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Workshop on Progress in Nanotechnology and Optoelectronics will take place at Lodz University of Technology, International Faculty of Engineering (IFE). The building is located on the A campus of the University of Technology. The main entrance to the building is located on the inner side of the campus. The campus has four entrances: the Żwirki street entrance, the Żeromskiego street entrance, the Wólczańska street entrance and the Radwańska street entrance. Paid car park with a limited number of slots is located near to the Politechnika avenue.

PROGRAM

Thursday 25 April 2019

08:30 – 09:50	Registration and Welcome coffee
09:50 – 10:00	Welcome and opening
	Functional nanomaterials I (chair – Jacek.Ulański)
10:00 – 10:40	Krzysztof Matyjaszewski *Molecular engineering of nanostructured materials by Reversible Deactivation Radical Polymerization*
10:40 – 11:05	Adam Proń *Ternary and quaternary inorganic semiconductor nanocrystals for electronics and biomedicine: core and surface engineering*
11:05 – 11:30	Stefan Jurga *Multifunctional nanomaterials for biomedical applications*
11:30 – 11:50	Coffee break
	Functional nanomaterials II (chair – Marcin Kozanecki)
11:50 – 12:15	Francesca Nanni *Multifunctional polymeric composite materials for 3d printing: the scenario in industry 4.0*
12:15 – 12:40	Andrzej Galeski *Nanomechanisms of plastic deformations of polymers*
12:40 – 13:05	Marcin Stępień *Curvature vs. π-conjugation: new routes to chiral and low-bandgap systems*
13:05 – 14:30	Sandwich lunch
	Synthesis of organic semiconductors (chair – Małgorzata Zagórska)
14:30 – 15:10	Klaus Müllen *Graphene nanoribbons - merging the conjugated polymer and graphene worlds*
15:10 – 15:35	Yingping Zou *High performance polymer solar cells*
15:35 – 16:00	Pierre Audebert *New insights in tetrazines and heptazines chemistry; synthetic improvements and original properties in fluorescence and photoactivation*
16:00 – 16:20	Coffee break
	Simulation and models (chair – Piotr Polanowski)
16:20 – 16:45	Andrzej Sikorski *Dynamics in complex macromolecular systems. Simulations with the dedicated parallel machine ARUZ*
16:45 – 17:10	Zbigniew Klusek *Graphene hybrid systems. Physics and applications*

17:10 – 17:35	Marek Szymański *Inverse problems in organic electronics*
17:40 – 19:40	Poster session
20:00 – 22:30	Official dinner for invited speakers and guests

Friday 26 April 2019

	Molecular Optoelectronics I (chair – Tomasz Marszałek)
09:00 – 09:40	Anna Köhler *Describing charge separation in organic semiconductors*
09:40 – 10:05	Juliusz Sworakowski *How accurate are energies of HOMO and LUMO levels in small-molecule organic semiconductors determined from cyclic voltammetry – continuation*
10:05 – 10:30	Eric Daniel Głowacki *Abundant organic semiconductor catalysts for a peroxide clean energy cycle*
10:30 – 11:00	Coffee break
	Molecular Optoelectronics II (chair – Heinz Bässler)
11:00 – 11:40	Paul Blom *Charge injection and transport in organic semiconductors*
11:40 – 12:05	Wojciech Pisula *Organic ultrathin transistors interconnecting Lodz and Mainz*
12:05 – 12:30	Jasper Michels *Structuring in thin-film solutions upon liquid-vapour mass exchange*
12:30 – 12:55	Jiří Pfleger *Organic Electronic Memory Devices: How to make advantage from unwanted behavior*
12:55 – 14:30	Sandwich lunch
	Molecular Optoelectronics III (chair – Jarosław Jung)
14:30 – 15:10	Marek Samoć *The use of upconversion processes in nanosystems for biological and theranostic applications*
15:10 – 15:35	Andy Monkman *Thermally activated delayed fluorescence from exciplexes, how dilution increases performance*
15:35 – 16:00	Luiz Pereira *Efficient design of OLEDs structure: electrical carrier transport and recombination*
16:00 – 16:30	Coffee break
	Simulation and models (chair – Piotr Polanowski)

16:30 – 16:55	Xinliang Feng *Polymer synthesis enabled by interfaces: towards a world of organic 2D materials for electronics*
16:55 – 17:20	Jean-François Gérard *Nanostructuration of polymers from assembling ionic liquids and metal-oxo clusters*
17:20 – 17:45	Malgorzata Jakubowska *Graphene composites in biomedical applications*
18:00 – 19:00	Meeting of Polish Platform for Printed Electronics
18:00 – 20:00	Poster session
20:30 – 23:00	Informal dinner

Saturday 26 April 2019

Department of Molecular Physics Alumnae & Co-workers – Overview

Session DMP I (chair – Lidia Okrasa)

09:00 – 09:15	Piotr Polanowski *Investigation of diffusion limited aggregation in frame of the dynamic lattice liquid model*
09:15 – 09:30	Jeremiasz K. Jeszka *Properties of polymer brushes obtained using Controlled Radical Polymerization – Monte Carlo simulation studies*
09:30 – 09:45	Gisèle Boiteux *Segregated polymer-carbon nanofillers composites with specific thermal and electrical properties*
09:45 – 10:00	Ireneusz Glowacki *Solution-processed OLEDs*
10:00 – 10:15	Jarosław Jung *Technology of Real-World Analyzers (TAUR)*
10:15 – 10:30	Aleksandra Wypych-Puszkarz *Functional materials investigated by means of broadband dielectric spectroscopy*
10:30 – 10:45	Marcin Kozanecki *Photo and thermal stability of Ag nanoparticles stabilized by sodium citrate*
10:45 – 11:00	Marcin Pastorczak *Femtosecond infrared pump – stimulated Raman probe spectroscopy (fs-IR-SRS): the method and its first application to study vibrational relaxation pathway in liquid water*
11:00 – 11:20	Coffee break

Session DMP II (chair – Ireneusz Głowacki)

11:20 – 11:35	Piotr Cywinski *A day in the life of a patent examiner*

11:35 – 11:50	Andrzej Rybak *Polymer composites for energy applications: challenges and opportunities*
11:50 – 12:05	Lidia Okrasa *Relaxation processes in macromolecules with complex structure*
12:05 – 12:20	Olivier Siri *Metallo-oligomers synthesis: from solution to surface*
12:20 – 12:35	Tomasz Marszalek *Organic Field Effect Transistors from a lab scale to the potential application*
12:35 – 12:50	Beata Luszczynska *Organic photodetectors - examples of devices with fast time response and high responsivity*
12:50 – 13:05	Jacek Ulanski *Recent progress in printed OLEDs*
13:05 – 13:15	Closing remarks
14:00 – 17:00	Informal party

THURSDAY 25.04.2019

Molecular engineering of nanostructured materials by Reversible Deactivation Radical Polymerization

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Many advanced nanostructured functional materials were recently designed and prepared by controlled/ living radical polymerization. More than 100 million tons of polymers are produced annually world-wide by conventional radical polymerization. However, macromolecular engineering is impossible in this process. Copper-based ATRP (atom transfer radical polymerization) catalytic systems with polydentate nitrogen ligands are among most efficient controlled/living radical polymerization systems. Recently, by applying new initiating/catalytic systems, Cu level in ATRP was reduced to a few ppm. ATRP of acrylates, methacrylates, styrenes, acrylamides, acrylonitrile and other vinyl monomers was controlled by various external stimuli, including electrical current, light, mechanical forces and ultrasound. ATRP was employed for synthesis of polymers with precisely controlled molecular architecture with designed shape, composition and functionality. Block, graft, star, hyperbranched, gradient and periodic copolymers, molecular brushes and various hybrid materials and bioconjugates were prepared with high precision. The organic/inorganic hybrids have excellent optoelectronic and thermomechanical properties. These hybrids provide access to new materials for application related to biomedicine, environment, energy and catalysis.

Ternary and quaternary inorganic semiconductor nanocrystals for electronics and biomedicine: core and surface engineering

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Colloidal semiconductor nanocrystals consist of an inorganic core to which organic ligands are attached assuring their colloidal stability and for this reason they can be considered as organic-inorganic hybrides. Physical properties of these nanoobjects depend on the size, shape and composition of the inorganic core and the type of the stabilizing surfacial ligands [1].

In the past 20 years, large majority of reports on colloidal semicoductor nanocrystals were devoted to binary nanocrystals (CdSe, CdS, PbSe, PbS) containing toxic elements. More recently it turned out that these toxic binary nanocrystals can be successfully replaced by Cd- and Pb-free stoichiometric (Cu (Ag)InS(Se)$_2$) and alloyed (Cu(Ag)-In-S(Se)) nanocrystals. Ternary (CuFeS(Se)$_2$) and quaternary ($Cu_2ZnSnS(Se)_4$) nanocrystals which do not contain indium - one of the most expensive elements used in modern electronics - have also been prepared [2,3].

In the presented lecture different methods of the nanocrystals preparation will be comparatively discussed as well as methods of the primary ligands identicfication. Special emphasis will be put on the exchange of the initial ligands for electroactive ones - an instructive case of nanocrystals stabilized with oligoanilines capped with different anchoring groups (thiol, carboxylic, amine) [4] will be described in detail.

Examples of the use of these organic/inorganic hybrids as components of thermoelectric materials [5,6] or drug carriers capable of recognizing cancer cells [7] will be given. Additionally, their surface functionalization in view of various applications of nanocrystals in bioimaging will be discussed.

Acknowledgement: we wish to acknowledge financial support from the National Science Centre, Poland (NCN, Grant No. 2015/17/B/ST4/03837).

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Multifunctional nanomaterials for biomedical applications

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Dedicated to Professor Jacek Ulański on his 70th birthday anniversary.

Nanotechnology became an important field in innovative medical science. Development of specifically designed “intelligent” nano-carriers introduced the concept of targeted therapy which in principle aims at dramatic reduction of side-effects by accurate and selective treatment of the diseased tissue. This approach can be done by incorporation of active ligands on nanoparticle (NP) for recognition of biological receptors [1]. Moreover, NPs due to their large surface area, provide excellent platform for further functionalization. Accordingly, it is possible to fabricate multifunctional nanoplatforms [2-4] by combining both multimodal imaging and therapeutic agents. Among contrast agents, the most frequently used are for instance gadolinium compounds [5] for Magnetic Resonance Imaging or photoluminescent species [6] for optical imaging methods. Interestingly, superparamagnetic NPs alone can act as a contrast agent [2] and might be utilized as drug-carrier or a tool for localized hyperthermia. Furthermore, specifically designed nano-carriers can exhibit a) desirable and controlled release profile of bioactive agents (coating chemistry), b) prolonged blood circulation time, c) improved delivery of therapeutics across biological barriers, and d) multiple receptor targeting. All abovementioned features provide significant opportunities for the next-generation health care strategies and therefore intensified inquiry and developments are required in the field of nanomedicine.

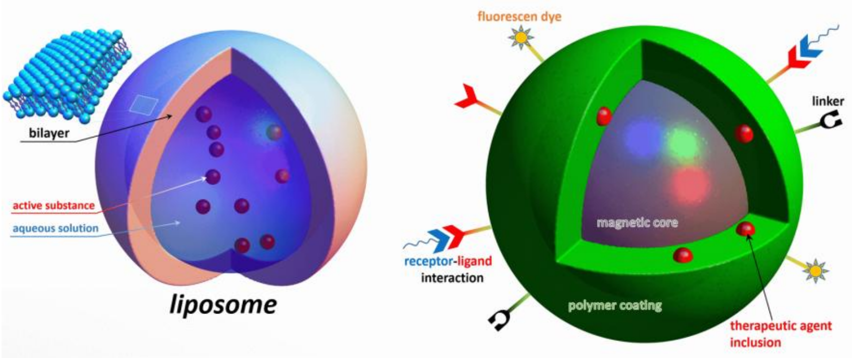

Figure 1: Schematically illustrated two possible nano-carriers: liposome and multifunctional nanoparticle.

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Multifunctional polymeric composite materials for 3d printing: the scenario in industry 4.0

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In past years the advent of fast growing innovative industrial scenarios, as those concerning Industry 4.0, resulted in a strong and prompt impulse towards the research of new "intelligent" or "multifunctional" materials, also referred as advanced materials, that are part of the so called key enabling technologies (KETs). Such materials are characterized by dispalying a major property (usually linked to the structural behaviour), together with additional chemical-physical properties, that make them able to offer unique functions as self-healing, self-monitoring, IR reflective properties, and so on.

Parallel to material innovation, another KET, which is additive manufacturing (AM), burst out among the advanced processing technologies. AM is characterized by the unique feature of producing a piece by adding the material only where it is needed, making possible the realization of innovative mechanical designs thus producing lighter components using less material. The combination of processing multifuncional materials with AM is nowadays showing to become a promising successfull sinergy in view of realizing smart structures.

Polymers and their composites are the most common mutlifunctional materials, due to their intrinsic versatility. The addition of fillers and/or the molecular manipulation of the polymeric chains can allow to reach new properites. A possible success key to technological transfer is therefore the formulation of bespoken materials to suit specifications in each industrial case. As it mostly happens, however, it is hardly possible to find or prepare a material that perfectly suits all design needs, as solutions are usualy a trade-off between opposite trends. As an example, some properites, as electrical conductivity, thermal conductivity or others can be achieved in polymers by adding specific fillers/nanofillers, that, however, usually impact other properties , as ductility or toughness. Such modifications on mechanical properties cannot be usually accepted in the mechanical design, where the primary structure function has to be guaranteed. Following a cyclic procedure, however, the mechanical design can be adjusted to some extent or changed to permit the use of the new material, provided that the new shapes can be succesfully manufactured. Here is where AM plays a role, as the freedom of processing turns into design freedom and, thus, in the end, in the possibility to use the new materials.

Recently, some examples of technological transfers of multimaterials processed via 3d printing have been achieved, concerning the use of technopolymeric (i.e.PEEK) composites with magnetic, electrical and thermal properties for space applications.

Moreover the 3d printing of rubbers is attempted in view of preparing energy harvesting and IR reflective materials, whereas they have already been successfully obtained via conventional rubber process.

Nanomechanisms of plastic deformations of polymers

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Plastic deformation of amorphous polymers is the most peculiar among all materials. The plasticity is achieved by a series of crack-like events in a micrometer range, called crazes, which are, however, span by nanofibrils that are transferring the stress and preventing for fracture.

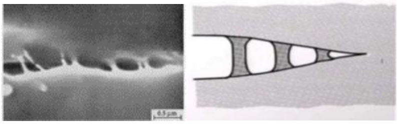


Figure 1. Nanofibrils, called tufts, are composed of bundles of highly elongated macromolecules.

The other important mechanisms of plastic deformation of a polymer is by shear banding, a strongly localized deformation in planes tilted at 45° with respect to the tensile force.

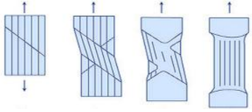


Figure 2. Development of high orientation by progressive shear banding in tensile deformation.

Often non-homogeneous deformation is caused by co-existence of both forms. Those two mechanisms are not excluding each other.

Most of commodity polymers are crystalline materials with unique structure of lamellar crystals arranged parallel in stacks with alternating amorphous layers, both entities having thickness in a nanometer range. It is in the interlamellar regions that the initial stage of deformation takes place. It follows that stress required to initiate deformation of amorphous phase constitutes from 2 to 10% of the stress needed to activate the mechanisms of crystalline phase deformation. However, yielding concerns exclusively the polymer crystals and it sets in when the stress exceeds yield stress. Mechanism for yielding of semicrystalline polymers consists an emission of dislocations from the edges of the lamellae across the narrow faces and their travel across crystals via crystallographic slips.

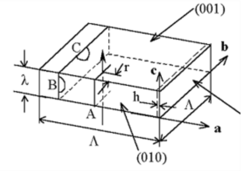


Figure 3. Types of dislocations generated at polyethylene lamellar crystals: A monolithic screw, B screw half loop, and C edge half loop [1].

The crystal thickness is then a crucial parameter for monolithic screw while not for half loops. Dislocation theory predicts the correct order of magnitude of the yield stress that agrees best for the Burgers vector of dislocations for various polymer crystals. However, there are experimental evidences that the yield stress of semicrystalline polymers depends not only on crystal thickness but also on the degree of crystallinity.

Recently [2, 3] it was shown that plastic yielding of semicrystalline polymers is greatly affected by the state of their amorphous phase. Changes made to the amorphous phase such as addition of low molecular fraction, swelling, additional entanglements, which does not affect crystalline phase, causes deformation of lamellae stacks, however, there is no expansion of stacks along lamellae basal planes while stretched chains of amorphous phase generate uniaxial tension transmitted to lamellae surfaces. It appears that measured yield stress plus the stress exerted by amorphous phase amounts exactly to the stress required for plastic deformation of crystals, therefore the yielding is determined by the same crystal plasticity despite different external load. The changes to amorphous phase may account to explanation why yielding depends on crystallinity degree.

It appeared that one of the main nanomechanisms of plastic deformation of crystalline polymers is cavitation during stretching. Cavitation nanopores are formed within amorphous interlamellar layers having initially the size less or equal to layer thickness (5-20 nm). They grow during stretching, finally contributing to as much as 20-100% of the initial material volume. The detailed studies [3, 4] indicated that the cavitation nanopores are initiated and formed from free volume pores of the amorphous phase.

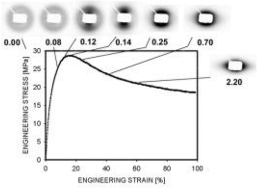
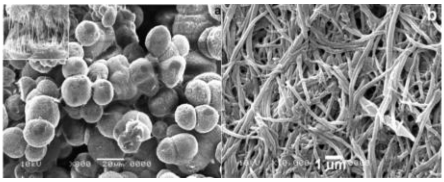


Figure 4. Cavitation seen as stress whitening, is also observed in SAXS (small angle X-ray scattering). Strong SAXS reflections appear around the yielding during stretching of polyethylene [5]. SAXS patterns recorded *in situ* at Hamburg synchrotron facilities.

Plastic deformation of polymers is strongly impeded by entanglement of macro-molecules. Free drawing is restricted by strain hardening and fracture resulted from stretching of entanglement network. There are ways of preparation of crystalline polymers devoid of most of entanglement knots. Such crystalline polymer can be easily drawn via dislocation-crystallographic slips to very high deformation ratio. The plastic flow can be so easy that grains of disentangled polymer embedded in another viscous media can be deformed into nanofibrils by shearing.



Figures 5. SEM images of grains of disentangled polypropylene and of nanofibrils after shear deformation during compounding of disentangled polypropylene grains with polystyrene [6]. Polystyrene matrix was removed by dissolution in toluene.

There are several independent nanomechanisms of plastic deformation of polymers: crazing, shear bands, crystallographic slips and cavitation. Entanglement of macromolecules, its density can be controlled and then it influences all elementary mechanisms of plastic deformation. By intensifying or restricting those mechanisms we obtain new materials with new properties.

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Curvature vs. π-conjugation: new routes to chiral and low-bandgap systems

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Curved π-aromatic systems are of significant current interest because of their theoretical appeal, synthetic challenge, and practical implications of non-planar aromatics for materials science [1]. This talk will highlight two approaches to curved aromatic molecules explored by our group. The first one, based on the so-called fold-in method, attempts to transform cyclophane-like macrocycles into aromatics with various curvature types, ranging from bowl-shaped molecules (e.g. **1**, Figure 1), [2,3] through planar systems,[3,4] to hyperbolically distorted coronoid macrocycles (**2**).[5] The other approach involves the use of the recently developed donor–acceptor pyrrole blocks[6] to construct helicene-like chromophores and fluorophores (**3**, **4**).[7,8]

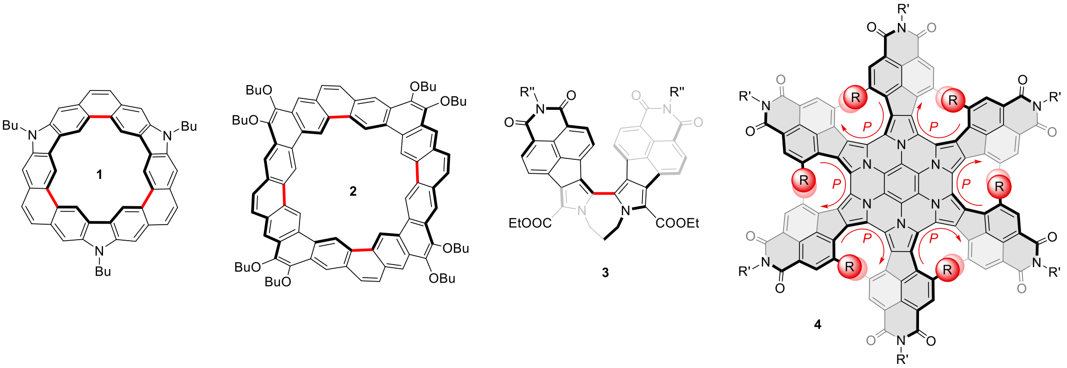

Figure 1: Examples of nonplanar aromatics developed by our group

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Graphene nanoribbons – merging the conjugated polymer and graphene worlds

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Graphenes and graphene nanoribbons (GNRs), their geometrical cutouts, are exciting additions to the rich carbon family. Graphenes hold enormous promise, for example, in energy technologies and non-linear optics. However, before they can be employed in electronics and their high charge-carrier mobility be utilized in field-effect transistors (FETs), an opening of their band gaps must be achieved. The best answer to this longstanding problem are GNRs, and this brings precision polymer synthesis into play. While protocols from lithography or unzipping of carbon nanotubes offer no control over length, width and edge structure, bottom-up synthesis is the method of choice.

