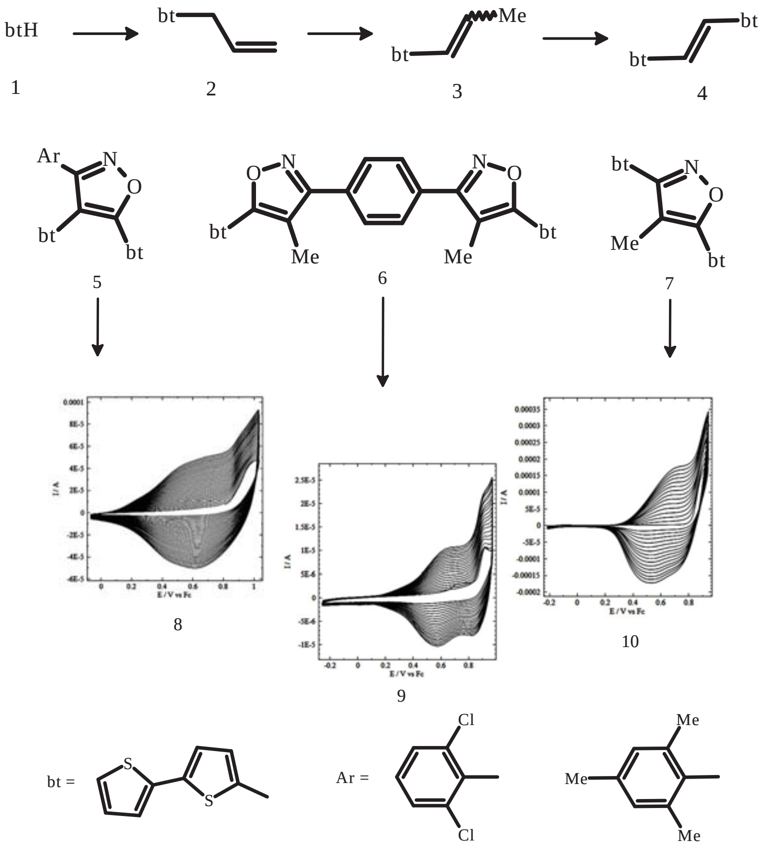

5-Allyl-2,2’-bitiophene 2 was obtained in the allylation reaction of 5-lithio-2,2’-bithiophene by allyl bromide. Then, 2 was quant. isomerized to 3 in the presence of [RuClH(CO)(PPh$_3$)$_3$]) and, subsequently, 3 subjected to self-metathesis (on 2nd generation Grubbs’ catalyst) yielding 4. Dipolar cycloaddition of appropriate nitrile oxides to 3 (BT-CNO and 1,4-(ONC)$_2$C$_6$H$_4$) and 4 (2,6-Cl$_2$C$_6$H$_3$ and 2,4,6-Me$_3$C$_6$H$_2$) led to the formation of dihydroisoxazoles, which were oxidatively dehydrogenated (with DDQ) to isoxazoles 5, 6 and 7.

Electrochemical properties of the isoxazoles were investigated using cyclic voltammetry on Pt and ITO electrodes. New redox-stable conjugated polymers (8, 9, 10), containing isoxazole moieties in the main chain, were obtained via electropolymerization. Thin films of the polymers were studied using cyclic voltammetry and UV-Vis spectroelectrochemistry.

The metathesis product 4 and the dihydroisoxazole intermediates were also subjected to electropolymerization, but their redox stability and charge transport properties were inferior, most likely due to disturbed bond alternation (poly(dihydroisoxazoles)) or redox instability of the CH=CH- linkage (poly(4)).

EXCITED STATES, OPTICAL NONLINEARITIES

ROTAXANES – MATERIALS FOR ADVANCED POLYMER BLENDS: MULITCOLOUR ASE AND ULTRA-BROAD OPTICAL GAIN

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Here, we show properties of conjugated polyrotaxanes combine into photonic application: ultra-broad band optical gain in a binary polymer blend that can be further exploited for two-colour lasing. We study the optical properties of two blends of polyfluorene and polyrotaxane (supramoleculary insolated chain) by means various spectroscopy techniques.

The ability to produce semiconducting polymer blends with white emission spectra, large emission cross sections and broad optical gain is critical to their application in white PLEDs, lasers and broadband amplifiers. Cyclodextrin-encapsulation is an effective means of suppressing detrimental intermolecular interactions, and energy transfer (ET) channels in polymer blends, thus enabling fabrication of white-emitting devices. We show that all such properties combine into a high impact photonic application: ultra-broad optical gain and two-colour amplified spontaneous emission (ASE) in a binary polyrotaxane blend. We study the photophysics of a blend of a conventional and an encapsulated polyfluorene by means of steady state and ultrafast spectroscopy techniques (pump-probe and ASE experiments). The morphology of the blend is investigated by μ-Raman imaging and confocal fluorescence microscopy. We ascribe the ultra-broad optical gain (>850 meV) and the simultaneous ASE from both constituents to the dual effect of reduced polaron formation and suppressed ET in the polyrotaxane binary blend.

Our results demonstrate that polyrotaxanes could realistically represent the building blocks for advanced polymer blends with highly controlled optical properties. The composite material investigated here represents only the first proof of principle of strategy and we expect the optical properties can be improved by blending encapsulated compounds only. These polymeric composite materials have highly controlled optical properties and could lead to disrupting technologies such as single broadband optical amplifiers covering the entire visible region, to be applied for data transmission by wavelength division multiplexing in plastic optical fibres, for applications in solid state lightning, lasers and photovoltaic technologies.

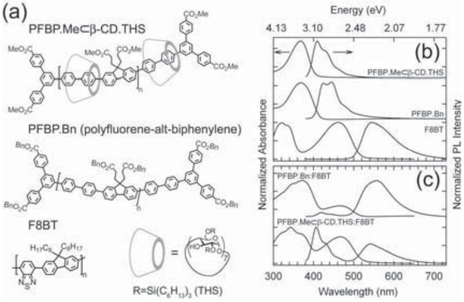

Figure 1. (a) Molecular structures of the investigated polymers. Absorption and steady-state PL spectra of spin-cast films of (b) neat polymers and (c) their relative 1:1 (wt%) blends.

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MODIFICATION OF CHITOSAN BY AZO MONOMERS VIA RAFT POLYMERIZATION

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The controlled grafting modification of chitosan has been achieved by RAFT polymerization using chitosan-RAFT agent. The chitosan was first modified with S-Dodecyl-S′-(α,α′-dimethyl-α″-acetic acid)trithiocarbonate to prepare RAFT agent, and then the controlled grafting polymerization of two acrylic monomers using RAFT procedure followed by azo coupling reaction between modified chitosan and the diazonium salt of 4-aminobenzonitrile and 4-nitroaniline (Fig. 1) [1].

The azo polymers were characterized by spectroscopic methods and GPC measurements. The results showed that the graft polymers were successfully synthesized with narrow molecular weights distribution in the range of PDI = 1.19 [2].

The polymers were deposited as films onto glass plates by spin coating technique and the photochromic properties were measured. The side chain azobenzene moieties showed the ability to reversible trans-cis isomerization by illumination with light. The maximum absorption band of the film were observed at 434 nm for polymer containing nitrile and 455 nm for polymer containing nitro group in the said chain. The obtained films were illuminated during ellipsometric measurements and the result was a change in refractive index. The change of real part of the refractive index after 5 minutes illumination was in the range of 0.0177 – 0.0206 [3].