We present unprecedented syntheses proceeding in, both, solution and on-surface. The latter approach, which can be scaled up by extension from UHV-conditions to chemical vapor deposition, also allows in-situ monitoring and proof of GNR-formation by scanning tunneling microscopy.

Based on these material breakthroughs, we fabricate FETs from single GNRs and GNR-networks and compare the performance with that of conventional conjugated polymers. Surprisingly, the design of GNRs with appropriate combinations of arm-chair and zig-zag edges furnishes robust topological insulators in 2D as well as spin states with high correlation times. There is hope that these features provide entries into spintronics and even quantum computing.

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High performance polymer solar cells

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Although polymer solar cells have witnessed significant advances during the past few years, improving the power conversion efficiency (PCE) is still an ongoing challenge to overcome. Here, we summarize our two most recent work in polymer donors and nonfullerene acceptors (NFAs). We synthesized a series of fluoroquinoxaline based polymer donors. Most of polymers showed over 10% efficiency with high Voc and high FF. For NFAs, we reported a facile method, where electron affinity is delicately tuned by introduction of multifused benzotriazole or benzothiadiazole into non-fullerene acceptors. Nonfullerene solar cells based on acceptors with DAD fused ring core exhibited a low voltage loss below 0.6 V and high short-circuit current density above 22.0 mA cm-2, resulting in over 14% efficiency with single-junction organic cells. These unconventional benzotrizole/benzothiadiazolebased non-fullerene acceptors with near-infrared absorption lead to low non-radiative recombination loss, which follows the common criteria for high efficiency solar cells. More importantly, a new record PCE of 12.6% was certified and added to the most recent National Renewable Energy Laboratory chart of “Best Research-Cell Efficiencies”.

New insights in tetrazines and heptazines chemistry; synthetic improvements and original properties in fluorescence and photoactivation

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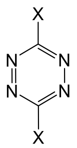
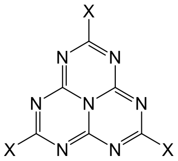
Tetrazines, and the far more enigmatic heptazines, which count much less described examples, are among the most electron deficient high-nitrogen content, stable aromatic heterocycles (Fig. 1). This peculiarity confers them very original physico-chemical characteristics, including frequently delayed fluorescence, a high electrochemical reduction potential, and so on.

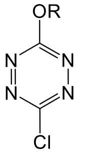


s-tetrazines

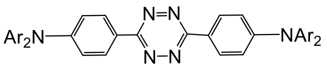


heptazines

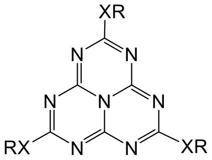
This lecture will present the fluorescence and electrofluorochromism of several tetrazine families (1-3), and finally introduce a new synthetic approach of original heptazines possessing exchangeable groups by nucleophilic aromatic substitution (4). Examples featuring the molecules concerned are gathered in the Scheme 1 below.



s-tetrazines for
electrofluorochromism



s-tetrazines for
2PA



new heptazines
X = S or NR

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Dynamics in complex macromolecular systems. Simulations with the dedicated parallel machine ARUZ

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In general, intracellular and extracellular environments are usually densely crowded and contain different elements such as lipids or proteins [1]. Theoretical studies of dynamics of such systems require special simulation algorithms. We present the applications of the Dynamic Lattice Liquid (DLL) model. Studies of molecules' movement in crowded environments by means of extensive Monte Carlo simulations were carried out. Two-dimensional coarse-grained model is supposed to mimic a lateral motion of probe molecules in a membrane. The systems studied contained obstacles that were fixed or underwent Brownian motion; they can also be formed of flexible chains [2]. For this purpose two mechanisms of molecular transport were employed: Single Agent Model where the motion of an object is considered as a random walk without any correlation with other moving elements [3] while the second model of motion was based on the DLL model, which was built on the cooperative movement concept [4]. Simulations were partially carried out on a dedicated machine ARUZ located in BioNanoPark in Łódź. This machine was designed for simulations that enable studies of large systems, i.e. consisting of ca. 5 million objects for ca. 10^{10} time steps [5]. The conditions at which anomalous diffusion appeared in the system were analyzed. The influence of obstacles mobility, size and concentration on the static and dynamic percolation threshold was shown. The mobility of objects, critical exponents and the shape of molecules trajectories were also studied. The impact of the mechanism of transport on the dynamics of such systems was suggested.

This work was supported by the Polish National Science Center (NCN) grant UMO-2017/25/B/ST5/01970.

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Graphene hybrid systems. Physics and applications

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Graphene is the first discovered 2D material which demonstrates linear dispersion relation similar to mass-less relativistic particles described by the mass-less Dirac equation. It shows very high carrier mobility and extremely low intrinsic spin-orbit coupling (SOC) together with absence of band gap and high electrical conductivity which causes limited application of this material in spintronics and optoelectronics. Recently, this drawback has been overcome by the application of different 2D materials in combination with graphene i.e. graphene van der Waals heterostructures have been extensively investigated.

In the presentation we show the basic physical properties of graphene, layered transition metal dichalcogenides (TMDCs) and selected topological materials. Then the methods of creation and experimental/theoretical characterization of van der Waals heterostructures will be briefly outlined. Finally we show application of graphene/transition metal oxide heterostructures in OLED devices. The presentation is thought as a non-mathematical introduction to 2D systems, topological matter and heterestructures.

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Inverse problems in organic electronics

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An inverse problem in science is the process of estimating, from a set of measurements, the physical parameters that produced them. In emerging electronics, often only measurements on complete devices are available. They are determined by physical parameters such as interfacial barriers, charge carrier mobilities, and trap state distributions. When these parameters cannot be directly determined, it is of interest to estimate their values by solving inverse problems.

Such estimation is, however, not trivial. In the first place, it needs a correct mathematical model of the measurement. This requires both carefully performed experiments and accurate simulation of the measurement. Then, the inverse problem is not guaranteed to have an unique solution and global optimization strategy must be employed to search through solution space.

In the talk, introduction to the topic of inverse problems, from the perspective of R&D on emerging electronic devices, will be given, with examples of solving inverse problems involving measurements on organic photovoltaic devices [1].

This work was supported by the Swedish Knowledge Foundation for the KKS SYNERGY project 2016 "BIO-QC: Quality Control and Purification for New Biological Drugs" (grant number 20170059).

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FRIDAY 26.04.2019

Describing charge separation in organic semiconductors

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In organic solar cells, light absorption by a donor materials and subsequent electron transfer from the donor excited state to an acceptor at a donor-acceptor interface creates coulomb bound charge transfer states. Their separation efficiency controls the performance of the solar cell. In this talk, I shall adress the energies of charge transfer states can be derived from spectroscopy, which binding energy they have, and how they separate.[1,2] I may also comment on how these states actually from the photoexcited donor. [3]

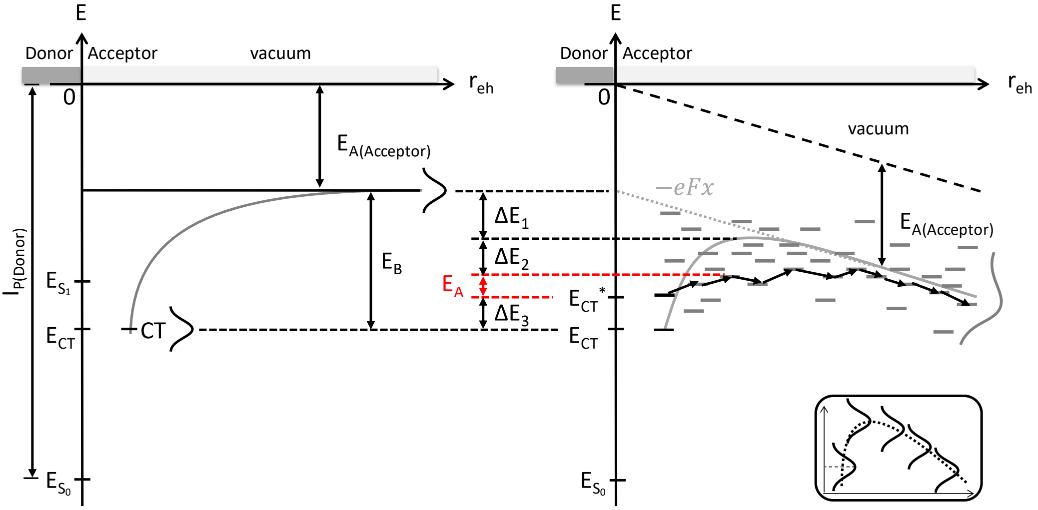

Figure 1: Energy level scheme to account for the difference between the binding energy EB of the CT state and the thermal activation energy E_{act} required for dissociation. From [1]

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How accurate are energies of HOMO and LUMO levels in small-molecule organic semiconductors determined from cyclic voltammetry - continuation

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Energies of ionized levels, i.e. of the levels allowed for excess holes and excess electrons (commonly referred to as HOMO and LUMO, respectively) are key parameters characterizing organic electronic materials. These energies can be directly probed by the photoelectron spectroscopy techniques: UV photoelectron spectroscopy (UPS) for occupied levels, and inverse photoelectron spectroscopy (IPES) for unoccupied levels. The techniques, however (and IPES in particular), are unavailable in most laboratories synthesizing novel materials, hence an electrochemical method, cyclic voltammetry (CV) has been widely used for this purpose. Being an indirect method, CV has a serious limitation: to yield reliable results, it requires a proper calibration.

Based on results published in the literature, we have shown [1] [2] that the correlation equations commonly employed to determine energies of the ionized levels from CV experiments are incorrect. Consequently, the energies of the HOMO and LUMO levels, and hence the energy gaps (energy differences between HOMO and LUMO levels) determined by CV ('electrochemical gaps', Δ^{CH}) differ from those determined by UPS and IPES ('transport gaps', Δ^{EL}). Moreover, we have shown that the general correlation, including all available data obtained for various groups of compounds is burdened with a spread which may be as large as seval tenths of eV. More trustworthy correlations can be obtained for classes of chemically similar molecules.

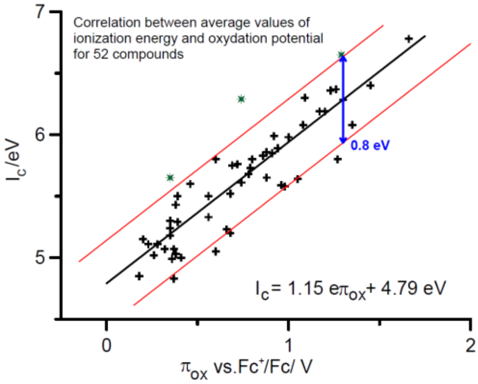

Figure 1: A general correlation between oxidation potentials and solid-state ionization energies.

This work was financed from the subsidy of Polish Ministry of Science and Higher Education for the statutory activity of the Chemical Faculty of Wrocław University of Science and Technology.

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Abundant organic semiconductor catalysts for a peroxide clean energy cycle

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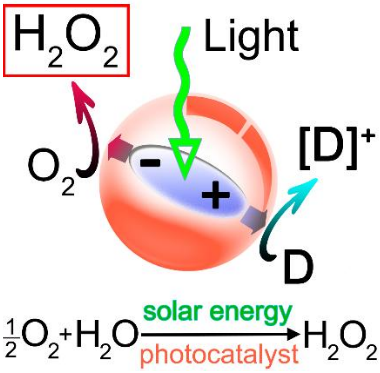
Semiconductor-based catalysts can convert solar energy into chemical fuels such as hydrogen, hydrogen peroxide, or hydrocarbons produced via carbon dioxide reduction. Long overlooked due to stability concerns, some organic semiconductors have recently emerged as excellent electrocatalysts and photocatalysts for stable operation in aqueous environments. We have found that organic semiconductors have, in general, a high selectivity for the two-electron reduction of oxygen to hydrogen peroxide. We find this occurs on numerous organic semiconductors [1-5] and conducting polymers [6] with outstanding stability in a pH range from 1 to 12. The possibilities of solar energy conversion into the high-energy molecule H_2O_2 enabling carbon-neutral energy storage in liquid form, in contrast to gaseous H_2, will be discussed [7]. Finally, I will cover recent results on purely photocatalytic systems, where hydrogen peroxide or hydrogen is produced reductively while various substrates are oxidized, including water to oxygen – showing that organic semiconductors can support the complete water splitting reaction.



$$\tfrac{1}{2}O_2 + H_2O \xrightarrow[\text{photocatalyst}]{\text{solar energy}} H_2O_2$$

Figure 1: Scheme showing photocatalytic reduction of oxygen to hydrogen peroxide, with concurrent oxidation of various electron donors

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Charge injection and transport in organic semiconductors

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Organic semiconductors are used in optoelectronic devices, such as organic light-emitting diodes, organic and perovskite solar cells, and organic field-effect transistors. The performance of such devices depends heavily on charge injection and transport. Here, we describe a universal strategy to create Ohmic contacts on organic semiconductors, even with ionization energies of up to 6 eV. The method is based on the use of an interlayer that causes electrostatic decoupling of the electrode from the semiconductor, while establishing alignment of the Fermi level with the energy levels of the organic semiconductor. This method to create Ohmic contacts enables us to characterize charge transport in a large range of of organic semiconductors. From these measurements we are able to extract important parameters, such as the charge-carrier mobility, energetic disorder and the molecular site spacing. These experimental parameters are then compared to theoretical multiscale simulations, which compute these parameters considering the molecular arrangement and electronic interaction between the molecules. Excellent agreement is found between experiment and theory, which paves the way for predictive charge-transport simulations from the molecular level.

Organic ultrathin transistors interconnecting Lodz and Mainz

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The first few semiconducting layers next to the dielectric interface are of vital importance, because they dominate the charge carrier transport of the device. At certain conditions it is possible to solution process organic semiconductor films in a monolayer precision. This allows to vary the film thickness from submonolayer to mulitlayers to systematically study the microstructure formation and charge carrier transport at the semiconductor/dielectric of the organic semiconductor in a field-effect transistor. In this context, it has been proven that the first monolayer has also essential importance for the microstructure evolution of the bulk film. This microstructure in turn is necessary for creating the required percolation pathways for the charge carriers in transistors. A further important aspect is the structural inhomogeneity of the semiconducting films. This is presentation it will be reported that the interfacial microstructure of organic semiconductors near the dielectric has a minor impact on the charge carrier transport [1]. The concluded transport mechanism is based on a by-passing of the interfacial smaller domains by the charge carriers through ordered larger domains within the multilayers. Interestingly, these findings are valid for a broad range of organic semiconductors which are crystalline or semi-crystalline, and for films deposited from solution or sublimated.

This work was supported by the National Science Centre, Poland, through the grant UMO-2015/18/E/ST3/00322. We acknowledge the BL09 beamline at DELTA synchrotron in Dortmund for the support in the GIWAXS measurements.

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Structuring in thin-film solutions upon liquid-vapour mass exchange

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Organic and hybrid thin film electronic devices, such as memory diodes, photovoltaic devices and transistors, typically contain a functional layer based on a blend of multiple polymeric or small-molecular species whose properties cooperatively give rise to a specific function. Depending on the desired functionality, phase separation during thin film solution processing is either encouraged or suppressed. Due to the fact that mutual repulsion often overcomes the entropic driving force to form stable mixtures in solution, droplet-like demixed morphologies may emerge due to (spontaneous) liquid-liquid (L-L) demixing. Besides, the performance of many devices depends on a high charge carrier mobility, usually achieved via crystallization, i.e. liquid-solid (L-S) demixing. Since device performance critically depends on the micromorphology of the active layer, it is of paramount importance to understand how structure evolution during such phase transitions is affected by mass exchange across the liquid-vapor boundary (Figure 1a), i.e. evaporation and condensation [1]. In this contribution I will communicate our recent insights on how the coupling between evaporation and condensation with other dynamic processing variables affect morphology evolution during L-L and L-S phase transitions. We employ a numerical multi-component-multi-phase model [2,3] that reproduces experimental thin-film microstructures (Figure 1b,c). The computational results allow for process design, based on quantification of the interrelations between internal and environmental factors in determining the final microstructure, especially with respect to phase domain size and shape, as well as composition.

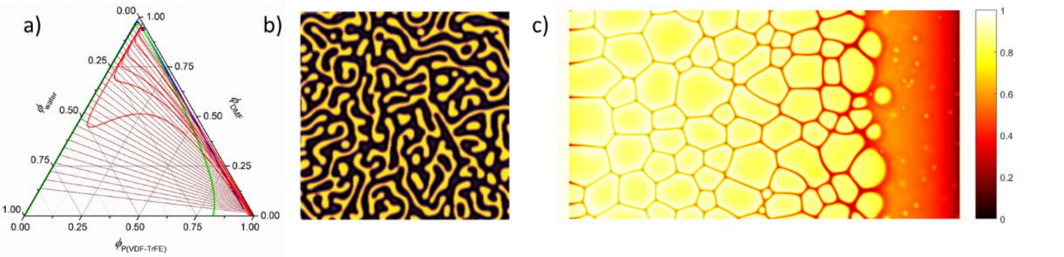

Figure 1: a) Ternary phase diagram (polymer/water/solvent) with calculated composition trajectories (red) due to simultaneous solvent evaporation and water condensation; b) simulated morphology in a polymer:fullerene blend; c) simulated spherulitic crystallization in a concentration gradient.

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Organic Electronic Memory Devices: How to make advantage from unwanted behavior

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Electronic memory represents an indispensable part of most electronic circuits. For some applications, like RFID tags used for smart packaging, for manufacturing and warehouse automation or security systems, simple low-level performance devices are required, which could be produced by a cheap large scale production technology, as e.g. printing. Resistive-type memory elements (ReRAM) made from switchable resistive organic materials can fulfill such requirements. Electrical bistability usually arises from changes of the intrinsic materials properties, such as charge transfer, phase changes, conformation changes or redox state, in response to an applied electric field [1-5]. The basic memory cells can be integrated into a cross-point memory array, where each memory cell is unambiguously identified by its x and y coordinates, suitable for easy programming and reading the addressed cell.

We focused on resistor-type memory (ReRAM) made from soluble polymer materials, in which data are stored as different electrical conductivity states. We show a simple organic memory based on thin films of molecularly-doped polymer based on soluble derivatives of polydiketopyrrolopyrroles mixed with a soluble low-molecular weight derivatives of perylene. The commercially available poly[2,5-(2-octyldodecyl)-3,6-diketopyrrolopyrrole-alt-5,5-(2,5-di(thien-2-yl)thieno [3,2-b]thiophene)] (DPPDTT) was used as a hole transporting soluble polymer matrix with 2-diethylaminopropyl perylene (Per-2DEAPA) acceptor additive, and a multilayer structure was prepared on the ITO bottom electrode with DPPDTT:Per-2DEAPA bottom layer, thin insulating layer with admixed Au nanoparticles, and upper layer of DPPDTT:Per-2DEAPA, completed with an Al top electrode. Poly[2-cyanoethyl(vinyl)ether (CEPVA) was used as a polymer insulator, having a high value of the dielectric constant ($\varepsilon_r = 15$), and Au nanoparticles prepared by laser ablation in ethanol with average diameter 8 nm. Laser ablation was selected for nanoparticles preparation since it provides surface of nanoparticles not contaminated by chemical products. The structure shows pronounced hysteresis in its current voltage characteristics. Depending on the composition, the maximum achieved ON/OFF ratio was about 10^3 with writing/erasing voltage +/-5 V and reading at applied 0.5 V. The functionality of the structure as rewritable resistive memory is well documented on repeated read/write cycles and a retention time exceeding several hours. There are several assumptions made to explain these effects based on the charge transfer mechanism, stabilization of the space charge trapped on metal nanoparticles by the interaction with dipolar cyanoethylether groups ($p = 12 \times 10^{-30}$ C m), and also the formation of conductive filaments cannot be excluded as suggested in recent literature [6].

A single component polymer rewritable resistive memory was prepared using a newly synthesized poly(N-(3-(9H-carbazol-9-yl)propyl)methacrylamide) sandwiched as a thin film between ITO and Al electrode. The polymer was prepared by a radical polymerization of the N-(3-(9H-carbazol-9-yl)propyl)methacrylamide using azobisisobutyronitrile as a radical initiator. The starting monomer was obtained by three-step reaction from carbazole. The molar mass of the polymer was influenced in limited extent by the reaction temperature but it was still relatively low (M_w = 6000). However, film forming abilities were sufficient, particularly in thin films (typical thickness used in the memory elements was below 100 nm). The polymer is stable at higher temperatures up to 300 °C, glass transition temperature of the polymer is 130 °C.

The device showed good and repeatable hysteresis in I-V characteristics with switching effect, maximum ON/OFF ratio was ~ 200. A typical write/erase cycle is shown in Fig. 1 which proves a good retention time exceeding 2 hours even during permanent reading in both ON and OFF states. Here, writing was at the applied voltage +5 V erasing with -5 V and reading at 0.5 V (sign refers to the polarity of the ITO electrode). After some initial instability during memory element forming, the ON and OFF current was stable during more than 40 repeated write/erase cycles..