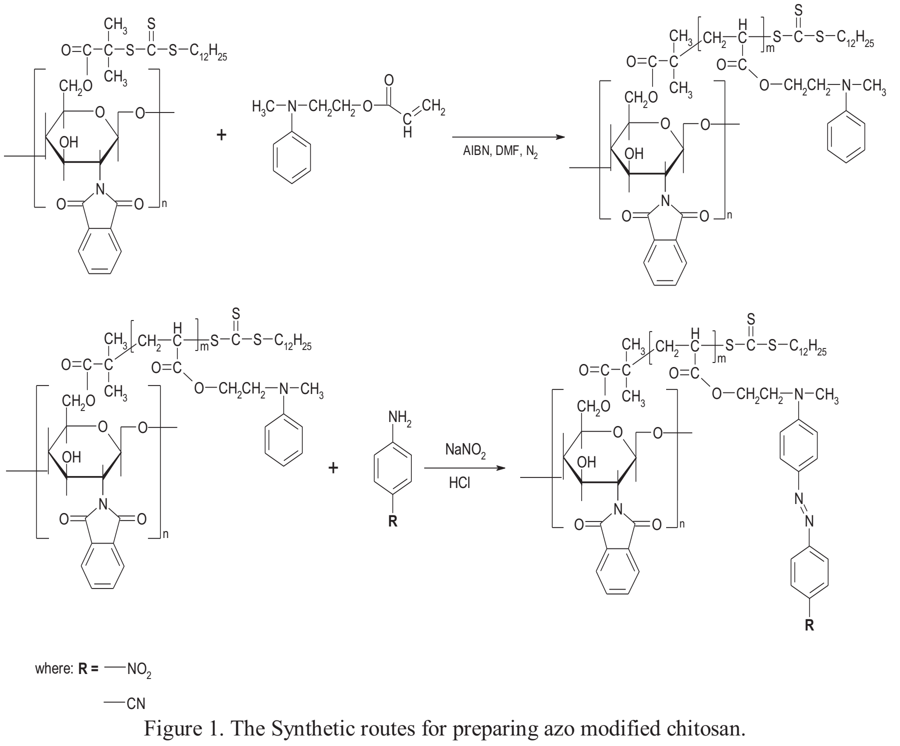

Figure 1. The Synthetic routes for preparing azo modified chitosan.

Acknowledgements
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THE AMPLIFIED SPONTANEOUS EMISSION FROM POLYMERIC FILMS DOPED WITH 3-(1,1-DICYANOETHENYL1)-1PHENYL-4,5DIHYDRO-1H-PYRAZOLE

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The (DCNP) crystal has been synthesized by S. Allen in 1988 as a novel organic material for applications in nonlinear optics [1]. In DCNP crystal the photoluminescence can also occur when excited with light from green to UV spectral region [2].

The authors presents results of studies realized on polymeric systems doped with the DCNP organic molecules, which served as the luminescent chromophores. We compare four types of polymeric systems like PMMA, PC, PVK and DNA-CTMA doped with 2 % w/w of DCNP. To excite the luminescence second and third harmonic of fundamental frequency line coming from nanosecond pulse Nd:YAG laser was used. The signal of luminescence was collected with "Ocean Optics" fiber spectrometer coupled with PC for data acquisition. In every system amplified spontaneous emission (ASE) was observed. The normalized spectra of ASE excited by light with λ = 532 nm and energy density ρ = 80 mJ/cm^2, for each sample are presented in Figure. 1. The threshold energy densities, gain coefficients and temporal stability were estimated for all systems.

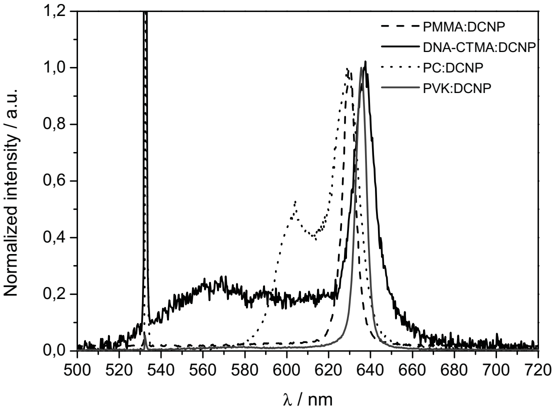

Figure 1. ASE spectra of DCNP molecules dispersed in different matrices. The excitation wavelength was λ = 532 nm and the energy density was ρ = 80 mJ/cm^2.

The lowest threshold energy density was obtained for PVK:DCNP system and it was around 4.5 mJ/cm^2, the best temporal stability was found for PMMA:DCNP system and was estimated to around 30 000 pulses. The highest gain coefficient was estimated to 15 cm^{-1} and it was reported for DNA-CTMA matrix.

Acknowledgements
The authors wish to thank Wroclaw University of Technology and Polish Ministry of Education and Science (grant no. N N507 475237 research project "Iuventus Plus" IP2010 0277 70) for financial support.

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THE DYNAMICS OF THE NO_2 GROUP IN THE SOLID - CONSEQUENCES FOR ITS THERMODYNAMIC STABILITY AND PROPERTIES

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Nitroaromatics are known to exhibit properties that are interesting for application. They can be found among pharmaceuticals, explosives, dyes and pigments and materials potentially useful in optoelectronics. They often crystallize in polymorphic forms. For industrial purposes it is extremely important to control the polymorphism as polymorphic forms of a compound differ in their properties. Crystal structures and molecular packings of substituted nitrobenzenes with substituents able to form strong hydrogen bonds (i.e. hydroxyl, amino and carboxyl groups) and substituents not able to form strong hydrogen bonds (e.g. nitro groups, halogen atoms and others) have been studied. The experimental as well as theoretical methods of the investigations have been used: multi-temperature X-ray crystal structure analysis including the rigid body analysis of anisotropic displacement parameters, quantum chemical calculations at different levels of theory, computer crystal structure prediction and crystal structure retrieval from the CSD. The results are consistent about the occurrence of attractive intermolecular interactions between nitro groups. The interactions even seem to compete with hydrogen bonding in the crystals of the *ortho* isomers of nitroanilines and nitrophenols, i.e. hydrogen bonds between nitro oxygen atoms and amino or hydroxyl groups. Especially in the crystals of nitroanilines the hydrogen bonds are relatively weak, though their impact on the crystal architecture is crucial[1].

Large amplitude torsional vibrations of nitro group's oxygen atoms constitute another aspect of the interactions. The vibrations seem to be a driving force of polymorphic transformation in nitrophenols and nitrobenzoic acids. The transitions occur at temperatures above ambient and preserve intermolecular hydrogen bonds. The vibrations are responsible for large thermal expansion along the direction of the oxygen atoms' displacements. The vibrations lie in the frequency range of lattice vibrations and they can couple along the direction of close intermolecular contacts and have an impact on crystal properties[2].

The problem has been studied in the case of 1,3-dinitrobenzene, an optically nonlinear material. The crystal's nonlinear optical susceptibility results from high hyperpolarizability of 1,3-dinitrobenzene molecule. The quantum chemical calculations at different levels of theory proved that the vibrational contribution to the molecular hyperpolarizability is predominant as compared with the electronic counterpart. The calculations also showed that the normal mode connected with torsional vibrations of two nitro groups has the main contribution to the vibrational part of the molecular hyperpolarizability. The calculated mechanical and electrical anharmonicity corrections to the vibrational hyperpolarizability have been found to be substantially larger than lowest-order harmonic terms and correspond to the direction of the largest thermal expansion in the crystal. The interactions between nitro groups seem to be the most relevant for material properties of 1,3-dinitrobenzene[3].

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SOLVENT EFFECTS ON TWO-PHOTON ABSORPTION SPECTRA OF ORGANIC COMPOUNDS

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Solvent effects on linear absorption spectra are well known and have been broadly investigated for a variety of molecular systems. The solvent effect (solvatochromism) is defined as a change in position and, in some cases, shape of the UV/Vis absorption band related to the polarity of the solvent where given molecule is dissolved [1]. Changes of the molar absorption coefficients also ensue. Depending on the properties of an investigated molecular system it is possible to observe so called bathochromic shift (red shift) as well as hypsochromic shift (blue shift) with increasing solvent polarity [1].

It has been theoretically suggested that solvent effects should be observed also in two-photon spectroscopy [2]. Recently such observations were reported, but until now the phenomenon of two-photon solvatochromism is relatively poorly investigated [3-5]. Furthermore, there are not many consistent investigations nor attempts to explain it in terms of theoretical models of two-photon absorption.