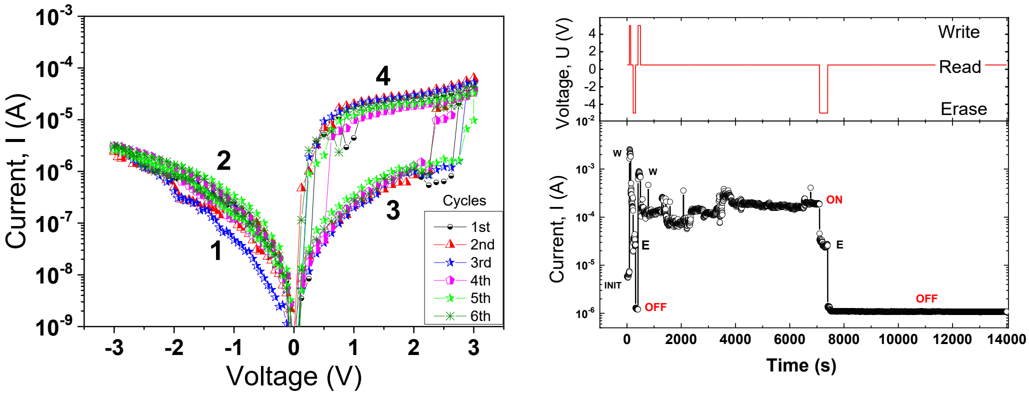

Figure 1: A typical V-A characteristic (left) and write/erase cycles (right) of the resistive memory element based on poly(N-(3-(9H-carbazol-9-yl)propyl)methacryl- amide) thin film sandwiched between Al/ITO electrodes.

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The use of upconversion processes in nanosystems for biological and theranostic applications.

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The oxygen molecule, which in its ground state has two unpaired electrons and therefore is a triplet, $^3O_2$, under certain circumstances can be excited to a singlet state, $^1O_2$. The singlet oxygen is one of the so-called reactive oxygen species (ROS) that play important role in many biological processes and can be used as a basis of photodynamic therapy of cancer, or for photoinactivation of disease causing bacteria.

The singlet oxygen can be generated by employing absorption of light by dyes called photosensitizers, however, there are limitations concerning the use of such dyes in practical applications. Our research groups have decided to investigate the possibilities of using more complex approaches to generation of ROS at the required site, using electromagnetic radiation from the so-called biological windows, which is weakly scattered and absorbed by tissues. The phenomena enabling such possibilities are nonlinear optical (NLO) effects and/or photon upconversion effects that can be obtained in specially engineered nanosystems containing lanthanide ions. The crucial feature of our approach is that the various species that are responsible for absorption, upconversion and photosensitization as well as for luminescence that can be used to monitor the photodynamic therapy, are co-encapsulated into specially crafted nanocarriers of suitable sizes that are additionally functionalized to provide optimal behavior upon application.

We have studied systems where the role of NLO absorbers is played by quantum dots which are encapsulated inside oil-filled containers [1] as well as systems where the cargo inside the nanocapsules contains lanthanide-ions-doped inorganic nanoparticles which are effective upconverters that can be used with cw diode lasers [2]. Co-encapsulation of NLO upconverters with photosensitizers has led to proof-of-principle theranostic (therapeutic+diagnostic) nanocarriers that showed efficient generation of reactive oxygen species upon excitation in the near infrared as well as good luminescent properties [3]. In the case of coencapsulation of upconverting nanocrystals (containing ytterbium and thulium ions) with photosensitizer (verteporphin) it was also shown that the ROS generating nanocapsules could be obtained in an environmental friendly, sustainable manner. [4]

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Termally activated delayed fluorescence from exciplexes, how delution increases performance

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Efficient design of OLEDs structure: electrical carrier transport and recombination

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Development of efficient Organic Light Emitting Diodes (OLEDs) in a simplest possible structure that can be minimally efficient for practical applications, is, nowadays a challenge. Due to the substantially different electrical carriers mobility and some mismatch of HOMO and LUMO energy levels for p and n-type organic semiconductors, is very difficult to make OLEDs with low number of layers that can be technological competitive. Moreover, the usual and sometimes abnormally high density of defects acting as carrier traps, poses additional issues. Nevertheless, achieving substantially high external quantum efficiencies (for instance up to 12 – 14 %) with only three or even two organic layers is possible as our current work shows. Although employing highly efficient emitters like Thermally Activated Delayed Fluorescent (TAFD) materials, the drawbacks are placed in the electrical properties related with charge transport and recombination. Focusing as the most important target, the idea of a well electrically balanced device should be used for an efficient device structure.

Considering the intrinsic physical models for electrical charge transport that are mobility and trap dependent, it is possible to estimate by simulations the electron and hole densities in a multilayer device structure, as a function of the fundamental properties of the organic semiconductors used and the relationship with different layers thickness. Including the expected voltage barriers at layers interface, a fully functional model for prediction of charge density (electrically balanced device) and recombination region (targeting high exciton density in the active layer) was obtained. The model as successfully tested in a simple three layer OLED with several possible structure design, using TXO-TPA (red TADF) as emitter.

Extending the model to solution deposited OLEDs, we was able to achieve efficiencies comparable to the more complex multilayer structure employing the same TADF emitter. Specifically, with TXO-TPA (three organic layers device) and with 2PXZ-OXD (in only two organic layers device), an EQE up to 16% and 8% respectively was obtained, that in spite of a little less values than reported in thermally evaporated devices with similar emitters, exhibits a particular interesting figures of merit.

The idea can be further discussed as a practical concept for understanding the effects of intrinsic electrical and molecular structural properties of organic emitters in the final device design.

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Polymer synthesis enabled by interfaces: towards a world of organic 2D materials for electronics

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Interface has been playing a key role in most “bottom-up” synthesis methods and is advantageous for directing the orientation of the molecules or precursors. By looking back at the history, the interfacial synthesis has been largely developed for the controlled polymer synthesis, which can be dated back to 1930s by Gee et al who achieved polymer monolayers at an air-water interface. Typically, the reactions at the interfaces between air-water (or gas-liquid), liquid-liquid, liquid-solid and gas-solid (or vacuum-solid) have been explored to offer paramount control over the morphology and the structure of polymers. While the synthetic linear polymers and cross-linked polymers are the main resultant structures in the historic interfacial polymer synthesis, it turns out only in recent years that a controlled 2D covalent reaction can take place if a finely designed interface is provided. A subsequent consequence of adsorption, nucleation, arrangement and polymerization of suitably designed precursors or intermediates, guided by a confined 2D geometry of interface, can yield a structurally well-defined, periodic organic 2D material such as 2D polymer.

In this lecture, we will present our recent efforts on the bottom-up synthetic approaches towards novel organic 2D materials with structural control at the atomic/molecular-level or at the meso-scale. First, we will introduce the latest development on the synthetic 2D conjugated polymers including 2D Schiff-base type covalent polymers and 2D metal-dithienene/diamine coordination polymers at the air-water or liquid-liquid interfaces. The resulting 2D conjugated polymers exhibit single- to multi-layer feature, good local structural ordering and with a large size. The functional exploration of such 2D conjugated (coordination) polymers for the electrical, magnetic and mechanical properties, as well as serving as efficient electrocatalytic water splitting catalysts will be demonstrated. Next, we will introduce the self-assembly of a host-guest enhanced donor-acceptor interaction, consisting of a tris(methoxynaphthyl)-substituted truxene spacer, and a naphthalene diimide substituted with N-methyl viologenyl moieties as donor and acceptor monomers, respectively, in combination with cucurbit[8]uril as host monomer toward monolayers of 2D supramolecular polymers at liquid-liquid interface. Third, we will present the supramolecular approaches to synergistically control the multi-component assembly, which results into 2D conducting polymers, such as polypyrrole and polyaniline nanosheets featuring 2D structures and with adjustable mesopores with/without on various functional free-standing surfaces. The unique structure with adjustable pore sizes (5–20 nm) and thickness (35–45 nm), enlarged specific surface area as well as high electrical conductivity make 2D conducting polymers promising for a number of applications. Finally, we will present a controlled synthesis of few-layer 2D polymer crystals on the water surface assisted by soft templates; we achieved micrometer-sized either horizontally or vertically grown 2D polyamide crystals by tailoring templating layers. The future perspective and outlook regarding the goal towards highly crystalline organic 2D materials will be also provided.

Nanostructuration of polymers from assembling ionic liquids and metal-oxo clusters

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Thermoset polymers such as epoxies are widely used as matrices of fiber-reinforced composites, coatings, encapsulants, and adhesives in aerospace, aeronautics, automotive industry, etc. Nanostucturation of those polymer networks allows to design high performances materials as combined functionalities could be introduced at nanoscale from the use of nanobuilding blocks (NBB) such as metal-oxo clusters, i.e. polyhedralsilsesquioxanes, POSS, and/or ionic liquids.

The nanostructuration from hybrid organic-inorganic nano-objects such as POSS proceeds from self-assembling processes occuring before the 3D polymerization (crosslinking) or via a (nano)phase separation phenomena during polymerization resulting from the competition between the reaction kinetics and the thermodynamics of phase separation [1]. A higher controlled nanostructuration for POSS-based networks consists in synthesizing organic-inorganic block copolymers (BCP) based on an inorganic-rich POSS-based block which results from the polymerization of a reactive POSS such as POSS-methacrylate [2-5]. In this case, from a proper selection of the ligands of the POSS cubes, the POSS-based blocks will self-assemble in inorganic-rich nanostructures inside the polymer network.

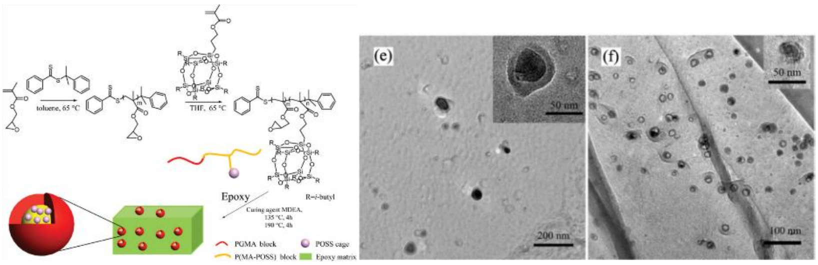

Figure 1. (a) Synthesis of PGMA macro-CTA and PGMA-b-P(MA-POSS) BCP via RAFT polymerization and the model of core–shell nanostructure formation for BCP in an epoxy matrix; (b) SEM morphologies of epoxy network nanostructured with 10 wt% of copolymer [4]

A second type of nanostructuration of polymer networks is the assembling of ionic liquids from a (nano)phase separation process. Ionic nanostructures as dispersed nanodomains or spider web-like nanophases could be generated from the proper selection of cation/anion pair and chemical architecture of these counterparts [6-10]. For example, phosphonium based ionic liquids combined with phosphinate, carboxylate, and phosphate counter anions could be considered. Due to the presence of ionic nanostructures formed by the ionic liquid within the thermoset networks, these ones could combine series of functionalities such as a high surface hydrophobicity, an excellent thermal stability (i.e. above 350 °C), and an improved deformation ability, as well as a thermomechanical behavior tuned from the chemical structure of ILs. In addition, ILs were considered to be inserted in the network from its participation to the cationic polymerization of epoxies or from the synthesis of epoxy-functionalized ionic liquids which can be copolymerized with diamines [8-10].

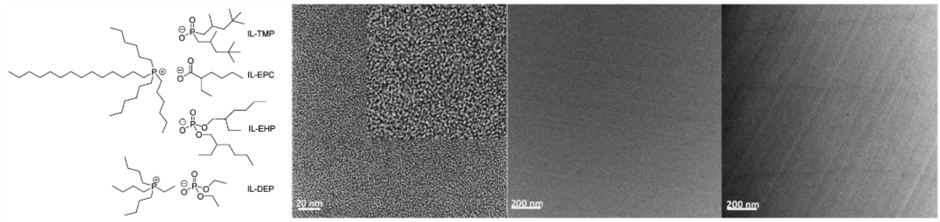

Figure 2. (a) Phosphonium-based ionic liquids considered to modify (b) epoxy networks (TEM micrographs)(10 phr for phosphinate and 30 phr for phosphate)[9]

More recently, ionic liquid-modified POSS were synthesized (Figure 3) and introduced in polymer networks such as epoxies [11]. The IL-g-POSS nanoclusters appears to be well dispersed in polymer networks synthesized by copolymerization of a diepoxy prepolymer and a cycloaliphatic diamine as spherical or ellipsoïdal inorganic-rich nanophases (from 10 to 80 nm)(Figure 3). The existence of these ionic organic-inorganic nanostructures induces a significant enhancement of the fracture properties and of the thermal stability (400 vs 300 °C), including large fire retardancy improvement.

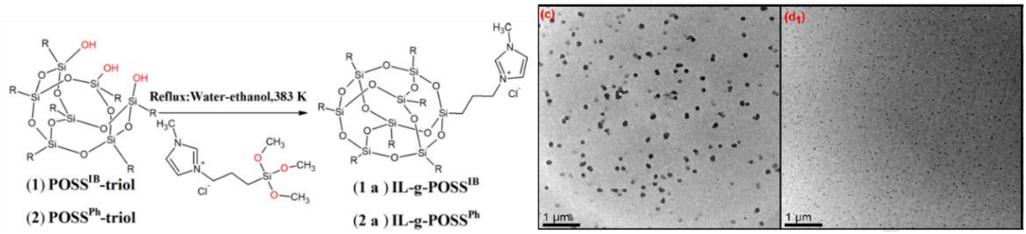

Figure 3: Synthesis of IL-grafted POSS and TEM micrographs of epoxy networks with 5 wt.% of (a) of POSS triol and (b) IL-g-POSS [11]

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Graphene composites in biomedical applications

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The use of printed electronics technics such screen printing, spray coating ink-jet printing and aerosol jet printing with the simultaneous use of the special prepared conductive, heterophasic inks, allows to production of various layers and coatings as well as systems for biomedical application. We are presenting a number of such applications: from antibacterial layers, through various sensors, to electronic tattoo for wireless human pulse measurement and electrodes for stimulation of rabbits nerves.

First of all through printed electronics technology, various sensors can be manufactured. Ranging from physical quantities such as temperature and pressure to chemical properties like pH or concentration of numerous compounds – printed sensors allow monitoring of many aspects of health or biological processes – both in mobile, point-of-care and laboratory manner.

Such a significant interest in printed electronics techniques in biomedical applications results from the ability to print on non-flat surfaces with high resolution. It allows to manufacture many applications in systems and sensors for medicine. Another of the applications of aerosol printed paths characterized by high electrical conductivity are connections made on optocycles used for optogenetics.

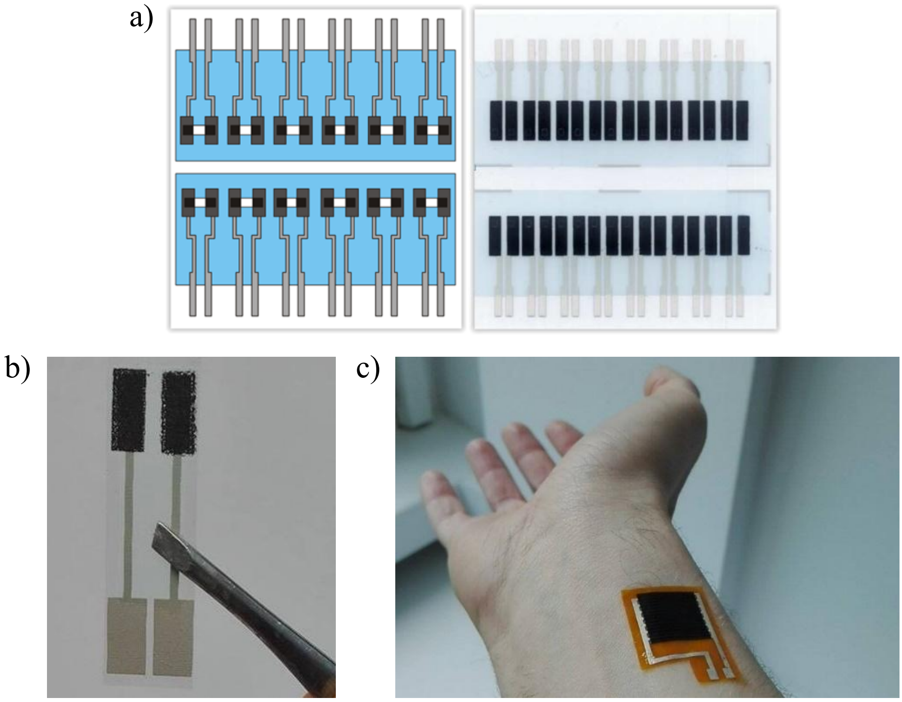

Figure 1. a) the urease sensor; b) electrodes for pH-metric sensors; c) electronic tattoo.

Moreover produced by us layers and coatings can by use for stimulation of cell growth. Conductive layers can be used for electrostimulation of the human cells. Coatings are also antiseptic, capable of blocking the procedure of bacterial biofilm formation and reducing the risk of urological infections.

Manufacturing of systems and coatings for biological applications is possible only using special materials – the biological inks. This materials should meet both engineering and biological requirements. First of all the ink cannot be toxic to the cells, thus biocompatibility of inks is a required characteristic. However, it is equally important that the ink is easily printable. Therefore, it must meet the rheological requirements such as suitable viscosity and surface tension and must exhibit good stability and particle dispersion. The stabilization of the particles in the suspension is actually the key of good ink formulation. All of above mentioned conditions can be achieved by selecting the correct ink composition.

Composite suspensions used for printing electronic components with ink-jet printing technique, called heterophasic inks, consist of two main materials: the functional phase and the binder. The functional phase influences the physical properties of the ink and determines the deposited layer functionality e.g. electrical conductivity. The binder plays the role of the matrix for the functional phase, and is responsible for the ink rheology and adhesion of printed layer to the substrate.

Special, biocompatible functional phase, which has attained an enormous popularity in the recent times is a carbon nanomaterial – graphene. Graphene exhibits unique electronic, mechanical, thermal and optical properties and is distinguished by high surface area to volume ratio. Moreover it characterized by antibacterial activity and low toxicity to human cells. Therefore graphene is promising candidates for biomedical applications. It can be implemented in various applications in diverse fields of science, not only in electronics but also in materials technology, nanomedicine and tissue engineering.

SATURDAY 27.04.2019

Investigation of diffusion limited aggregation in frame of the dynamic lattice liquid model

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Stochastic models of fractal growth have inspired a number of studies and applications in physics, biology, chemistry, nanotechnology, medicine, metallurgy and others domains. The best known model of fractal growth is the diffusion-limited aggregation (DLA) which was introduced in the early 1980s by Witten and Sander [1, 2]. It is very popular because it contain the main features of the random growth using very simple definition. The importance of the DLA model for the physics of structure growth is comparable to the Ising model in the theory of phase transitions. The dynamical rules for DLA are simple but the patterns produced are complex and have thus far defied full theoretical understanding. The stochastic growth rules can be couched in terms of random walk dynamics. Usually the initial conditions is a single seed particle at the origin. The growth of the aggregate occurs one particle at a time and proceeds by starting the first particle at a random position on the "birth circle". This particle does a random walk, until it either drifts out to the "death circle", or comes in contact with the particle at the origin. If it contacts the particle at the origin, it sticks and the aggregate grows. If it reaches the death circle, it is reborn at a random point on the birth circle and the process is repeated until the particle sticks. Described scenario assumes that the fractal grows in medium being an infinity dilute solution. Moreover problem with time scale matching occurs because in one time quanta (regarded as one particle trail) only one particle can be touches to the cluster. It seems to be strange in real situation with finite concentration of particles in solution. Above assumptions lead to difficulties of investigation of fractal growth dynamics and indicate a need for another scenario to model dynamic behavior of this phenomena.

The DLA process can be readily modeled using the DLL simulation, provided that an appropriate rule is added to take into account the particle-particle aggregation. At the beginning of the simulation one rest particle (C) is introduced to the system to act as aggregation seed. The system contains two kinds of moving particles (A) built up fractal cluster units with average concentration ρ and (B) inert solvent with concentration $1-\rho$. When diffusing A particle becomes the nearest neighbor of the rest particle C, they sticks. It leads to the cluster growth by transforming the A specie into C-type rest particle. Because DLL algorithm is parallel several particles can sticks in the same time. To describe structural properties of growing cluster and their behavior in time, some characteristic quantities such as mass of the cluster, radius of gyration, distribution of mass in distance form center of mass, autocorrelation functions of particle of the cluster and fractal dimension of the cluster are monitored.

Properties of polymer brushes obtained using Controlled Radical Polymerization – Monte Carlo simulation studies

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Polymer brushes i.e. ensembles of chains grafted on plain solid surfaces, nanoparticles or pore surface attract attention since many years. They are interesting from theoretical point of view and can find many practical applications[1-9]. An often used method of synthesizing such polymer systems is controlled radical polymerization, in particular atom transfer radical polymerization (ATRP). Usually the initiator is anchored to the surface in a separate process and then the polymerization is carried out (grafting-from method).

Properties of such brushes are different form the model systems in which all the chains have the same length. Simulation of the polymerization and subsequent relaxation of the obtained can be helpful in understanding the effect of various parameters on the properties of synthetized materials.

Segregated polymer-carbon nanofillers composites with specific thermal and electrical properties

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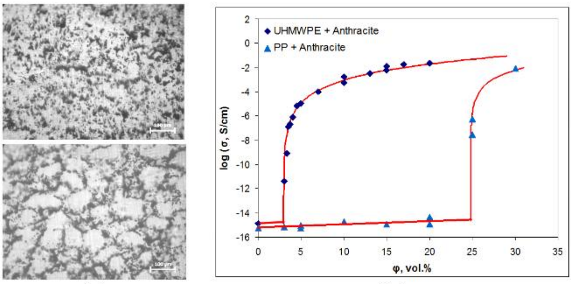
Conductive polymer composites (CPC) play important role in various areas of electronic industry due to their distinguished properties. However, CPC with random distribution of conductive particles within the polymer matrix require high values of the filler content (more than 10 vol. %) to achieve high conductivity. However, such high filler content can significantly worsen the mechanical properties and manufacturing processes. Segregated polymer composites (SPC) can be a good solution for this problem. In SPC conductive filler creates an ordered framework in polymer matrix. The local concentration of filler φ_{loc} in the wall of SPC framework is higher than mean filler concentration φ calculated for the whole volume of the sample, $\varphi_{loc} > \varphi$. Owing to this, the percolation threshold φ_c, defining the insulator/conductor transition, is much lower than for the random distribution of the filler.

The segregated structure of composites, based on the ultra-high-molecular-weight polyethylene (UHMWPE), was formed by hot compacting method. There were used two types of carbon fillers: microfiller anthracite (A) and nanofillers – graphene (Gr) and thermally expanded graphite (TEG). For comparison, there were produced the composites based on polypropylene with random distribution of anthracite filler (PP-A). Electrical conductivity measured on DC and thermal conductivity by hot-disc method.

The influence of filler distribution on electrical conductivity is shown in the Figure 1. The concentration dependence of conductivity is defined by a percolation equation: $\sigma = \sigma_0(\varphi - \varphi_c)^t$, where σ_0 – parameter of conductivity, φ – filler concentration, φ_c – value of percolation threshold, t – critical exponent.



(a) (b)

Figure 1 (a) optical microscopy of composite structure – random (top) and SPC (bottom) with anthracite; (b) electrical conductivity of SPC and polymer composite with random distribution of anthracite.

The values of percolation thresholds of SPC and random composite PP-A are given in the Table 1. It is seen that SPC filled with nanofillers Gr and TEG have the lowest values (0.21 and 0.49 for graphene and TEG, respectively), while for microfiller A φ_c is significantly higher ($\varphi_c = 2.95$). The system with random distribution PP-A has the much higher value of $\varphi_c = 24.8$ vol.%. These results can be explained by existing of ordered conductive framework in SPC with $\varphi_{loc} > \varphi$, which decreases the values of φ_c in comparison with composites having random distribution of filler.

Table 1.

Composite	*φ_c, vol.%*	*λ_f, W/(m·K)*
PP-A	24.8	7.2
UHMWPE-A	2.95	31.6
UHMWPE-Gr	0.21	44.7
UHMWPE-TEG	0.49	33.5

Thermal conductivity of systems filled with A and Gr does not reveal the percolation behavior and can be well described by Lichtenecker equation $\log\lambda = (1-\varphi)\cdot\log\lambda_p + \varphi\cdot\log\lambda_f$. Parameter λ_f is calculated thermal conductivity of the filler phase (including the contact resistances between particles). The composites PP-A with random filler distribution shows essentially lower value of λ_f while the values of λ_f for SPC are 4-6 times higher that indicates a better heat transfer through the filler phase in the segregated systems.

Ordered distribution of filler in SPC provides much lower value of percolation threshold for both nano- and microfillers and better heat transport in comparison with filler random distribution.

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Solution–processed OLEDs

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Organic light emitting diodes (OLEDs) based on small molecular materials which are fabricated by using vacuum techniques, have already found application in commercial products. They exhibit excellent performance, however their fabrication is very complicated and expensive due to the need of using high vacuum technology and fabricating multi–layered structure. Therefore, simple and cost effective solution–processed OLEDs may become a good alternative. Moreover, application of polymers as active layers and usage of polymeric substrates create a possibility of obtaining fully flexible devices. This is the main reason why nowadays the research work is strongly devoted to find new materials for solution processing, especially compounds that can be printed. Polymers are particularly attractive due to their ability of forming thin layers with desired thickness. However, for some time low molecular weight materials have been successfully applied to emissive layers (based on host–guest systems) as well as the additional layers that contribute to the increase of OLED performance [1].

This work will present the progress and problems in fabrication of OLEDs via solution methods. Usually, OLEDs prepared by solution–processing techniques have a simple, one– or two–layered construction. In the latter case, apart from the emission layer (LEL), there is often an additional layer enhancing injection of holes (HIL) from the anode. These layers are the most frequently fabricated by spin–coating method. However, from last decade, there is an intense research work focused on fabrication of LEL and/or HIL using printing methods such as aerosol–jet, slot–die, ink–jet and others [2]. Construction of OLEDs with a higher number of layers fabricated from solutions is very limited due to the difficulty of dissolving the materials in orthogonal solvents. Therefore, additional layers are mainly fabricated by vacuum evaporation.

One of the latest attempts leading to a significant increase of the OLED performance based on host–guest systems is using thermal activated delayed fluorescence (TADF) materials as an assistant dopants [3], [4]. Using TADF as an assistant dopant in the emissive layer based on 4,4–*N*,*N*–dicarbazole–biphenyl doped with red iridium complex [5] as well as on poly(*N*–vinylcarbazole) doped with green Ir complex [6] enable significant increase performance of solution processed phosphorescent OLEDs. In the latter case, this effect has been achieved not only for devices with the emissive layer deposited by spin coating but also using slot–die coating.

Widely used material for HIL in solution–processed OLEDs is poly(3,4–ethylenedioxythiophene)–poly(styrenesulfonate) (PEDOT:PSS). Despite its thin layer has high transparency and appropriate electronic properties, there is a problem of its long–term stability in OLEDs. This is due to its acidity and hygroscopicity which may accelerate the degradation of the emission layer and induce corrosion of the indium thin oxide (ITO), consequently leading to a reduction of the device lifetime. Recently, transition–metal oxides such as molybdenum oxide (MoO_x) are intensively studied as promising alternatives to PEDOT:PSS in OLEDs [7], [8]. We present the results obtained for OLEDs with the solution–processed MoO_x as HIL and *p*–phenylene vinylene copolymer (the trade name "Super Yellow") as emissive layer, both fabricated by spin–coating. In order to determine the effect of the MoO_x layer on the OLED performance, diodes without any HIL and with PEDOT:PSS as HIL were also made. Comparison of the working parameters of the devices indicates that the presence of the HIL made of MoO_x results in a significant increase of luminance compared to device without any HIL. However, OLEDs with HIL fabricated from PEDOT:PSS exhibited the highest luminance. Nevertheless, the current efficiencies of these three types of OLEDs were at a similar level.

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Technology of Real-World Analyzers (TAUR)

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In this work we describe the most important project assumptions for the reconfigurable construction of dedicated electronic machines intended for performing analyzes of phenomena occurring in multi-component systems containing at least several million of mutually interacting elements. Devices built in the presented technology are characterized by: the use of reconfigurable integrated circuits, spatial construction ensuring scalability, redundant panel system, as well as specially developed data transmission and supervision control systems [1,2,3]. Machines work in a parallel manner solving problems in various fields of science and technology and are alternative for supercomputing systems with high speed of data processing for parallel algorithms.

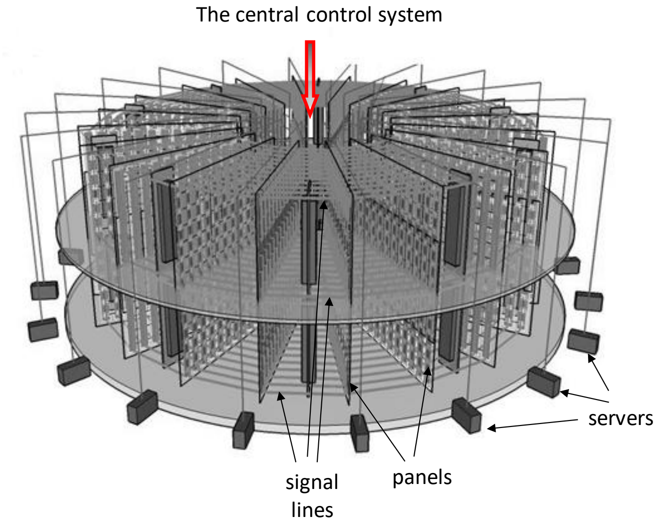

Figure 1: Exemplary TAUR system design.

As an example, the ARUZ system [4], containing 26,000 FPGAs, made using this technology is briefly presented. The currently available set of ARUZ configuration bitstreams allows simulation of the statics as well as the dynamics of molecular systems using the DLL algorithm [5,6]. Nevertheless, the work to extend its applicability is still ongoing. Among others, the usage of ARUZ for Lattice Boltzmann method seems to be very promising [7].

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Functional materials investigated by means of broadband dielectric spectroscopy

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Functionality of many polymer-based materials is directly, or indirectly, related to their dielectric properties. Therefore, Broadband Dielectric Spectroscopy (BDS) is one of basic methods of characterization of such materials as polymers and copolymers of different composition and architectures[1], ceramic materials[2] and their derivatives i.e. organic-inorganic (so called hybrid) materials[3].These exemplary systems investigated by Broadband Dielectric Spectroscopy will be briefly described.

BDS is a tool to relate molecular dynamics and structure of the materials under study, which in the case of functional materials with specific morphology or architecture provides not only a basic dielectric parameters but allows to determine the relationship between molecular structure and material properties as seen via their molecular dynamics (molecular relaxations). It exhibits the influence of processing parameters on the dielectric properties of the material, determines the effect of the existing interface's boundary in the tested compound and indirectly also describes the specific interactions between molecules/dipoles occurring in the investigated system.

Within functional materials hybrid composites containing high k inorganic particles are under great interest over the last decade. These materials, ideally link high permittivity of the inorganic particles with mechanical flexibility and easy processability of the organic counterparts. The dielectric properties of these systems depend on a dispersion of the ceramic particles in the polymer, its volume fraction, morphology/spatial architecture and also on the specific interactions between them. Broadband Dielectric Spectroscopy, working in a wide range of frequencies and temperatures, gives an overall characterization of these functional materials. Through analysis of the relaxation processes occurring there, their frequency dependence, relaxation strength and distribution of relaxation times one can gain information on specific interactions between ceramics and polymer.

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Photo and thermal stability of Ag nanoparticles stabilized by sodium citrate

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Variety of nanoparticles (NPs) covers a wide spectrum of substances, including metals, metal oxides, carbonaceous nanocrystals and clusters and many other inorganic as well as organic materials. The stability of nanoparticles attracts an attention because of the broadening field of their application in catalysis, medicine and pharmacy, electronics and optoelectronics, sensors, environment protection technologies, textronics. Many of these applications are connected with a treatment of the NPs by the radiation of different energy. Depending on the absorptivity the radiation can impact on the nanoparticle variously. Also the temperature may be a strong agent influencing the nanoparticle stability, as it changes the intermolecular interactions.

This work is devoted to the stability of electrostatically stabilized aqueous dispersions of Ag nanocrystals. The Ag NPs with different sizes were treated by laser and electron-beam irradiation as well as by temperature. Obtained results have shown that the nature and mechanism of size and shape changes induced in Ag NPs treated by temperature and radiation are different. However, both agents lead to narrower size-distribution of Ag NPs.

It was also found that the effects induced by laser light strongly depend on the relationship between the maximum of the plasmonic absorption band and wavelength of laser light. Also, the laser power influences observed changes in Ag NPs.

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Femtosecond infrared pump – stimulated Raman probe spectroscopy (fs-IR-SRS): the method and its first application to study vibrational relaxation pathway in liquid water

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The major goal of the contemporary ultrafast vibrational spectroscopy is to provide material scientists, biologists and physical chemists with a detail dynamical image of inter- and intramolecular interactions, of molecular dynamics and to some degree of supramolecular structuring of matter. On the top of the inherent features of vibrational spectroscopy, the perfect vibrational time-resolved method should provide time resolution better than 100 fs, spectral resolution better than 10 cm^{-1} and the possibility of simultaneous observation of dynamical changes in the whole range of molecular vibrations after some perturbation of a system. For some scientist an access to low frequency intermolecular vibrational modes below 500 cm^{-1} would be a huge additional advantage of a method.

In recent years, a step toward the desired method was made thanks to progress in generation of broadband infrared (IR) continuum through laser beam filamentation in air. As a result, broadband IR probe pulses (from around 1500 cm^{-1} to around 3300 cm^{-1}) were successfully applied in femtosecond IR and 2-dimensional IR spectroscopies [1]. Earlier, this sort of method was attempted to achieve by Kaiser and Laubereau [2] followed by Dlott [3] who applied IR pump – Raman probe scheme in time-resolved experiments. Thanks to inherent features of Raman scattering these methods provide multiplex detection but the time-resolutions achieved by the researchers were picoseconds either due to the limitations of IR pulses generation at the time (Kaiser & Laubereau) or because of picosecond Raman probe pulse being a painful trade-off between time and spectral resolution of the method (Dlott).

In this work we propose a new method: femtosecond infrared pump – stimulated Raman probe spectroscopy (fs-IR-SRS). In the femtosecond Stimulated Raman Spectroscopy (FSRS) the Raman transition is induced with two pulses: a narrow-bandwidth picosecond pulse which initializes the Raman transition and a broadband ultrashort probe pulse to stimulate the Raman transition [4]. All information about the system available in this process is contained in a wideband ultrashort probe pulse. The time resolution of FSRS is limited only by the cross correlation of the excitation pulse and the probe pulse, which can be easily below 50 fs. It was demonstrated [5] that the spectral resolution is limited mainly by the Raman pump spectrum and is independent of other pulses used in FSRS. This way one can circumvent a traditional frequency – time transform limitation which applies to standard pump-probe experiments. In our modification of the initial concept of FSRS we replace the visible actinic pulse with a femtosecond infrared pulse which promotes vibrational transition in a system. In the fs-IR-SRS the time resolution of an experiment is limited by duration of IR pulse; which is in around 90 fs.

In the proof-of-concept experiment, we apply the fs-IR-SRS method to study vibrational relaxation pathway in isotopically diluted water (HDO in D_2O). We determine lifetimes of OH stretching vibrations to be in the range 310 fs – 500 fs depending on the isotopic dilution, which is in a good agreement with the results from pump-probe femtosecond infrared spectroscopy. [6] Moreover, we observe a strong coupling of OH stretch to OD stretch vibrations and possibly also to the librational modes of water. We show that thanks to the multiplex advantage of Raman spectroscopy and features of stimulated Raman process the technique provides sub-100 fs time resolution, spectral resolution better than 10 cm^{-1} and at least 200 cm^{-1} to 4000 cm^{-1} probe bandwidth. Hence, the presented method is the first vibrational spectroscopy providing simultaneously sub-100 fs time resolution with broadband probe that covers full spectral range of molecular vibrations. Fs-IR-SRS also constitutes a complementary method to the one developed by Tokmakoff's group infrared pump-broadband probe spectroscopy with >2000 cm^{-1} infrared continuum probe. [1]

We think that fs-IR-SRS should be a suitable method to study phenomena such as protein hydration, ion-pairing in water but also intermolecular interactions in non-aqueous systems. Polarization-resolved fs-IR-SRS experiments should be able to provide simultaneous information about rotational dynamics of many chemical groups in a multiatomic molecule. The fs-IR-SRS, thanks to its extremely broad probe range, would also be a perfect tool to study kinetics of thermally driven chemical reactions.

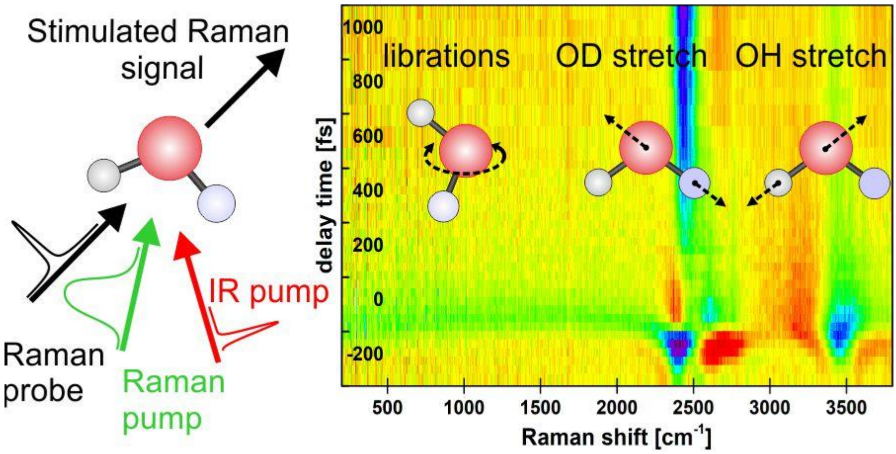

Figure 1: General scheme of fs-IR-SRS experiment with an example of the results obtained for 17 mole % of HDO in D_2O system - spectral map presenting time evolution of the stimulated Raman transient spectrum within initial 1.2 ps after excitation of the OH stretch vibration of HDO. Bleaching signal is marked blue to violet and increased Raman signal is marked in yellow to brown.

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A day from the life of a patent examiner

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Due to a recently observed significant increase in developing new technologies, the demand for patent protection continues to grow. The patent protection, an invest in knowledge and expertise transfer and a modern working environment foster development-stimulating innovations in all fields of science and technology. A general assumption behind patent protection is to support innovation, competitiveness and economic growth over the globe. In many cases, however, an unintentional patent infringement can lead to serious legal consequences associated with high costs and the loss of confidence in offered products - partly being urged by an unprofessional patent assessment process. In this view, a thorough, professional and competent patent examination process becomes a curial factor and common interest for inventors as well as for SME and large companies.

This contribution provides a short overview about daily duties of a patent examiner, and the rules examiner needs to follow to properly examine a patent application. Additionally, this overview includes a brief general insight into the relevance of patent protection for academic institutions, R&D institutes as well as small, medium and large enterprises.

Polymer composites for energy applications: challenges and opportunities

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Polymer composites are commonly used in the electronic and power devices as an electrical insulation. The management of heat dissipation is crucial for ensuring the proper operation of electrical devices. Improper heat management can potentially lead to malfunctions. Optimized thermal management in electronic components can lead to a reduced carbon footprint or to an enhanced rating of their power ranges. The addition of particles into a polymer matrix can result in a significant improvement of its thermal conductivity.

The appropriate selection of the filler and the processing methods used for preparation of the polymer composite is a key step to control and obtain the optimized and desired properties. Distinctively, the quality of the filler–matrix interface seems to be crucial in ensuring the conductive properties of a composite. In particular, it is necessary to consider the phonon scattering processes as well as the interface resistance. To increase thermal conductivity in polymer composites, the conductive paths must be maximized, and the thermal contact resistances must be reduced. Thus, one should select the most suitable filler and processing method that will lead to a polymer composite with appropriate thermal conductive functionality.

For this reason, the modification of the filler materials can give a promising solution. A several methods for the thermal conductivity enhancement will be discussed, namely:

a) incorporation of the hybrid nanofillers (e.g. graphene nanoplatelets) [1], and the microfillers (e.g. boron nitride flakes) [2],
b) use of the magnetic field-assisted filler alignment technology [3],
c) synthesis and application of a novel core-shell materials [4, 5].

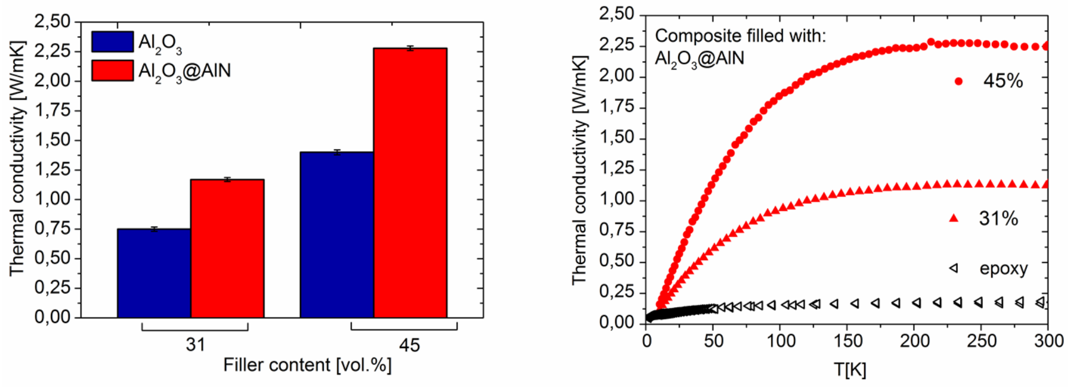

Figure 1: Thermal conductivity of composites measured at 300K with core-shell fillers in relation to standard system (left). Temperature dependence of thermal conductivity measured for composites filled with Al2O3@AlN core-shell particles with different filler content (31 and 45 vol.%). For comparison the dependence for neat epoxy is shown [4].

The composite samples based on epoxy resin filled with the modified fillers have been investigated in order to determine the effective thermal conductivity. The obtained composite samples exhibited a significant improvement in the thermal conductivity (see examples in Figure 1 and Figure 2). The results were analyzed with use of the various theoretical models. Additionally the mechanical and the dielectric measurements were performed showing a high potential for the composites with incorporated new modified fillers to be applied for the electrical insulation with the enhanced thermal conductivity.