In the present work our preliminary investigations varied out for model dipolar molecules are introduced. On the basis of Z-scan measurements and a variety quantum chemistry calculation methods the preliminary findings for gas phase and representative solvents are presented. Experimental nonlinear spectra were obtained using the Z-scan technique, where a single Gaussian laser beam is used to measure the transmittance of a nonlinear medium both through an aperture (resulting in determination of nonlinear refraction) and without aperture (nonlinear absorption) as a function of the sample position with respect to the focal plane [6,7]. The experimental results are supported by quantum chemistry calculations based on *ab-initio* and Density Functional Theory methods.

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QUANTUM-MECHANICAL INVESTIGATIONS OF DISSOCIATIVE IONIZATION OF THE METHIONINE MOLECULE

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Proteinogenic amino acids, which methionine belongs too, are those that can be found in proteins widely used as biomimetic materials. On the other hand, the methionine is used to evaluate various metalobacitracin complexes, therefore the properties of this molecule, especially those leading to dissociative ionization/fragmentation, are very important in understanding and explaining the processes occurred in proteins.

Quantum-mechanical and experimental studies on the methionine molecule fragmentation are performed with a special emphasis given to the determination of the appearance energies for the ionized fragments. Such data are of specific interest in view of tracing the possible consequences of the live tissue interaction with ionizing radiation.

Theoretical investigations were performed by means of the generalized gradient approximation for the exchange-correlation potential in the density functional theory (DFT) as it is described by Becke’s three-parameter hybrid functional, using the non-local correlation provided by Lee, Yang, and Parr (B3LYP method) [1]. The cc-pVTZ basis set has been used as well [2].

An experiment was carried out using a crossed-beam technique combined with the mass separation of electron-molecule interaction products. Measuring procedure was fully automated using the PC control. We have determined the energy dependences of the ionized fragment yield with the 0.1 eV energy step and the <0.5 eV (FWHM) energy resolution in the energy range from the threshold up to 100 eV. Application of a special least-square fitting procedure enabled the absolute values of the appearance potentials for the fragments under study to be found. Since the initial molecule may undergo strong fragmentation due to the thermal processes, the special studies of possible temperature-induced destruction of the methionine molecule were carried out as well.

It has been found that among the main ionic fragments of the initial $C_5H_{11}NO_2S$ molecule one may note $C_2H_5S^+$ (m=61 a.m.u), $C_3H_6N^+$ (m=56 a.m.u.), $C_4H_7NO_2^+$ + $C_4H_7NS^+$ (m=101 a.m.u.), and $C_3H_7S^+$ (m=75 a.m.u.). We have determined the appearance potentials for the above ionic fragments presented in Table 1 as compared to the calculated values.

Table 1. Theoretically (E_t) and experimentally (E_{ex}) determined appearance potentials (in eV) for the positively charged fragments of the D-methionine molecule.

Fragment	$C_3H_6N^+$	$C_2H_5S^+$	$C_3H_7S^+$	$C_4H_7NO_2^+$;$C_4H_7NS^+$	$C_4H_{10}NS^+$
E_t	12.04	12.52	11.83	7.91	10.01
E_{ex}	12.0±0.1	12.5±0.1	–	7.5±0.1	9.7±0.1

Based on the theoretical results obtained it has been predicted that the $C_4H_7NO_2^+$ fragment should be the ionic fragment of the initial $C_5H_{11}NO_2S^+$ (multiplicity=2) molecule cation, while other fragments should be the ionic fragments resulted from the excited neutral molecule decay.