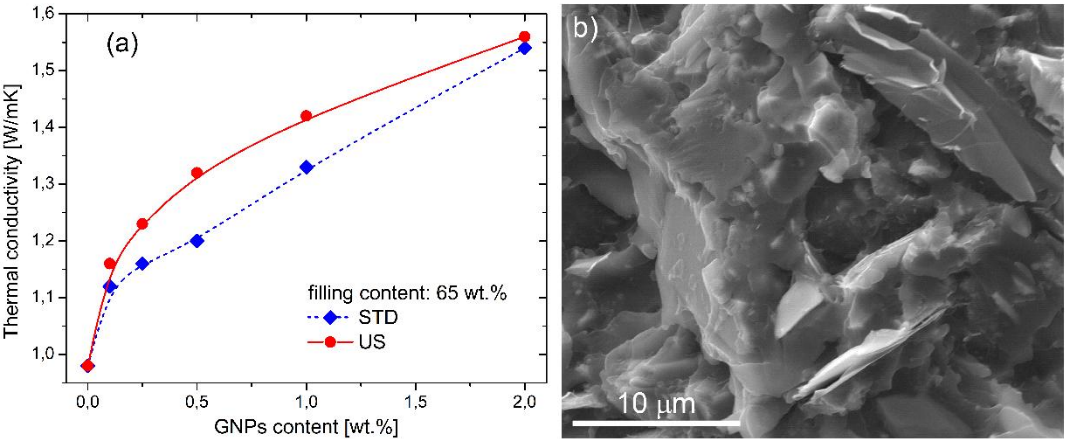

Figure 2: (a) Influence of the preparation method on the thermal conductivity of nanocomposites filled with a mixture of microsilica and graphene nanoplatelets (STD – standard method, US – method with ultrasonication step), (b) SEM image of the sample fractures with visible graphene nanoplatelets between microsilica grains [1].

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Relaxation processes in macromolecules with complex structure

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The use of modern organic materials in advanced technologies requires a good understanding of the impact of the broadly defined material structure on its properties. Molecular dynamics (molecular relaxation processes) plays a very important role here. Molecular dynamics in the case of polymers, especially those with a complex structure, *e.g.* hyperbranched polymers, dendrimers, copolymers, polymer networks, *etc.*, and their composites, can be very complex and difficult to analyse. Molecular dynamics depends on many factors - on the one hand, on the chemical structure of the studied systems, their synthesis and processing methods, and on the other on the type and amount of various additives, and above all on the interactions between individual elements. In the case of many functional polymers with a complex structure as well as their composites, the key aspect is to understand the mechanisms of phase transitions and the role of intermolecular interactions. This important information on the influence of the supramolecular structure of the tested materials on their physical properties can be obtained just by analysing the relaxation processes of these systems. An excellent tool for studying molecular dynamics, both low molecular weight materials and polymeric materials, is the dielectric relaxation spectroscopy (DRS) [1,2]. However, it should be emphasized that often complementary techniques should be used to give credibility to the interpretation of the obtained results [1].

The main purpose of my work is to describe the molecular dynamics of macromolecules with a complex structure, such as polyurethanes crosslinked with hyperbranched polyesters, aromatic polyethers with a very complex chemical structure or poly(oligo(ethylene glycol) methyl ether methacrylate) networks. In order to make the assessment, analysis and, above all, molecular identification of particular relaxation processes present in the polymer systems, I first had to enrich my workshop and become familiar with the molecular dynamics of systems with less complex construction, one can say model ones. I have also learned various complementary techniques that allow me to study the molecular dynamics of such systems, their advantages and limitations.

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Metallo-oligomers synthesis: from solution to surface

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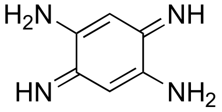
The rich chemistry of molecules exhibiting a quinoid structure has attracted the interest of a large scientific community for decades owing to their implications in a wide range of science including in nanoscience. A critical element in designing and fabricating new conductive materials is the control of the pi-distribution and the nature of the heteroatoms. 2,5-Diamino-1,4-benzoquinonedimine **1** is a very long known molecule (1887)[1] that has been poorly investigated owing to its low solubility and its unstability in solution. We decided to revisit the chemistry of **1** in order to elaborate new materials based on coordination chemistry.[2]



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Our strategy is based on the incorporation of **1** in extended molecules for the construction of near infra-red (NIR) dyes with different electronic properties.[3] The different approaches and the key role of **1** as ligand – in solution or in surface - will be described and discussed in the presentation. The possibility to elaborate a new class of vapochromic materials based on **1** – by tuning the nature of the N-substituents - will be also reported (Fig. 1).[3]

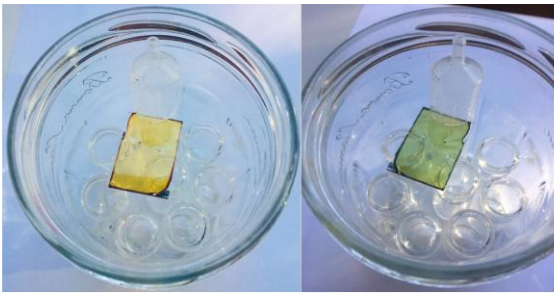

Figure 1: DMF vapors detection based on **1**. [3]

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Organic Field Effect Transistors from a lab scale to the potential application

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"Plastic electronics" is not only an exciting field of science, but also promising for future applications in spintronics and nanoelectronics. The basic elements of future electronics are field-effect transistors based on organic semiconducting and isolating materials. Solution-based deposition processes of active layers significantly reduce the fabrication costs of transistors. Mechanical flexibility of these devices is another major advantage.

This work presents a comparative study of flexible transistors using parylene C as both substrate and dielectric layer yielding, in the best case, devices with charge carrier mobilities $\mu_{(FET)} = 0.1\ cm^2/Vs$ [1]. Bending tests allow to determine the minimal curvature radius for the transistors at which their performance is not deteriorated irreversibly. The investigated devices are sensitive to ambient atmosphere, showing reversible increase of the source to drain current upon exposition to air, what can be explained as doping of the TTF derivative by oxygen or moisture [1,2].

Additionally, a novel one-step solution-based technique to produce bi-functional flexible semiconductor–dielectric composites for organic field effect transistor (OFET) applications has been developed [3,4]. By changing the deposition parameters and components, one can produce composites with the semiconducting layer on the top or at the bottom of the polymer film suitable for fabrication of oxygen sensitive OFETs. In the final remarks, possible industrial applications of the developed X-ray sensors will be discussed.

This work is supported by the Foundation for Polish Science in the frame of First TEAM program, First TEAM/2017-3/26. The mentioned project in realized at the Department of Molecular Physics at Lodz University of Technology.

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Organic photodetectors - examples of devices with fast time response and high responsivity

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Organic semiconductors are an interesting new class of electronic materials that combine some of the features of classical semiconductors with the chemical and mechanical properties typical of organic materials, including polymers and plastics. Their properties, such as their ability to absorb light or emit light in the desired spectral range and their electrical conductivity, as well as their solubility in organic solvents, facilitate their potential use in future electronic devices.

We investigated organic, bulk heterojunction, characterized with unbalanced charge carrier mobilities, for application in photovoltaics and photodetectors

The presented drift-diffusion simulation of bulk heterojunction photodiodes with Langevin recombination indicates that the bandwidth of photodiode is approximately independent of the mobility of slower charge carriers in the blend. The negative effect of low mobility on the responsivity can be compensated by increasing the reverse bias [1]. Our study shows that well performing organic photodetectors can be fabricated using organic semiconductors having too low mobility for photovoltaic applications. Moreover the simple device structure allows to fabricate the devices with fast time response.

Moreover we will present also the examples of the photodetectors with high responsivity and detectivity. Such high preformance was achieved by the application of the reversed device structure through the modificatin of the electrode work-function [2].

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Recent progress in printed OLEDs

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Organic light emitting diodes (OLEDs) fabricated by vacuum deposition technology are applied on large scale in displays and monitors since many years. On the other hand the technique of printing OLEDs cannot overcome laboratory scale and in fact in most published reports on printed OLEDs, only some layers in these devices are printed, while the other are deposited by vacuum evaporation technique. This is due to a number of serious obstacles hindering possibility of fabrication by means of solution based techniques and with high precision multilayer OLED structures [1].

Among the most critical issues, which are still not fully solved, one should name low efficiency of OLEDs due to difficulties in employing triplet states, lack of proper printable interlayers (*e.g.* needed to facilitate injection of one sign charge carriers and to block charge carriers of opposite sign), technical problems with deposition from solutions subsequent layers, continuous and with precisely determined homogeneous thickness (next layer can dissolve/damage the lower layer, or when orthogonal solvents are used, lack of wettability will prevent formation of the upper layer), lack of conducting inks, compatible with active organic layers, poor precision and low resolution of available printers, and lack of flexible, transparent and highly efficient barrier materials.

In the Department of Molecular Physics we are involved in last years in research aiming to solve the most important problems related to printed OLEDs in frame of several grants, national as well as European, realized in close cooperation with other laboratories in Poland and abroad, and also with industry [1 - 3]. In this talk we will present selected results illustrating application of new solution processable active layers exhibiting electrophosphorescence or thermally delayed fluorescence (TADF), printable interlayers and electrodes, as well as our approach for ink formulation and high precision printing technique.

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Bending experiments of organic thin film transistors

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Organic electronics is based on conjugated small molecules or polymers that can be deposited from solution or thermal evaporation. The advantage of organic electronics over inorganic silicon components is, among others, mechanical flexibility [1]. In this work, mechanical properties of thin film transistors are discussed in relation to their electronic parameters such as charge carrier mobility, threshold voltage and on/off ratio.

To realize elastic transistors parylene C as elastic gate insulator was applied [2]. On the elastic samples metallic conductive paths and electrodes were evaporated. These paths were necessary because the sample dimensions depend on the geometry of the bending setup. The selected organic semiconductor is deposited by spin-coating and thermal vacuum evaporation to vary the microstructure and molecular organization in the active layer. During bending the transistor channel took on a constant radius of curvature along its entire length. The sample deformation was induced during buckling.

Because of the specific thickness of the sample, not only bending stresses were induced, but also stretching and compression was observed [3]. Understanding the stress distribution is an important step to describe the observed process.

During repetitive stress of the transistors, the electrical parameters (charge carrier mobility, threshold voltage) can change. Changes can also be observed when the sample is stretched. All issues need to be considered during the analysis of the transistor undergoing cyclic measurements during bending.

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Electroconductive composite nanofibers

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Conductive polymers, especially polyaniline (PANI) has been of particular interest in lasts years. Furthermore PANI is ono of the most chemically stable polymer and thus a good material for preparing conductive blends or fibers. Chemical synthesis of PANI leads to obtain a powder of polymer, therefore possible is to apply it to make a composite fiber. Electrospinning is an attractive method for fabrication of polymer or mixed polymer nanofibers with controllable diameter and composition. Such fibers could be appropriate to construct among other electronic devices.

In this work conducting composite fibers made of PANI and polyacrylonitrile (PAN) were prepared using electrospinning method. PANI were synthesized through chemical oxidative synthesis and characterized by fourier-transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) as well as scanning electron microscopy (SEM). Composites of PANI and PAN, diverse by rate of polymers were electrospuned. Morphology and diameter of prepared fibers were characterized by SEM micrographs analysis. Results indicates on composition impact on diameter of fibers. Electrical conductivity, determined by four point probe method, reveal on conductivity increasing with increasing the polyaniline content. The TGA measurement indicate on stability of composites after electrospinning. The fiber were electrospuned to make surface layer and characterized in aspect of morphology of surface by SEM.

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Physicochemical and biological characteristics of bioactive flavonol fisetin

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Fisetin (FIS), a bioactive flavonol was found in the smoke tree (*Cotinus coggygria*), vegetables, fruits and nuts. It exhibits various therapeutic activities. Several polymeric nanoparticles have already been developed for encapsulation of drugs [1]. But physicochemical properties and biological activity of fisetin are still unclear. Factors such as pH of the environment and the pKa values mediate the interaction between fisetin and cell membrane. PH directly affects the magnitude of the electrostatic charges of both fisetin and lipid molecules of the membrane and thus determines the penetration extent of flavonoid. PH directly affects the magnitude of the electrostatic charges of both fisetin and lipid molecules of the membrane and thus determines the penetration extent of flavonoid [2]. It is shown that the cell membranes are more penetrable to unionized molecules and these molecules have the capability to pass through the membrane in a passive manner. Therefore, the ionization state of fisetin is important factor because it affects its localization and interaction with membranes and can subsequently influence the activity of the compound.

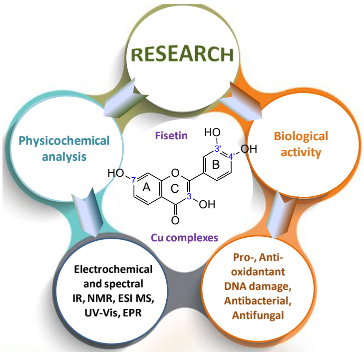

Figure 1: Scheme of research

This work was aimed at determining and characterizing ionization forms of fisetin species formed in various pH ranges in absence and presence of metal ions. Fisetin was characterized by potentiometric titration and spectroscopic techniques: UV-Vis, EPR, ESI-MS, FTIR [3]. Their impact on DNA was investigated using methods of circular dichroism, spectrofluorimetry and gel electrophoresis. The antimicrobial activity of the compounds was tested on selected bacteria and fungi (**Figure 1**).

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Dielectric properties of TiO_2 nanoparticles obtained by chemical solution based method

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Inorganic-organic hybrid gate dielectrics by combining high-κ metal oxide and polymer components are promising candidates for solution processable flexible organic electronics. High-quality hybrid gate dielectric must characterize by low surface roughness, a low leakage current density and reasonable dielectric properties: gate capacitance along with dielectric constant.

Anatase and rutile are the most known polymorphs of TiO_2. The most important application of TiO_2 concerns its optical properties that make it important additive in paints and varnishes as well as paper and plastics, what covers about 80% of the world's titanium dioxide consumption [1]. In recent years nanostructured titanium dioxide have attracted great attention due to its remarkable chemical and physical properties with respect to the bulk. Special attention is attracted by nano-TiO_2 importance in photocatalytic, optical and electrical applications [2]. Nano-TiO_2 has numerous advantages like large surface area, high chemical stability, low cost, and elevated values of dielectric permittivity [3] which makes this material a noteworthy component of hybrid gate dielectrics.

The physical and chemical properties of nanomaterials are substantially influenced by method of preparation. Solution-based synthetic methods are used broadly due to their simplicity and low cost and number of parameters that can be easily adapted to get product with desired size, shape and structure.

The main scope of this work is synthesis of TiO_2 nanoparticles by simple chemical, solution based method and investigation of their phase composition, morphology and dielectric properties by use Raman spectroscopy, scanning electron microscopy (SEM) and broadband dielectric spectroscopy (BDS).

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Enhanced P3HT aggregation in dielectric polymer solution

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P3HT (*poly(3-hexylthiophene-2,5-diyl)*) is one of the most commonly investigated conjugated polymers with well-known physical properties. As such, it is commonly investigated and often used as a model organic semiconductor to describe new strategies for the fabrication of organic field effect transistors.[1] P3HT is known to create long-range ordered fibers during aggregation. Thus, one efficient way to improve P3HT based electronic devices is preaggregation in solution before thin film deposition.[2] The formation of the P3HT fibrils depends on factors such as molecular weight, concentration, UV irradiation, sonication, type of solvent and solution composition.[3,4,5]

In this work, we describe the aggregation of P3HT in the presence of dielectric polystyrene in solution. It is found that the concentration of polystyrene in combination with the type of solvent plays an important role on the formation of P3HT fibers in the solution. The aggregation was monitored by time-dependent UV-Vis spectroscopy measurements of aged P3HT solutions with different amount of polystyrene added in different solvents. The aggregation influenced the morphology and microstructure of spin-coated P3HT film as revealed by atomic force microscopy and grazing incidence wide-angle X-ray scattering. Changes in film microstructure were correlated with charge carrier transport in field-effect transistors.

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Role of the semiconductor/dielectric morphology on the charge carrier transport

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Organic electronics is a field of science which in the near future is able to compete with traditional silicon/germanium electronics. However, a serious problem seems to be a selection of a suitable substrate for the production of organic electronic devices. Most studies present solutions in which organic equivalent still contain silicon or glass in their configuration. As of today, this kind of approach blocks the possibility of the rapid development of the described field of science due to the mechanical properties of such substrates. Fragility and stiffness are the properties that unfortunately prevent the production of integrated circuits with adaptive shapes. In order to solve the described problem, scientists try to implement new ideas based on flexible organic electronics. The possibility of using bendable substrates allows creating prototypes of discrete electronic components such as Organic Light Emitting Diodes (OLEDs), Organic Field Effect Transistors (OFETs), resistors and capacitors [1].

In order to produce OFETs, a promising solution seems to be the use of systems showing the phenomenon of controllable phase separation [2-3]. The following work presents the results of basic research on the production of bi-layers, based on semiconductor-isolator blends that can be used as an active composite in OFETs fabrication. For simple and reliable comparison of obtained results with scientific reports, a well-described in literature tips-pentacene was used as a semiconductor and polystyrene as an isolator. In order to obtain long oriented crystallites and thus improve the morphology and reduce the number inter-crystal boundaries the technique used for the production of such films was one of the meniscus guide techniques called a zone-casting [4]. In the wake of the research, the impact of the semiconductor-isolator ratio on the morphology of the obtained layers and therefore on the electrical parameters of ready-made devices was noted.

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Scanning electrochemical microscopy-based characterization of biosensor coating consisting of single-walled carbon nanotubes modified with reduced graphene oxide

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Scanning electrochemical microscopy (SECM) is an innovative method, which could be applied for localized surface-activity analysis of enzymatic biosensors [1-4]. The SECM is based on electrochemical measurements performed by ultramicroelectrode (UME), which is scanning 3D space close to surface of the interest, which could contain catalytic, redox or other electrochemically active sites. The advantage of SECM is that the technique can be applied for in-situ study without any damage to the system of interest. The transducer was based on polycarbonate filter membrane, which was punctuated by 400 nm holes (PcFM), was modified by single walled carbon nanotube (SWCNT) and then formed PcFM/SWCNT structure was covered by thin layer of graphene oxide (GO) or reduced graphene oxide (rGO) in order to get PcFM/SWCNT/GO and PcFM/SWCNT/rGO structures, respectively. In order to form biosensing surface the PcFM/SWCNT/GO and PcFM/SWCNT/rGO structures were modified by immobilized glucose oxidase (GOx) and examined using a SECM.

When horizontal scan was performed in the intersection of the areas - modified and non-modified with GOx, without glucose in solution - the oxygen reduction current is higher at non-modified area. Herewith non-modified surface is conducting and the measurement shows ‘positive feedback’ effect. At the area modified with GOx, the current is lower, and this means that GOx is blocking conducting surface. Thus, enzymatic reaction on GOx-modified surface appeared when glucose has been added to the solution; after some time, the signal from enzymatic reaction decreased, and peaks, showing conductive membrane holes, reappeared again. Horizontal scanning of GOx-modified surfaces shows the bio sensing phenomena.

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Effect of the chemical structure of the chromophore on selected physicochemical properties of azopolymers

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Recently, a dynamic increase in demand for efficient and cheap devices causes the rapid development of modern technologies in the field of optoelectronics, photonics, and holographic techniques along with searching of new materials. One of the most promising ones are photochromic materials among which azobenzene-based polymers play an essential role [1]. Due to the ease of modification of their chemical structure [2] and the ability to change optical properties, as a result of irradiation with a polarized light [3], they show a huge potential applications in optical information storage and processing, optical switches, the fabrication of diffractive optical elements and others [4].

In this work, we present a series of "guest-host" systems based on poly(ether imide)s matrices differing in the molar mass and a type of the azochromophore (derivatives of azopyridine or azobenzene) [5]. Chemical structures of the investigated compounds are depicted in **Figure 1**. The aim of the study was to investigate the effect of the polymer molar mass and a type of azochromophore on thermal behavior (TGA, DSC) and optical properties including the thermal *cis-trans* isomerization reaction in DMF solution and in the solid state. It was found that the insertion of the pyridine ring into the azochromophore structure affects the process of thermal relaxation, causing the acceleration of the *cis-trans* isomerization both in solution and in the solid state in comparison with the azobenzene-based chromophore. The effect of the molar mass of polymers was also observed.

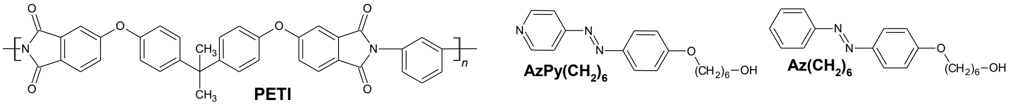

Figure 1. Chemical structure of the polymer matrix and azochromophores.

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Inkjet printed polymer OLEDs: ivestigation of trap signature using Differential Analysis of Steady State Current-Voltage Characteristics

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Printing technology has a high potential to be implemented for production of optoelectronic systems based on organic light emitting diodes (OLEDs). Currently, majority of the OLED based applications (displayes and light emitting systems) are manufactured through vacuum evaporation methods [1]. However, vacuum based techniques result in low throughput and increase of the cost per pixel area. For this reason printing techniques are considered as a potential low cost technology for large-area OLEDs based flexible displays. One of the commonly used printing methodology is inkjet because it offers a non-contact, high-resolution process and fast processing throughput[2].

In this work, we used inkjet printing technique to deposit uniform films of a light emitting polymer on glass substrates. Stable inkjet polymer ink was fomulated by using a mixture of high boiling point and low boiling point solvents. High quality printed films were achieved by controlling the various printing parameters like: print resolution, substrate temperature and the ink concentration. We found that the parameters of printed OLEDs were comparable to that of spin-coated reference device having maximum current efficiency of 5.6 Cd/A and maximum luminance of 66000 cd/m^2.

Different processing techniques may result in different morphology of the OLEDs active layers and therefore influence also charge carrier transport mechanism. Disordered organic semiconductor layers have charge carrier traps due to different defetcs and inhomogeneities of the morphology. Such trap states are localized within the energy gap and affect the performance of the device and its long-term stability. For this reason we applied differential anlysis of steady state current density - voltage characterstics to study trap signature [3, 4]. We present and discuss the traps distribution and their depths in printed and spin coated organic layers.

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Phthalimide based acceptors for tuning the exciplex emission in OLEDs

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The organic light emitting diodes (OLEDs) have been widely studied for their promising application in lighting and display technologies [1]. High-efficiency OLEDs can be realized by employing thermally activated delayed fluorescence (TADF) mechanism, by which it is possible to harvest both singlet and triplet excitons. Such mechanism can operate in appropriately selected donor and acceptor systems, with the subsequent formation of excited intermolecular charge transfer complexes (exciplexes). To provide high exciton utilization in organic light emitting diodes, phthalimide derivatives were designed and synthesized as exciplex-forming materials. Due to high triplet levels (2.92–3.11 eV) and ionization potentials (7.18–7.29 eV), the developed phthalimide derivatives were found to be appropriate accepting materials for the formation of exciplexes emitting different colour of light. Solid-state blends of the synthesized phthalimides as acceptors and a carbazole containing donors (mCP,CBP, PVK, TCTA) showed exciplex emissions colour of which covered large part of visible spectrum from sky-blue (490 nm) to red colour (575 nm), depending on the donor used. The most efficient sky-blue emission with small singlet-triplet splitting (0.06 eV) was observed for the exciplex-forming blend of (2-(4-benzoylphenyl)isoindoline-1,3-dione)(4-BpPht) as an acceptor and 1,3-di(9H-carbazol-9-yl)benzene (mCP) as a donor. Such exciplex-forming molecular mixture was implemented as the light-emitting material in the sky-blue organic light emitting diodes which showed the brightness of 2500 cd m^{-2} and maximum external quantum efficiency of 2.9% due to the employment of both singlet and triplet excitons [3].

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Molecular dynamics and thermal properties of semi-crystalline poly(oligo(ethylene glycol)methyl ether methacrylates) (POEGMAs) networks

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Presented results raise the issue of an impact of oligoether side chain length and in consequence also their ability to crystallize on the molecular dynamics in poly(oligo(ethylene glycol) methyl ether methacrylate) (POEGMA) networks. POEGMA networks were synthetized by radiation-induced crosslinking polymerization of pure monomers (with various number of oxyethylene groups n from 2 to 19) without any additives (crosslinkers, initiators). Obtained materials were investigated and characterized mainly by Dielectric Relaxation Spectroscopy (DRS) in broad frequency and temperature ranges. Two patterns of behaviour may be distinguished, namely amorphous and semi-crystalline networks. Therefore, in case of the samples with $n > 7$, which are partially crystalline, relaxation processes are strongly disturbed by cold crystallization and/or melting [1] [2].

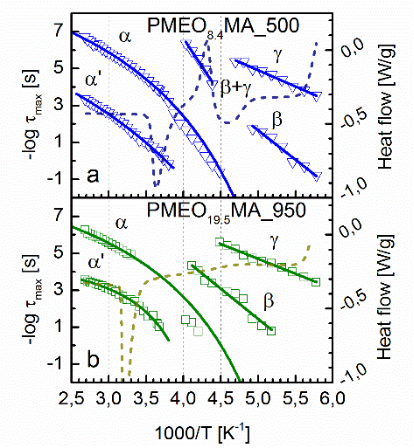

Figure 1: Activation maps and DSC thermograms (dashed lines) determined for all relaxation processes found in PMEO$_n$MA-based networks, which are partially crystalline.

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Lessons from Modelling of Diarylethene-based Molecular Photoswitches with Density Functional Theory

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The diarylethene-based molecules are a highly promising group of photoswitches and therefore it is essential to be able understand and describe the photoreactions of closing and opening their central phenyl ring, which constitute the photoswitching mechanism in this group of molecules. [1]

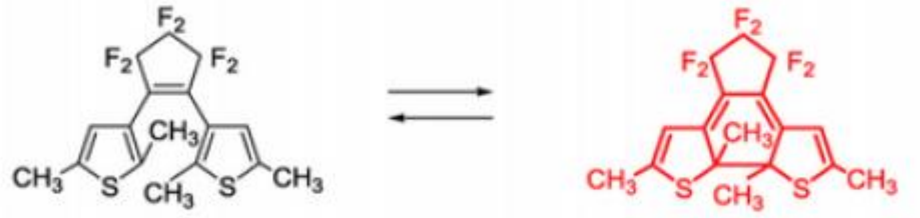

Figure 1: Scheme of the reaction for a molecule from diarylethene group [1].

Computational methods of quantum chemistry, such as the Density Functional Theory (DFT), can assist in this quest. To verify the reliability of DFT in describing the essential properties of diarylethenes, six popular density functionals were selected and their performance in modelling the essential properties - such as the geometry, the infrared (IR) and UV-VIS spectra - of three diarylethene molecules was examined.

We show that the use of the dispersion correction has an influence on the structure of diarylethenes: it makes the molecules flatter but also shortens the distance r_{CC} between the key carbon atoms in the central ring of the molecules. Secondly, also the influence of the solvent (hexane) on the results was considered and turned out to be quite insignificant.

The dispersion-corrected B3LYP functional produces the most accurate IR spectra and in most cases also the UV-VIS spectra. All of the tested functionals, however, except for LC-ωPBE, proved to be reliable. In each case, the dispersion-corrected functionals allowed obtaining better results.

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New cyanoacrylic acid derivatives with thienyl units for dye sensitized solar cells

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In recent years, the rapid development of energy technologies based on renewable sources has been observed. This is due to increased ecological awareness as well as economic issues [1]. Photovoltaic cells, in particular dye sensitized solar cells (DSSCs) meet with unflagging interest [2-3]. The key component in DSSC is dye because it has a significant impact on the performance of the entire device [4]. In recent times metal-free compounds are a more popular type of sensitizers compare to ruthenium or zinc complexes because they are easier to obtain and do not generate high-costs [4]. A promising alternative is compounds with cyanoacrylic acid as an anchor group obtained as a result of the condensation reaction of cyanoacetic acid with aldehydes [5].

In this work six cyanoacrylic acid derivatives were prepared by Knoevenagel condensation of cyanoacetic acid with the following aldehydes: thiophene-2-carbaldehyde, 2,2'-bithiophene-5-carboxaldehyde, 3,4-ethylenedioxythiophene-2-carboxaldehyde, 2,2':5',2''-terthiophene-5-carboxaldehyde, 2,5-thiophenedicarboxaldehyde, 2,2'-bithiophenyl-5,5'-dicarbaldehyde. All synthesized compounds were characterized and their thermal, optical and electrochemical properties were studied. Finally, selected compounds were tested for application in DSSCs. The conducted research allowed to evaluate the effect of the number of thiophene rings and anchoring units on the properties of the synthesized compounds.

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Solvent vapor annealing as a promising tool to investigate interactions in blends of organic semiconductors and polymer dielectrics

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Solvent vapor annealing (SVA) is a widely used post-treatment technique that allows to improve the morphology of thin films [1]. It can be also used to trigger the self-assembly of molecules and to induce the phase-separation between the blend components. This advantage of SVA is promising for the fabrication of organic field effect transistors (OFETs) by solution processing of semiconductor-dielectric blends. This approach can improve the OFET performance due to a well-defined interface between dielectric and semiconductor. To well control the SVA process and the final blend morphology, a comprehensive understanding of the interactions in the corresponding blends components is required. Thus, this study is focused on the investigation of the film morphology formation during SVA. All experiments were performed in a specifically designed SVA chamber that allows monitoring the film thickness while the solvent vapor is passing through the chamber. The influence of type of solvent, temperature, volume and flow rate, film thickness, surface nature and film swelling was investigated for polystyrene (PS) and its blends with 6,13-Bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene). The procedure can be further exploited for the investigation of the phase separation and for the calculation of the Flory-Huggins interaction parameter (χ_{i-j}) between the blend components [2,3]. Due to the fact, that χ_{i-j} is a measure of the miscibility of the components, its identification is expected to allow better prediction of the final morphology of the film and the corresponding OFET performance.

This work is supported by the Foundation for Polish Science in the frame of First TEAM program, First TEAM/2017-3/26. The mentioned project is realized at the Department of Molecular Physics at Lodz University of Technology.

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Spectroscopic analysis of graphene oxide layers on textiles obtained by reactive inkjet printing

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Inkjet printing technique is a versatile method for controlled deposition of functional materials with suitable geometry on various substrates. It does not require any contact between the deposition system and the substrate. The only constraint of this technique is the requirement of fluids (inks) with suitable viscosity and surface tension. The inkjet printing technique is very attractive as it allows not only patterns of high resolution and high repeatability to be obtained, but also repeatable layer-by-layer structures [1][2].

Reactive inject printing is synthesis process of functional materials on substrate. During printing process, produced droplets of uniform size can be treated as building blocks. The size of these droplets can be tailored and they can be positioned accurately on a substrate in pre-determined locations. In chemistry, precise control over dispensed aliquots is desirable in ensuring that the correct stoichiometry is obtained in synthesis. Reactive inkjet printing transforms inkjet printing from simply being a deposition technique, capable of delivering reproducibly sized droplets in the pico-litre range, to one, where tiny droplets of one reactant can be added to another; allowing reactions to be performed with precision at a small scale [3].

During project, printed layers of graphene oxide on textiles substrates: polyacetonitrile (PAN) and polyethylene terephthalate (PET) were reduced. Obtained materials were characterised by Raman and infrared spectroscopies.

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Electrochromism in dithienopyrrole based polymers

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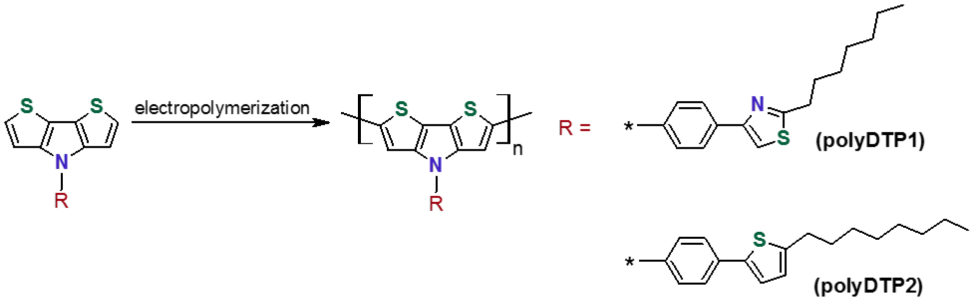
Two new dithienopyrrole derivatives were synthesized, namely dithieno[3,2-b:2',3'-d]pyrrole *N*-functionalized with 4-(2-heptylthiazol-4-yl)phenyl (**DTP1**) and 4-(5-octylthiophen-2-yl)phenyl (**DTP2**) groups. Both monomers readily electropolymerize to yield the corresponding **polyDTP1** and **polyDTP2** (**Scheme 1**).



Scheme 1. Electrochemical synthesis of **polyDTP1** and **poly DTP2**.

Thin polymeric films deposited on platinum or ITO electrodes exhibit electrochromic behavior. As evidenced by UV-vis-NIR spectroelectrochemistry, both polymers undergo classical (for conjugated polymers) oxidation, involving the formation of polarons in the first step and bipolarons in the second one. An interesting feature of the oxidation of **polyDTP2** is the highly delocalized nature of bipolarons, indicative of the metallic state (featureless absorption tail extending towards NIR part of the spectrum). In order to elucidate the exact nature of the electrochemical oxidation process detailed Raman spectroelectrochemical investigations of **polyDTP2** were carried out, supported by the vibrational model calculations using two methods: DFT and General Valence Force Field (GVFF). The results show that the polarons (radical cations) are formed in the pyrrole ring whereas bipolarons (dications) exhibit classical configuration with charges located in Cα positions of the thiophene rings [1].

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Characterization of nonlinear optical KAP crystals doped with organic dyes

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Potassium acid phthalate (KAP) crystals belong to organic-inorganic group of materials and due to their nonsymmetric structure exhibit second order nonlinear optical properties, like second harmonic generation (SHG), linear electrooptic effect (Pockels effect) and possibly optical rectification. The advantage of these materials is the ability to grow into large single crystals from water solution. KAP can be doped by different dyes including typical laser dyes like DCM, Acridine Orange and Nile Blue. The aim of present work is to characterize the luminescent properties of doped KAP crystals. Pure KAP as well as dye-doped KAP's were grown and their UV-Vis absorption and luminescence were measured. We also observed their behavior under optical microscope using laser light excitation at wavelength 473 nm. We observed that dyes can be incorporated into the crystal bulk either isotropically or anisotropically. In Figure 1 we show two examples of dye-doped KAP crystals under laser light excitation with clearly shown localized luminescence traces.

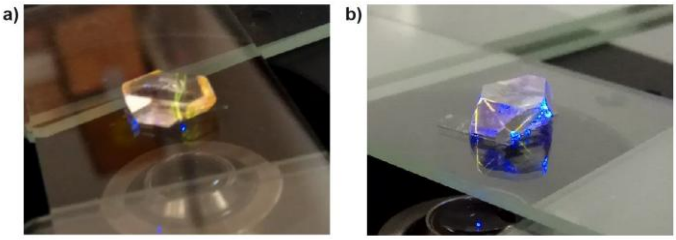

Figure 1. Traces of luminescence excited by 473 nm laser light in KAP crystals doped with: a) Acridine Orange and b) Nile Blue.

The SHG in KAP crystal has been demonstrated at 1064 nm laser light excitation with 10 ns light pulses. KAP crystal is transparent in the visible spectral range (cf. Fig. 2) therefore it is an excellent candidate for many optoelectronic and photonic applications, where nonlinear optical properties are combined with luminescence, e.g. SHG induced luminescence.

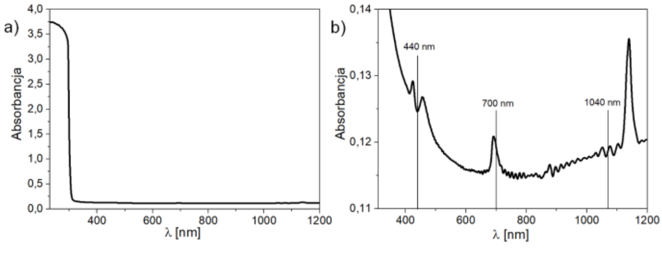

Figure 2. Single crystal absorption spectra of pure KAP.

Modeling the dynamics of systems containing macromolecules with complex topology

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Simulations of polymer systems like blends, solutions, alloys and composites (and *soft matter* problems in general) are a demanding task because they often involve a wide range of time scales and spatial distances. For this reason, various methods are still being developed and combined with others for obtaining information on diffusion properties, morphology, solvent and polymer chains dynamics, or the kinetics of reactions (like polymerization) in complex liquid systems. An interesting model is the Dynamic Lattice Liquid (DLL) proposed by prof. Tadeusz Pakuła [1]. This model is based on the concept of cooperative movements and allows to study longer time scales than the widely used method of molecular dynamics, but at the expense of a smaller time resolution. DLL has been used in simulations of many non-equilibrium processes, for both polymer and simple liquid systems. This work presents the use of DLL on the example of solvent dynamics in the vicinity of polymer chains [2], polymer stars and polymer brushes simulations, or atomic transfer radical polymerization modeling (ATRP) for polymer chains grafted on surfaces [3].

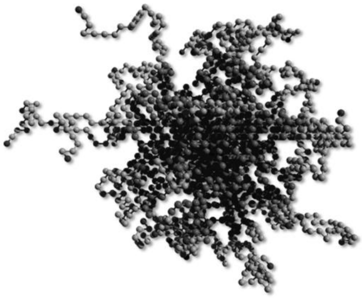

Figure 1: An example of polymer star with 32 arms which can be used as a nanoparticle template.

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grant UMO-2014/14/A/ST5/00204, is gratefully acknowledged.*

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Graphene Oxide Reduction during SI-ATRP

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The study is focused on the utilization of polymer hybrids containing the graphene oxide (GO-*g*-polymer) in smart stimuli responsive applications, i.e. photomechanical actuators and electrorheological suspensions (ER). Graphene oxide particles (GO) are considered as promising components for such applications due to their large surface area, low density, electrical properties, and cost effective way of preparation [1] [2]. The utilization of Surface Initiated Atom Transfer Radical Polymerization for GO-*g*-polymer preparation enables to control the molecular chain architecture [3], and as was revealed recently, also the electrical conductivity of GO [4].

Herein GO-*g*-polymers with various surface chemistry were prepared to study in details the affinity of such hybrids to silicone based polymers. Namely, a silicone oil was used in case of ER and silicone elastomer in case of photomechanical actuators. GO particles were modified with poly(methyl methacrylate), poly(*n*-butyl methacrylate), poly(glycidyl methacrylate) and poly(trimethylsilyloxyethyl methacrylate) as it was confirmed by thermogravimetric analysis with FTIR recording and by X-ray photoelectron spectroscopy. Electrical conductivity of obtained materials was measured using four-point probe method. Contact angle measurements demonstrated the varied compatibility of GO-*g*-polymer hybrids with silicon-based surroundings depending on the nature of grafted polymer. The tunability of the ER properties as well as photoactuation capability was investigated and it was shown, that not only the electrical conductivity but also dipole moment in the polymer brushes is an important factor affecting ER performance. For the photoactuation efficiency, the compatibility with the polymer matrix and thus proper particles dispersion is the most important factor. The GO-*g*-polymer hybrids showed plasticizing effect, i.e. reduced the matrix stiffness, that resulted in improved ability to reversibly respond the external light stimulation.

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Excited state dynamic of photochromic dimethyldihydropyrene derivatives in solutions

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Molecular switches can be commonly applied to control different functions and properties of materials which can be used in organic electronics (as for example in new memory elements based on single molecule) or in biology to manipulate the biological systems. Photochromism of dimethyldihydropyrene derivatives is a reversible transformation under UV and visible light irradiation between two, opened-ring cyclophanediene and closed-ring dimethyldihydropyrene, isomers with different spectroscopic properties. Dimethyldihydropyrene compounds could be applied in wide range of areas such as organic electronics, for example single molecule memory elements, and biology – diagnostics, control of metabolic reactions. To achieve even more suitable physical properties for different applications, DHP molecules could be modified by adding substitutes. However, the most common problem of these modified compounds is stability. To solve this problem, there is a need of deeper understanding of processes appearing during photochemical reaction [1].

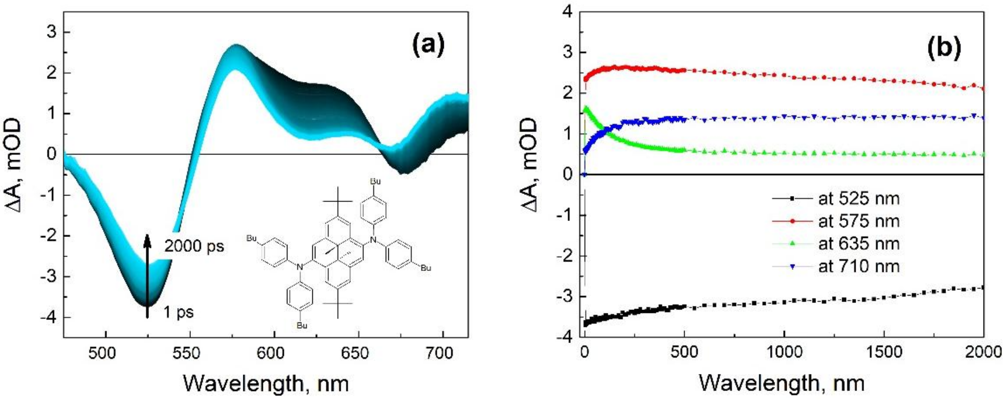

Figure 1. Transient absorption spectra (a) and kinetics (b) of studied compound under 380 nm excitation

New dimethyldihydropyrene derivatives were synthesized, and their optical properties as well as excited state dynamics were investigated in the solutions. We focus on the emissive properties of dimethyldihydropyrene derivatives with the possibility to switch them between fluorescent and non-fluorescent states. During the first 100-300 ps after excitation under visible light the closed-ring cyclohexadiene isomer were opened. Reverse transformation took place through intermediate stage during several nanoseconds.

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Thermal diode like behaviour studies in silicon membrane based phononic crystals

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The main challenge in modern electronics is the excess heat removal and the nonlinear heat devices are the potential solution. The thermal rectification [1] is a fundamental phenomenon in this field and can be described as the amount of heat transported along specific axis dependence upon the direction. Phononic Crystals (PnCs) with different periods in one larger structure can be an example of thermal rectifier. PnCs temperature dependence of the thermal conductivity [2] makes them a CMOS compatible building blocks for the thermal rectifiers.