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COVALENTLY COUPLED MULTI-DMABI HROMOPHORES: SYNTHESIS, LINEAR AND NONLINEAR OPTICAL PROPERTIES

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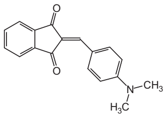
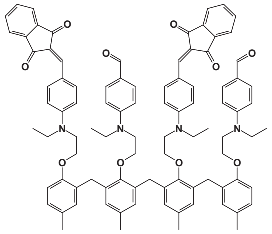
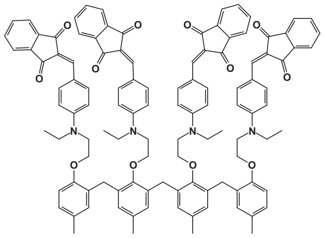
Over last two decades there is a stable interest to make use of organic molecular materials in a wide variety of nonlinear optical (NLO) applications [1]. Typically search for such material is based on development of chromophore with large first hyperpolarizability β. At the same time extent of material overall NLO efficiency is very much dependent on spatial arrangement of chromophores - they should be acentrically aligned and number density of them should be as high as possible. Unfortunately these two prerequisites are contradicting - molecules with large β possess a high dipole moment and tend to aggregate in cetrosymetrical, NLO inactive, structures. The DMABI chromophore (see figure), which possesses remarkably high NLO activity [2] and all optical poling capability [3] is in a scope of our research for many years. In spite of moderate dipole moment aggregation of DMABI strongly influence linear and nonlinear optical properties of host / guest polymer films [2,4]. To increase number density of active chromophores one could try to covalently bind them together in such a way that centrosymmetrical aggregation of individual chromophores are ruled out. Forming of such multiple chromophores could yield in formation of dipolar, octupolar or mixed NLO active molecular structures. Within this investigation multi-DMABI chromophore molecules (see figure) have been synthesized and studied by means of quantum chemical calculations, absorbance and fluorescence spectroscopy and hyper Rayleigh scattering (HRS) techniques.



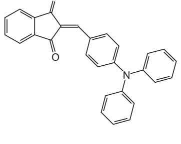
DMABI



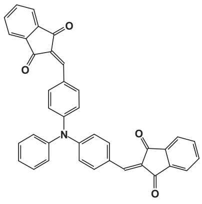
MtetraP-diDMABI



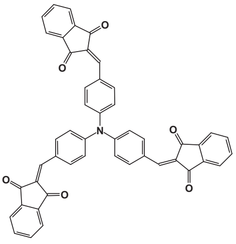
MtetraP-tetraDMABI



TPA-monoDMABI



TPA-diDMABI



TPA-triDMABI

Figure 1. Structures of investigated compaunds

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LINEAR AND NONLINEAR OPTICAL PROPERTIES OF BINUCLEAR RUTHENIUM (II) COORDINATION COMPLEX DNA PROBES

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Third-order nonlinear optical properties of some binuclear coordination complexes of ruthenium (II) (Fig. 1) and their interaction with oligonucleotides of specified sequence composition are reported. DNA in stretched films when equilibrated at 75% or 100% relative humidity (r. h.) adopts either A or B type conformation. [1]. Transition dipole moments of homochiral ΔΔ- and ΛΛ-Ru when interacting with DNA revealed differences in binding angles with respect to humidity conditions. Large differences are also detected when guanine/cytosine (GC) or adenine/thymine (AT) ratio is varied in oligonucleotides. Thus, selectivity of ΔΔ-Ru and ΛΛ-Ru towards specific DNA regions may serve as a model for designing sequence-selective DNA-binding drugs [2]. The investigated Ru complexes provide the possibility of performing *in vivo* research on cancer treatment through two-photon absorption in the infrared (IR) region where cells and tissues are not damaged by long light irradiation [3]. To evaluate the suitability of these ruthenium(II) complexes their nonlinear optical properties were investigated using an amplified femtosecond tunable laser setup (a Quantronix Integra regenerative amplifier and a Quantronix Palitra optical parametric amplifier). Z-scan measurements performed on solutions of the complexes revealed large values of the two-photon absorption cross section in both intra-ligand charge transfer (ILCT) and ligand to metal (MLCT) charge transfer regions. This makes the investigated ruthenium (II)-based compounds excellent candidates for further analysis in the context of potential utility in biology and medicine.

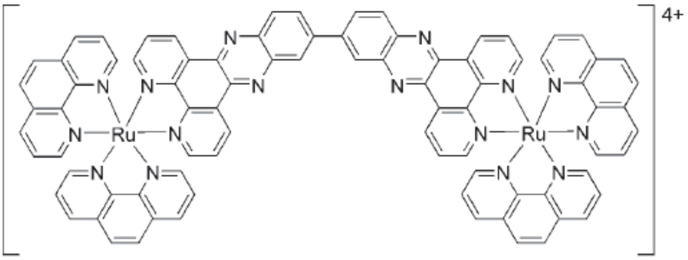

Figure 1.Structure of the ruthenium complex [-bidppz(phen)$_4$Ru$_2$]$_4$

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MODELLING OF PHOTOCHROMIC PROPERTIES OF BENZOXAZINE COMPOUND BY MEANS OF QUANTUM CHEMICAL METHODS

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Photochromic compounds are light-sensitive molecular systems which exhibit changes of absorption properties during photoinduced processes. Changes in absorption spectrum indicate energy transfer and structural transformations of the system [1], which are reversible (by thermal dissipation or by photoexcitation of a different wavelength) in most cases. Possible applications of such compounds include molecular-scale electronics and high density data storage [2].

Here are presented the results of quantum chemical calculations of structural and electronic properties of photochromic indolo[2,1-b][1,3]benzoxazine compound. Spectral measurements upon the excitation of this compound show the presence of two distinct chromophoric groups in the system, which are created by breaking C-O bond of the oxazine ring in the initial complex [3]. Within few hundred nanoseconds system reverts back to the ground state. Molecular structure and excitation properties of the complex and its subgroups are determined using several quantum chemical methods. The calculations were performed using Gaussian03 and GAMESS-US programs.

Structure optimization of benzoxazine compound was performed using density functional theory (DFT) with B3LYP functional and two different basis sets (6-31G(d) and 6-311G(2d,p)). In addition to the optimal ground state geometry three local minima (representing variants of broken-up structure, see Fig. 1) were located, as well as transition points in the ground state potential surface. Geometric structure of molecular subgroups in the system – 3H-indolium and 4-nitrophenolate anion – was optimized using the same method and basis sets. Electron-energy states for all compounds were obtained using several methods, including time dependent DFT (TD-DFT), GUGA-CIS and ZINDO. Calculation results in vacuum and using polarization continuum solvent model (PCM), with acetonitrile acting as solvent, were also compared. Theoretical absorption spectra of the initial compound and its subgroups in ground state, based on TD-DFT calculations, agree fairly well with experimental observations.

Optimal geometry of benzoxazine compound in lowest active excited state was calculated using CIS method and 6-311++(2d,p) basis set; it was found to be similar to the geometric structure of the complex in first local ground state energy minimum. Changes to absorption spectrum caused by the deformation of the complex approaching the excited state energy minimum were shown to be in correspondence with experiment results in time range of 200 fs to 725 fs.

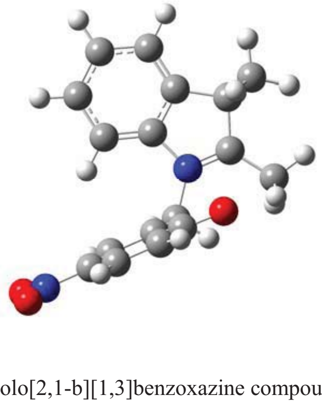

Figure 1. Structure of indolo[2,1-b][1,3]benzoxazine compound with open oxazine ring

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TEMPERATURE IMPACT ON PHOTOISOMERISATION OF CARBOXYL GROUP AZOBENZENE MOLECULES

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Azobenzene molecules are used in different optical fields, for example, photoinduced switches and holographic recording of refractive or surface relief grating [1,2]. In these cases the process may be arisen by photoisomerization mechanism of azobenzene molecules. At the same time photoorientation process may take place. Temperature could play important role in understanding of the photoinduced processes in host – guest films [3].