We report on the fabrication of silicon membrane PnC-based thermal diode using Focused Ion Beam milling and further experimental examination using novel contactless technique of two laser Raman thermometry.

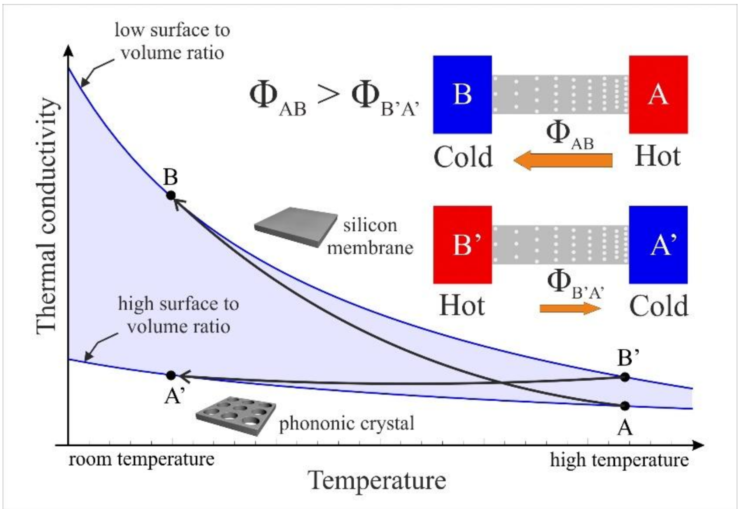

Figure 1: Thermal conductivity as a function of temperature for silicon membrane and PnC. Inset shows two cases of heat transfer corresponding to opposite heat flux direction.

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Functional organic semiconductors derived from exceptionally stable π-delocalized radicals

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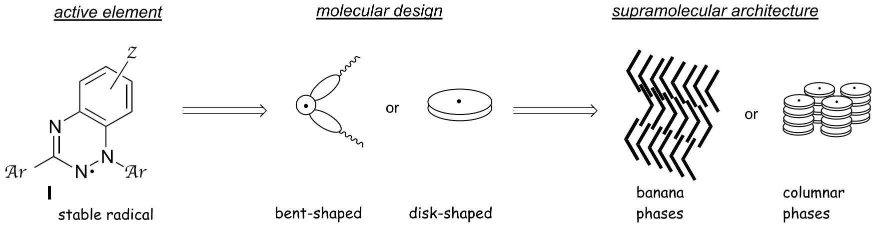
Open-shell organic systems are becoming increasingly important structural elements in advanced materials for applications in molecular electronics, energy harvesting, memory and energy storage, and spintronics. In this context, we have been investigating thin films of supramolecular assemblies of stable π-delocalized radicals, such as 6-oxoverdazyl and benzo[*e*][1,2,4]triazinyl (**I**). We have developed access [1] to derivatives of **I** with new molecular architectures [2] and to liquid crystals exhibiting discotic (Col_h) [3] and bent-core (SmA) phases [4]. SQUID measurements revealed that the discotic materials exhibit magnetic behavior that is structure–dependent and the spin-spin interactions range from antiferromagnetic to ferromagnetic in the solid phase. Photoconductivity studies demonstrated that the hole mobility is about $\mu \approx 1.3 \times 10^{-3}$ cm^2 V^{-1}s^{-1} in the fluid Col_h phase [3]. Films formed by molecules with new architectures of the cores (planar geometry and multi-spin molecular cores) give rise to appearance of new liquid crystalline phases, modulation of magnetic behavior as function of the phase structure, and improvement of mobility of the photoinduced charges.



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Industrial PhD in the cooperation with QWERTY Ltd.

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The presentation includes the results obtained in the frame of PhD project which is realized in the cooperation with industrial partner. QWERTY Ltd. is Polish company, leader on local and European market of electronic components manufactured by printing methods. Part of the presented results concerns the fabrication of simple electrical systems by inkjet printing method in industrial conditions. The obtained results can be considered as a preliminary stage leading to development of photovoltaic and photodiodes printing technology.

The tested simple electrical system was a flat capacitor whose electrodes were printed with conductive ink based on silver nanoparticles, while the dielectric layer was deposited from UV light curable resins or soluble polymer solutions. In this approach several commercially available polymers were tested as well as a number of acrylic copolymers synthesized in QWERTY Ltd. At the current step of this project, the required high insulation between the printed electrodes was only obtained for the UV-curing resins.

Parallel studies were carried out to form multi-layer photovoltaic devices by means of solution methods. Processing optimization of the device structure included the study of the effect of PDINO layer thickness (perylene diimide derivative), acting as the interlayer between the active layer and the vapor-deposited aluminum electrode. Its role was to reduce the potential barrier between the active layer and the electrode. The best manufactured polymer photovoltaic cells showed a conversion power of 7.5%.

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Photomechanical effect in glassy "T-type" azopolyimides

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High molecular masses azopolymers may be prepared as free-standing cantilever samples for the photomechanical effect investigations, where proper irradiation causes a sample deformation [1]. Bending of cantilever results from a strain gradient generated across the sample due to a strong attenuation of light absorbed by azomoietes. The magnitude of the deflection angle depends on irradiation conditions, polymer morphology, its thermomechanical properties and cantilever dimensions [2]. Azopolymers exhibiting the photomechanical effect may be applied as various mechanical light-controlled devices e.g. polymer cantilever oscillators, micropipettes or light-driven plastic motors [3].

We demonstrate an intriguing photomechanical response of a series of glassy azobenzene polyimides containing the chromophores covalently attached to the polymer backbone – "T-type" polymers. To our knowledge, it is the first report on photodriven bending of cantilevers for this class of azomaterials. It was found that the bending angles may reach extraordinary large values of 90 ° upon ca. 60-second exposure to 445 nm polarized light of moderate intensity. The underlying mechanism of the observed photomechanical response was proved to be reorientational as a bidirectional cantilever deflection either towards or away from a linearly polarized laser source was observed. No relaxation of cantilevers bent by a maximum angle to their original shape was visible during several days after irradiation.

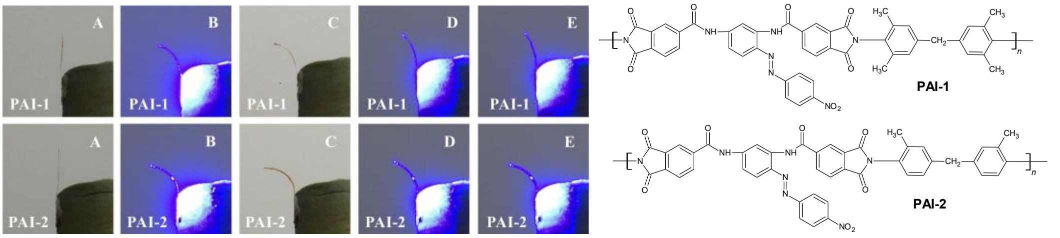

Figure 1: Photoinduced deformations of cantilevers prepared from the studied poly(amide imide)s (A) before irradiation, (B) at the end of irradiation with vertically polarized light, (C) after ca. 2 min relaxation period in the dark, (D) at the beginning of irradiation with horizontally polarized light, (E) at the end of irradiation with horizontally polarized light. (F) Chemical structures of azopoly(amide imide)s.

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Biosensors and Organic Electronics Laboratory:

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Laboratory conducts research in the area of the organic materials and composites structure optimization and their use in electronic devices. In particular, it focuses on the preparation and characterization of the printed electronics elements operating parameters (organic light emitting diodes, organic photovoltaic cells and organic field effect transistors).

Among others offer is addressed to the industrial broadly defined optoelectronic sector, which results in solutions of lighting, displays (organic light emitting diodes), as well as in photovoltaic cells. Organic materials investigated in laboratory are equally applicable to the construction of sensors based on the field effect transistors applied for the condition of the environment monitoring.

Research offer:

- High resolution contact measurement of the surface profile with the roughness sample analysis
- Performing the first and subsequent levels of photolithography
- Optimization process of thin layer manufacturing in ambient conditions using spin-coating deposition
- Optimization process of metal and/or organic thin layer preparation in ambient conditions using chemical vapor deposition method
- Full characterization of optical and electrical properties of organic thin layers
- Production of optoelectronic devices with vacuum and/or solution methods with full electrical characterization and encapsulation
- Process of the surface activation/surface cleaning using the active plasma
- Optimization Ink jet printing process

Figure 1: Headquarters of Biosensors and Organic Electronics Laboratory at Bionanopark.

Small organic compounds for optoelectronics

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Among various conjugated materials, particular interest is paid for azomethinoimides and malononitrile compounds for organic electronics. Azometins and azomethinoimides are compounds with a wide variety of applications in many fields of science such as pharmacy, medicine, synthesis and chemical analysis as well as in modern technologies that use their photographic and thermochromic, liquid crystal, chelating and optical non-linearity properties [1]. Compounds made of six-membered imide ring which are 1,8-naphthalimide derivatives, are very popular due to good thermal stability with the ability to emit light [2]. Moreover, the main advantage of malononitrile derivatives is the ability to photoluminescence in the solid state with high quantum yield [3].

Herein, we present small organic compounds with imine (-CH=N-) and vinylene (-C=C-) groups as a materials dedicated organic optoelectronics (Figure 1). As part of the work their selected properties, such as thermal, optical, electrochemical and electroluminescence were examined. The obtained compounds were characterized by high thermal stability and showed 5% weight loss above 288ºC. They were melting at a temperature from 137 to 230 ºC. DSC studies have shown that the compounds are a molecular glasses. Photoluminescence studies in solution, films and blends with PVK:PBD showed their ability to emit light in the range from blue to orange. The ionization potentials and the electron affinities by means of cyclic voltammetry were determined in the ranges -5.58 - -6.32 eV and -3.06 - -3.89 eV, respectively. The ability to electroluminescence was examined by constructing devices with the structure ITO/PEDOT: PSS/PVK: PBD: compound/Al and ITO/PEDOT: PSS/compound/Al. Prepared diodes emitted light with a maximum emission band from 501 to 655 nm.

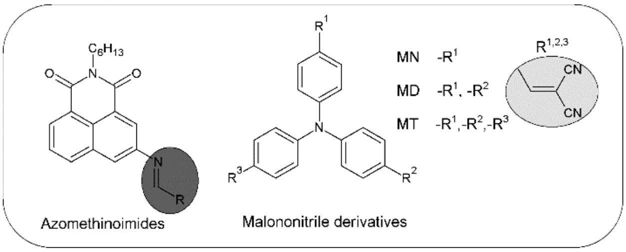

Figure 1: Chemical structure of the azomethinoimides and malononitrile derivatives.

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New semiconducting nonlinear azaacene based on derivatives of vat dyes

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The main goal of this research was to synthesize new organic semiconductors of nonlinear azaacene structure, to characterize their spectroscopic, electrochemical and structural properties and to verify, whether they could be applied as luminophores in electroluminescent light emitting diodes.

In this work a new synthetic method was elaborated, which neither required numerous steps procedure nor expensive catalysts. It is based on modification of known for more than 100 years and practically forgotten vat dyes, containg nitrogen atoms, namely 6,15-dihydrodinaphtho[2,3-*a*:2′,3′-*h*]phenazine-5,9,14,18-tetraone (indanthrone) and benzo[*h*]benz-[5,6]acridino[2,1,9,8-*klmna*]acridine-8,16-dione (flavanthrone). Conversion of these compounds into tetraalkoxy derivatives in the case of indanthrone and dialkoxyderivatives [1,2] in the case of flavanthrone [3] produces solution processable organic semiconductors with very interesting electronic and opto-electronic properties. Transformation of indanthrone into non-linear diazaacene consisted of the reduction of the carbonyl group by sodium dithionite followed by the nucleophilic substitution with alkyl groups under phase transfer catalysis conditions. Beside the indanthrone, this kind of reaction was performed for the linear and bend isomer of indanthrone. Also, dichloro-derivatives of these compounds and dialkoxy-derivatives of flavanthrone have been obtained using this procedure. Synthesis of alkylthienyl-derivatives of flavanthrone have been elaborated through the addition reaction between carbonyl group and lithium derivative of aromatic substituent followed by the core aromatization [4].

In the series of obtained derivatives of vat dyes, one can distinguish acceptor and donor units, which structure strongly influences spectroscopic and electrochemical properties. All obtained compounds are photoluminescent in the range of visible light (from green to orange colour) and quantum yield in the range of 60 – 80 %. Light emitting diodes of guest-host type were fabricated for chosen indanthrone and flavanthrone derivatives. Luminance and current yield of 1800 cd/m2 and 3 cd/A have been achieved [3].

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Iridium-based phosphorescence emitters – synthesis and properties

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Organic Light-Emitting Diodes (OLEDs) show great potential for application as alternatives to traditional inorganic devices, mainly due to the fact that thin-layer technologies for their fabrication are relatively simple, they require a small amount of organic components, and can offer significant energy savings, which makes them environmentally friendly [1]. For the last two decades, a significant increase in the interest in organic light-emitting diodes (OLED) has been observed. Of the few known types of OLEDs, the most efficient are phosphorescent ones which contain heavy transition metals species as dopants. Particularly attractive are the iridium(III) complexes stabilized with 2-phenylpyridine as ligands because of their good performance and tunability. So far only two examples of iridium(III) compounds containing coordinated benzo[*h*]quinoline, a 2-phenylpyridine analogue have been known. These complexes showed interesting electroluminescent properties which are promising for OLED application.

In this communication we present results of our research on the synthesis of new benzo[*h*]quinoline derivatives [2] and iridium(III) complexes containing the former ligands. We designed and synthesized a several examples of ionic compounds bearing two *C,N*-cyclometalated ligands and one *N,N*-donating ancillary ligand [3], a series of neutral compounds stabilized with *β*-ketoiminate ligand beside benzo[*h*]quinoline [4] as well as a few homoleptic meridional complexes containing only *C,N*-cyclometalating benzo[*h*]quinoline derivatives. The substitution effect on the performance of emitters was studied by photophysical characterisation in solution and thin layers. The operating parameters of the exemplary OLED devices, constructed on the basis studied iridium dopants are also presented.

This work was supported by the National Science Centre (Poland) through grant no. UMO-2013/11/B/ST5/01334.

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Highly bendable solution processed organic field effect transistor based on conjugated polymers

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Recent development of organic flexible and stretchable electronics opened a way for a wide range of new applications such as artificial electronic skin, wearable biosensors or paper-like flexible displays [1]. Fabrication of highly flexible organic field effect transistors (OFETs) is possible thanks to conjugated polymers, because of their mechanical elasticity [1,2]. Nevertheless, mechanical deformation induces surface strain of the semiconducting layer, leading to changes of its structural and morphological properties. These changes strongly influence the charge carrier transport in OFETs [2]. To investigate these electro-mechanical properties, mechanical tests of the transistors are performed by means of pre-strained and relaxed elastic substrates. This test enables the formation of wrinkles on the flexible device with small diameters down to several micrometers. These micrometer-sized wrinkles are formed under uniaxial compression of elastic substrate [3,4].

This work, presents basic electro-mechanical studies of flexible OFETs based on Poly(3-hexylthiophene) (P3HT) (Figure 1). The device was peeled off the support glass substrate and placed to a pre-stretched elastomer, enabling deformations on the whole transistor including the active transistor channel. The transistors were fabricated in bottom gate – top contact electrode configuration, which ensured the exposure of the active layer to the applied stress. As substrate and dielectric 1µm thick layer of parylene C was used. The thickness of the whole device did not exceed 2,2µm, ensuring high mechanical flexibility. The active P3HT layer was deposited by spin-coating. Different device parameters such as threshold voltage, charge carrier mobility, on/off ratio were recorded as function of applied mechanical stress before and after deformation of the transistor.

Figure 1. Wrinkling test of P3HT based flexible OFET

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Highly luminescent Ag-In-Zn-S quaternary nanocrystals: growth mechanism and surface chemistry elucidation

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Synthesis of alloyed Ag-In-Zn-S colloidal nanocrystals from a mixture of simple metal precursors such as $AgNO_3$, $InCl_3$, zinc stearate combined with 1-dodecanethiol, (DDT) and 1-octadecene (ODE) and with sulfur dissolved in oleylamine (OLA) results in a complex reaction system whose appropriate control leads to nanomaterials of improved luminescent properties. We determined the mechanism of the Ag-In-Zn-S nanocrystals formation and established the rules determining high photoluminescence (Q.Y.) values in the resulting nanocrystals. The main changes required for the Q.Y. improvement are: replacing ODE with a different, noncoordinating solvent, namely 1,2-dichlorobenzene (DCB) and dissolving sulfur in n-octylamine (OCA) instead of OLA. The choice of the solvent significantly affects reactivity of the precursors, especially the indium one. While sulfur precursor S/OLA, which is used for the reaction, except being a source of sulfur is also a source of two types of ligands binding to the surface of the nanocrystals, during which hydrogenation reaction of (*Z*)-1-amino-9-octadecene (OLA) to 1-aminooctadecane ($C_{18}H_{37}NH_2$) occurs as a transitional stage. Two types of linkages between the ligands and the nanocrystal surface can be distinguished: covalent one ("*crystal - bound*") when the alkyl chain is connected to the nanocrystal surface *via* sulfur ($C_{18}H_{37}$-NH-S-crystal). This linkage is dominant in the case of stoichiometric nanocrystals with ion-balanced surface. The second type involves a typical coordination bond where $C_{18}H_{37}NH_2$ ligand is "*surface-bound*" to indium ions. This linkage is dominant in nanocrystals of non-stoichiometric composition with a cation (predominantly indium) enriched. In nanocrystals of high photoluminescence the second type of linkages predominates. Hydrogenation of OLA to $C_{18}H_{37}NH_2$, occurring in the reaction mixture, is favorable for both types of ligands because it eliminates the adverse rigidity of the chain.

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An organic inverter made by inkjet printing

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Organic electronics is one of the most growing part of the electronic industry. Devices can be deposited onto substrate by solution process such as ink jet printing which is much cost effective technique than vacuum methods used to manufacture devices with inorganic semiconductors [1].

The aim of this work was fabrication of inkjet printed inverters (logic NOT gates), containing in their structure organic transistor and resistor (Fig 1b). Multilayer structures were printed layer on the layer in the following order: gate electrodes and conductive paths from nanosilver ink, polymer dielectric, source and drain electrodes, and organic semiconductors. Devices were printed in ambient atmosphere therefore all materials, used to produce logic gate should be stable in air.

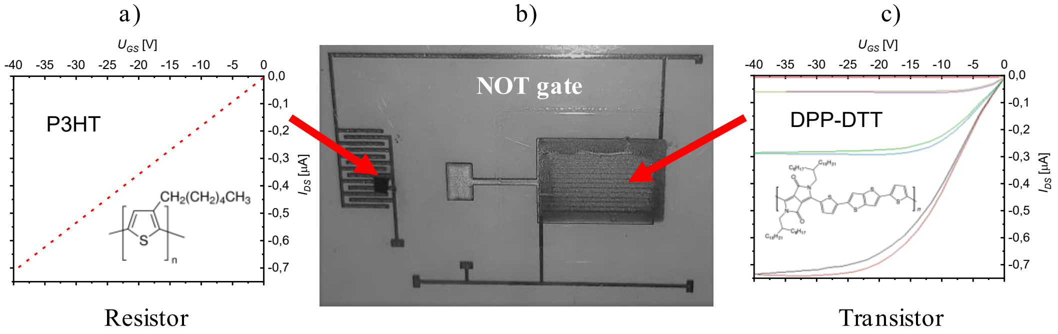

Figure 1: Current-voltage characteristics for a) oxygen doped P3HT and c) air stable DPP-DTT; b) structure of printed NOT logic gate.

In order to find influence of ambient air on organic semiconductors, the aging test of organic transistors with spin coated semiconductor layers were made.

Organic NOT logic gates were prepared using ink jet printer Dimatix 2831 with 16 printed nozzles. As active layers two materials were used: air stable poly[2,5-(2-octyldodecyl)-3,6-diketopyrrolopyrrole-alt-5,5-(2,5-di(thien-2-yl)thieno [3,2-b]thiophene)] (DPP-DTT) (Fig. 1c) for transistors and oxygen doped poly(3-hexylthiophene-2,5-diyl) (P3HT) for resistors (Fig. 1a).

Logic states of working gates were as follows: logic 1 – 38V – 50V, logic 0 – 0V - 8V. In perfect logic gates, these voltages should be: for logic 1 – 3V – 5V, for logic 0 – 0V – 2V. To achieve this range of voltages, the further work is required.

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Study of Clustered Water Structure in Chlorine Derivatives Using Infrared Spectroscopy and Molecular Dynamics Simulations

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Water, as one of the most common substance on Earth, has been a subject of numerous studies for years. In order to explain its unusual properties, numerous theories have been developed concerning the supramolecular structures of water molecules resulting from the presence of hydrogen bonds. One of the most interesting is the theory of water cluster structure [1]. Currently, the biggest challenge for scientists is to study the supramolecular structures of water with simple experimental techniques and under normal conditions.

One of these techniques is infrared absorption spectroscopy. With small amounts of water dispersed in the liquid matrix, such as chlorine derivatives of methane and ethane, it is possible to observe absorption peaks characteristic for small water clusters [2]. Computer simulation methods can be used as a complementary tool to investigate water structure. Molecular dynamics (MD) simulation methods allow detailed analysis of the water clustering process. In order to calculate the vibrational spectra of clusters obtained from the MD simulation and to compare with the experimental results, computational techniques based on density functional theory (DFT) are used [3] [4].