Our investigation is dedicated to thermal impact of photoisomerisation of carboxyl group containing azobenzene molecules **A-45** (see. Fig.1) in thin films. Polymer films with 1, 3, 5, 10, 15 and 20 wt% **A-45** molecule concentration were made by spin – coating method. Polymethilmetacrylate (PMMA) was used as a polymer and chloroform as a solvent. Film thickness was between 0,5 and 3 µm. Maximum of optical density of *trans* isomer at 360nm was recorded as a function of time by irradiating the sample with 360 nm (absorption band of *trans* isomer) and 450 nm (absorption band of c*is* isomer) wavelengths at different temperatures. The dependence of response time and changes of optical density and temperature of host – guest films with different concentration of azobenzene derivative will be analyzed in the work.

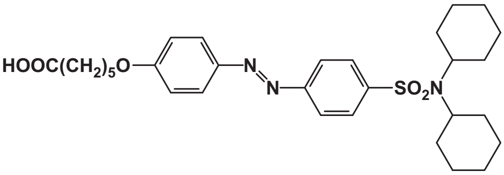

Figure 1. (6-[4-(4-Dicyclohexylsulfamoyl-phenylazo)-phenoxy]-hexanoic acid)

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NONLINEAR OPTICAL PROPERTIES AND HUMIDITY EFFECT IN BACTERIORHODOPSIN FILMS FOR HOLOGRAPHIC RECORDING

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Bacteriorhodopsin (BR), a light-driven proton pump and photoreceptor protein from *Halobacterium salinarum* is an outstanding photonic material for optical applications due to its multifunctional properties [1-3]. Upon absorption of visual light, BR molecule undergoes reversible light-induced transitions through a series of photocycle intermediates (K, L, M, N, O). These intermediates in turn are photoactive. The initial state of BR has an absorption peak at 570 nm, and the long-lived intermediate M is strongly blue-shifted, it has an absorption peak at 412 nm [4]. This large shift, photoreversibility of reactions, photoanisotropic response [1, 3] and accompanying refractive index changes constitute a basis for application of BR as a recording holographic material. It is known that humidity strongly affects the photoreactions of BR. We proposed the humidity-holography method in which a small cell for humidity variations containing a BR film was mounted inside the holographic set up [5].

In this work, we studied the effects of light intensity and humidity on nonlinear optical properties and dynamic holography recording in BR films. We found that humidity exerts a dramatic influence on the holographic parameters of BR films from its effects on yield and lifetime of the M intermediate. In light-adapted BR films, the highest value of the diffraction efficiency is observed at the humidity values of 96-99%. Both the peak and steady-state values of the diffraction efficiency kinetics are reduced with decreasing humidity. This is particularly pronounced at 96-99% humidity where the peak and steady state values of the diffraction efficiency are greatly reduced upon incubation in the dark. We suggested that illumination of the BR film at this humidity resulted in increased water content in the film. The holographic parameters are more stable in the dark in the 90-93% range of humidity.

The average decay time of the photobleached intermediate M depends on the intensity of actinic 632 nm light which does not excite M. We have shown that M decay time, τ, decreases with increasing the He-Ne laser recording intensity, I. It might be connected with the light-induced hydration of BR film since the M decay time is faster at humidity values of 96-99% than at lower humidity. The existence of $\tau(I)$ results that τ is modulated in space for the intensity grating (only light intensity is modulated in space), whereas the spatial modulation of τ is practically absent for the polarization grating (only light polarization is modulated in space). A comparison of the experimental ratio of the diffraction efficiencies of intensity and polarization gratings as a function of the recording intensity with calculated one is very sensitive technique to study the intensity-dependent decay (recovery) time not only in BR but in other optical material too. We propose to control a data storage time in optical memory systems with BR by varying the light intensity of recording beams and humidity.

We revealed that nonlinear optical properties of BR film which emerge only in Raman-Nath thin holographic grating allowed the real-time selection based on the object motion velocity. It is possible to select a particular motion velocity by choosing the recording beam intensity or humidity value in the tiny cell containing the BR film. We show that certain modifications and mutation (E204Q) enhance useful features of BR films.

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