In this work the combination of spectroscopic techniques with simulation methods in the study of water clusters was presented. This is an important step in the development of research into the understanding of supramolecular structure of water. The use of the chlorinated hydrocarbons with different polarity, in which water is dispersed, allowed to explore the relationship between the polarity of the matrix and occurrence of the preferred supramolecular structure in water. Comparison of the results obtained from infrared absorption spectroscopy and from calculations using MD and DFT allowed detailed analysis of the structure of water clusters occurring in real systems.

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Low molecular weight semiconductor / polymer dielectric blends for flexible organic field-effect transistors

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Organic electronics has developed rapidly over last two decades due to the expanding trend to replace silicon-based devices by low-cost, flexible and more environment-friendly substituents. Organic semiconductors and dielectrics appear attractive for these novel technologies due to their great potential for light-weight, stretchable and bendable circuits. Although the development of flexible electronic devices is currently ongoing, a deeper understanding of the relationship between thin film morphology and charge carrier transport in organic field-effect transistors (OFETs) is required for the fabrication of such reliable, flexible devices. [1-2]

One approach to fabricate ultrathin free-standing flexible organic transistors is based on the deposition of a polymer dielectric (polystyrene - PS) and organic semiconductor (tips-pentacene) blend from solution. In this work, the impact of molecular weight of PS and solvent vapor annealing process on the phase separation of the compounds in the film and electrical properties of OFET is presented. The film deposition and morphology was optimized to induce a phase separation between tips-pentacene and PS so that the dielectric polymer was applied as a flexible substrate and dielectric layer at the same time. Polarized optical microscopy and atomic force microscopy revealed a difference in the morphology due to the variation in the processing procedure. Time-of-Flight secondary ion mass spectrometry (TOF-SIMS) showed the distribution of the components over the film thickness and allowed to describe the phase separation. Finally, electrical properties of blend OFETs were compared with devices with plain sublimated tips-pentacene. It was confirmed that it is possible to obtain devices of solution processed blends with similar charge carrier mobility to plain sublimated tips-pentacene on standard Si/SiO_2 substrates.

The research was performed as part of the Foundation for Polish Science program First TEAM/2017-3/26.

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Impedance analysis of the photovoltaic cell with planar DBP/PTCBI heterojunction

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The objective of this work was to research processes determining current flow in the device based on a planar heterojunction of electron donor and electron acceptor organic materials. Studies have been carried out for the device ITO/MoO_3/DBP/PTCBI/BCP/Ag. The analysis was based on direct current-voltage measurements and small-signal admittance spectra in the dark and at photovoltaic conversion of energy. Such analysis may provide information on potential barriers, parasitic resistances and presence of space charge affecting the electric current flow within the device [1-3]. Therefore, this approach could be applied for determination of physical processes related to current flow in multilayer structures, such as photovoltaic cells or photodetectors.

The small signal admittance spectra of photovoltaic organic cells can not be interpreted in a simple way, like spectra of semiconductor diode p-n [4,5]. Both components of admittance, conductance and susceptance, can be modified under the illumination in the presence of various bias voltage applied to the device. It is obvious that the observed effects must be related to the processes determining the flow of charge through the system. In particular, it is known that the conductance value at low frequency must be equal to the DC differential conductance. Analysis of the small signal admittance spectra can provide important information about the processes determining the flow of charge through the sample.

Our analysis is based on direct current-voltage characteristics and small signal admittance spectra obtained within the 50 Hz - 1 MHz frequency range. Our reasoning regards simultaneous analysis of both components of complex admittance and their relation to direct current-voltage curves collected in the dark and under illumination at 615 nm wavelength.

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Synthesis and characterization of new ambipolar Ir(III) complexes – potential emitters for PhOLEDs

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It has been repeatedly emphasized in literature that incorporation of semiconducting moieties into an emitter molecule enhance its intermolecular charge transferring properties within the emissive layer of OLED device, consequently providing better luminance and external quantum efficiency [1][2]. In this communication, the effect of type, quantity and position of semiconducting substituents in ionic iridium(III) phosphorescent emitter molecule on the performance of PhOLED device is discussed. For this purpose, a series of new cationic cyclometalated iridium(III) complexes with the general formula $[Ir(C^\wedge N)_2(N^\wedge N)]^+$ equipped with electron-donating and accepting moieties was designed and synthesized [3][4]. The new iridium(III) phosphors were subjected to photophysical studies, then they were applied in construction of solution-processed PhOLED devices, whose basic operating parameters were recorded. Analysis of the obtained results allowed determination of the effect of a given emitter structure modification on the PhOLED device performance.

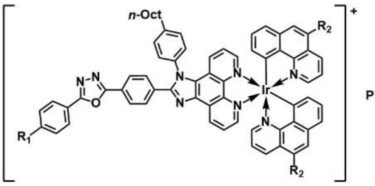

Figure 1: General formula of the studied Ir(III) complexes

This work was supported by the National Science Centre (Poland) through grant no. UMO-2013/11/B/ST5/01334.

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Synthesis and characterization of new hosts for deep blue OLEDs

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Further progress in application of OLED technology requires the development of devices featuring higher luminance, longer lifetime and better color purity. The economic factor also plays an important role in this area, therefore reduction of material costs and simplification of the production process are highly desirable. Efficient and stable red and green diodes have already been commercialized, while the so far designed blue devices are not characterized by high quantum yield and long lifespan in the same time, as achieved for the other primary colors.[1] Therefore, there is still a lot of room for improvement, especially considering deep blue OLEDs. Apart from variation of device structure, much can be done in the field of materials chemistry, aiming at obtainment of new molecules for the device components. [2]

Here we present a series of new hosts suitable for blue emitters. These materials were designed to exhibit variable hole and electron transport properties, and wide HOMO-LUMO bandgap, enabled by the methylene spacer between the carbazolyl and triphenylphosphine oxide moieties. The initial assumptions have been satisfied because all materials were characterized by wide bandgap, caused by reduction of HOMO-LUMO overlapping, the effect of spacer presence. Moreover, almost identical energy levels of frontier orbitals as well as absorbance and photoluminescence spectra proved that this approach might allow variation of the hole/electron mobility ratio without affecting the other properties. The substances were examined for their thermal, photophysical, electrochemical properties, and their capability to host FIrpic and $[Ir(pmp)_3]$ blue phosphorescent emitters

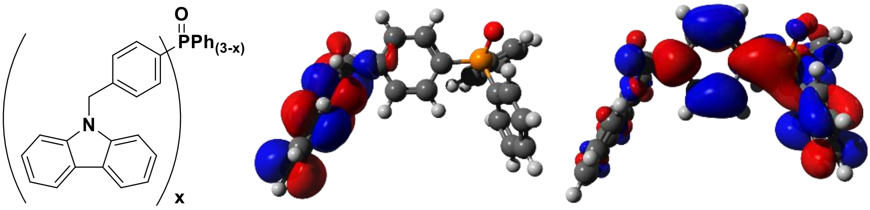

Figure 1: Chemical structures of examined compounds (left, **x=1-3**), calculated HOMO (center) and LUMO contours for **x=1** (right)

This work was supported by National Science Centre, Poland (grant numbers 2013/11/B/ST5/01334 and 2018/29/N/ST5/02926)

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Compounds with thiophene core – a promise for optoelectronics

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In the past few decades, there has been increased interest in new, functional organic materials with unique properties and application possibilities in organic electronics. Despite appreciable development of optoelectronics in recent years, many problems have related to semiconductor processing and efficiency of the devices are still unresolved. Therefore new stable, processable organic compounds, which are able to meet the continually increasing demands are being sought [1] [2].

Thiophene derivatives possess interesting optical and electronic properties that are perfectly in many applications. Moreover, thiophene compounds have good thermal and chemical stability. Any structural changes allow adjusting their optical and electrochemical properties for suitable applications. The promising of them compounds are azomethines with thiophene core. They are tested such as organic semiconductors to organic field effect transistors (OFETs), organic light emitting diodes (OLEDs), photovoltaic devices and electrochromic devices [3] [4].

The aim of the presented work was synthesis and investigations the properties of thiophene derivatives with azomethine linkage(s). Obtained compounds were explored in terms of potential application in OLED technology. Relationships between chemical structures of prepared imines and their crucial properties (thermal, electrochemical, photo- and electroluminescent) was determined. They exhibited good thermal stability and melted at the temperature of 170-260 °C. DSC investigations showed that some of them are molecular glasses. The selected compound were applied as active layer OLEDs and the diodes emitted light in the range of 540-682 nm.

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Electromodulation and magnetomodulation of exciton dissociation in organic materials

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It is widely recognized that exciton dissociation and charge recombination are the fundamental electronic processes limiting the efficiency of organic photovoltaic (OPV) and electroluminescent (EL) devices. These processes in low-mobility organic materials proceed through the intermediate stage of electron-hole (e-h) pair with a finite lifetime, wherein the Onsager approach to geminate recombination as well as Langevin approach to bimolecular recombination are usually applied. The issue of the size of the e-h pairs radius is also worth attention, because the knowledge on this subject is far from complete, for example, the involvement of an e-h pairs in the recombination charge carrier processes is still an open question. A useful tool to track the intercarrier distance in coulombically bound e-h pairs is investigation of magnetic field effect on photoconduction (MPC), electroluminescence (MEL) or photoluminescence (MPL) [1].

In order to clarify the magnetic field effects which operate on the hyperfine interaction scale (magnetic field with a several mT strength), the electron-hole pair (EHP) conversion model has been developed. In this model, intersystem conversion between singlet and triplet pairs, ^{1}(e-h) ↔ ^{3}(e-h), is suppressed by the applied magnetic field, due to Zeeman's splitting of the triplet state. It should be noted that for e-h pairs having a short radius, the singlet-triplet splitting is so large that the intersystem transition is blocked. The intersystem conversion can occur more efficiently in the case of singlet and triplet states of similar energy (quasi-degenerate e-h pair states, see figure 1), which is characteristic of pairs with a correspondingly larger radius (electrostatic exchange interactions decrease exponentially with increase in the e-h pair radius [2]).

In this work electromodulated exciplex fluorescence measurements were performed for two-component: electron donor – electron acceptor systems. Based on the formalism of Onsager theory and its extension proposed by Sano-Tachiya-Noolandi-Hong (STNH model), the lengths of the e-h pairs radii were determined. In addition, measurements of magnetomodulated exciplex fluorescence were carried out for the studied layers. A correlation has been observed between the length of the e-h pair radius and the magnitude of the MPL signal.

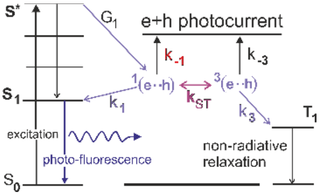

Figure 1: Diagram of energy levels and photophysical processes in organic photoconductors including quasi-degenerate states of singlet ^{1}(e-h) and triplet ^{3}(e-h) pairs

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Synthesis of semi-crystalline POEGMA networks

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Poly(olygo ether mathacrylates) POEGMA based networks are known mainly as materials for thermo-responsive gels [1]. POEGMA hydrogels exhibit thermally induced Volume Phase Transition, which allows to use them as controlled drug delivery systems or artificial muscles. Moreover, due to their biocompatible, they may be used in contact with human body.

Poly(ethylene glycol) is a polymer able for crystallization. Thus, it may be expected that the sufficiently long oligoether side groups of POEGMA can also crystallize. Confirmation of this hypothesis allowed to use them as self-composites - amorphous polymer reinforced by crystalline phase of the same polymer [2].

In this project a few series of POEGMA networks were made by Radiation Induced Polymerization and Crosslinking of monomers with different length of side groups. Obtained results show an impact of side group length and irradiation dose (cross-linking density) on physico-chemical properties of the POEGMA networks. In addition, the reaction atmosphere impact on gelation dose (minimal dose necessary to obtain macroscopic gel). The most promising results were obtained for POEGMA with the side chains containing more than seven oxyethylene groups. The materials are semi-crystalline as results of Differential Scanning Calorimetry (DSC) and Wide Angle X-ray Scattering (WAXS) confirmed.

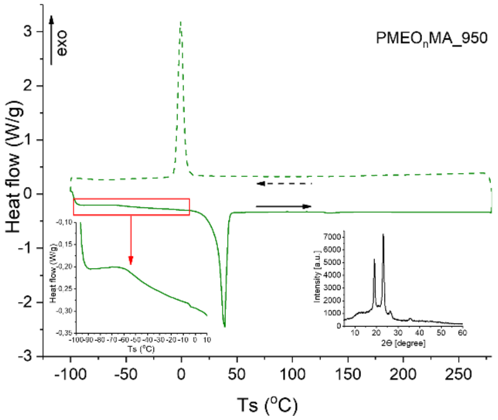

Figure 1: Selected DSC and WAXS results for POEGMA networks

Acknowledgements, This project was supported by Polish National Science Center grant no. 2016/21/N/ST5/03078.

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Dependence of electrical properties of donor-acceptor mixtures on HOMO energy of conductive polymers

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The unwavering interest in organic photovoltaics results from the fact that solvent methods of deposition of organic compounds (including printing) are less burdensome for the environment than the methods of inorganic electronics production. Products made of organic materials are also easier to recycle than inorganic electronics. The flexibility of the devices allows for the creation of uniform and large format systems with their reversible deformation [1].

The problem with the current organic photovoltaic is the inability to describe the electric properties of the devices by classic energetic models developed for inorganic semiconductors. Therefore, the purpose of the study was to analyze the effect of differences between the energy of highest occupied molecular orbital (HOMO) of conductive polymers and the energy of lowest unoccupied molecular orbital (LUMO) of low molecular weight compounds on the photoelectric properties of their mixtures. Polymers with the given energy levels were used for the tests: poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl] thieno [3,4-b]thiophenediyl]] (PTB7), poly[2,5-(2-octyldodecyl)-3,6-diketopyrrolopyrrole-alt-5,5-(2,5-di(thien-2-yl)thieno [3,2-b]thiophene)] (DPP-DTT), (poly(3-hexylthiophene-2,5-diyl) (P3HT), poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta [2,1-b;3,4-b′]dithiophene)-alt-4,7(2,1,3-benzothiadiazole)] (PCPDTBT), poly[2,7-(9,9-dioctylfluorene)-alt-4,7-bis(thiophen-2-yl)benzo-2,1,3-thiadiazole] (PFO-DBT), poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT), poly[(5,6-dihydro-5-octyl-4,6-dioxo-4H-thieno[3,4-c]pyrrole-1,3-diyl)[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl]] (PBDTTPD. Low molecular weight compounds were naphthalene diimide derivatives: N,N'-Bis(sec-butyl)-1,4,5,8-naphthalenecetracarboxyl-1,4:5,8-bisimide (LUMO -3.66) [2] and N,N'-Bis(4-n-hexyloxyphenyl)-1,7:4,5-naphthalenecethracarboxyl-1,4:5,8-bisimide (NBI-4n-OHePh) (HOMO -6.37, LUMO -4.12). [3].

Photosensitive systems were made, in which the active layer was a mixture of polymers with small molecule compounds in mass proportions of 1 to 1. This allowed to correlate the open circuit voltage with the energy levels of polymers. The mobility of charge carriers in the tested materials was also estimated.

Polymer	HOMO [eV]	LUMO [eV]
PTB7	-5,15	-3,31
DPP-DTT	-5,2	-3,52
P3HT	-5,2	-3.53
PCPDTBT	-5,3	-3.55
PFO-DBT	-5,4	-3.6
PCDTBT	-5,5	-3.6
PBDTTPD	-5,56	-3,75

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Comparison of electrical performances of organic field-effect transistors with inkjet printed and thermally evaporated electrodes

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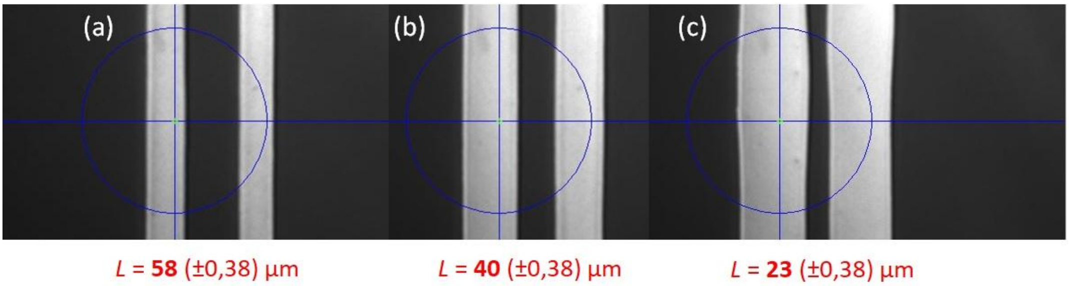
Inkjet printing is becoming an important technology for various applications, among which one of the most promising remains organic electronics [1]. This additive method of processing of the subsequent layers and elements in devices bearing different functions, e.g. switching (Organic Field-Effect Transistors) or light emission (Organic Light-Emitting Diodes), enables to achieve satisfactory operational results while minimizing the waste of material [2]. This is a vital fact, considering the high cost of production of fine chemicals in the case of organics, and increasing shortage of resources-based substrates, like e.g. case of the indium-tin oxide (ITO).

Here we report the developed series of silver conductive tracks based on the ultraprecise inkjet printing of silver nanoparticle-based inks. Due to the complexity of the inkjet printing process, in the first part we show the optimization of the geometrical and morphological features of the silver tracks by adjustment of printing parameters and substrate properties. In the following part, we present the results of resistivity measurements, confirming the proper thermal post-processing of the printed tracks. Ultimately, the inkjet printed silver tracks were used as the source and drain electrodes in the Organic Field-Effect Transistors in the bottom gate-bottom contact configuration. The electrical characteristics of devices with the inkjet printed electrodes is compared with performances of OFETs with the same device architecture, but thermally evaporated silver electrodes. The potential differences in the performances of both types of devices may be connected with different surface topography of inkjet printed and evaporated silver, or in the different values of workfunction of printed and evaporated metal, coming from the organic additives in the silver nanoparticle ink.



L = **58** (±0,38) µm L = **40** (±0,38) µm L = **23** (±0,38) µm

Figure 1: (a) Single, (b) double and (c) triple imprints of silver nanoparticle ink on silicon dioxide surface. L denotes values of distance between the edges of silver tracks, identical to channel length.

The research is financed by the Foundation for Polish Science – project First TEAM/2017-3/26 "Self-standing, flexible and solution processable organic field effect transistors for complementary inverter applications".

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Fully etched vertical Silicon nitride grating coupler

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In a field of integrated optics grating couplers are very common systems used for coupling light into a waveguide. Numerous of highly efficient couplers were proposed in a literature [1][2][3]. In a majority of them, materials with a very high refractive index like Silicon [4] are used with a few hundred nanometer thickness of the waveguide. In this research we present a grating coupler dedicated for systems with 100 nanometer silicon nitride waveguide. A design of presented grating coupler differs from commonly used grating couplers due to the fully etching, which includes bottom region under the waveguide. This approach led to the theoretical increase of coupling efficiency by 12% (for wavelength 1300 nm) in comparison to the traditional unetched grating coupler. All computations were performed with the Plane Wave Admittance Method [5], which is time efficient in comparison to the traditionally used Finite Difference Time Domain method and allowed us to investigate grating coupling efficiency as a function of: period, fill factor, etching depth and height of layers.

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Photovoltaic properties of DBP/PTCBI planar heterojunction devices

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The investigated system was based on a fullerene-free planar donor/acceptor heterojunction of two perylene dyes, i.e. PTCBI (perylenetetracarboxylic bisbenzimidazole) and DBP (tetraphenyldibenzo-periflanthene) of chemical structures shown in Fig.1a. Relative positions of HOMO and LUMO levels of these materials seem to provide suitable conditions for efficient exciton dissociation, and relatively high values of the open-circuit voltage of about 1.0 eV [1,2]. ITO and Ag were used as the front and back electrodes, respectively, while thin MoO_x and BCP (bathocuproine) buffer layers were introduced to eliminate exciton quenching at electrodes, facilitate extraction of free charge carriers at respective contacts and to prevent the damage of the acceptor layer upon Ag deposition [3-6]. Photovoltaic properties of the system in question were characterized on the basis of short-circuit current and open-circuit voltage action spectra, current-voltage measurements carried out in the dark, under monochromatic illumination of low intensity, and white light illumination, along with light intensity dependence of short-circuit current and open-circuit voltage.

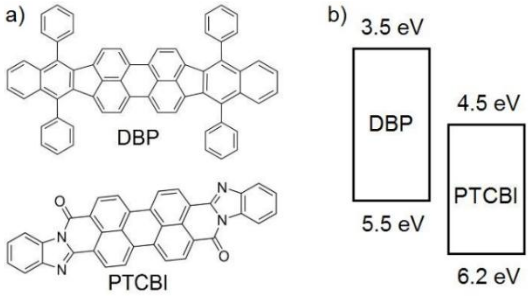

Figure 1: Chemical structure of DBP i PTCBI, (a), and energetic structure of layers formed by these materials [1,2] (b).

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From Liquid to Solid State: preparation of highly homogeneous, smooth, transparent films of liquid-exfoliated WS2 in the polymer matrix.

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Since graphene discovery and its presentation as a wonder material scientist started looking for similar structures. The Liquid Phase Exfoliation method enabled isolation of 2-dimensional (2D) nanomaterials with precise control of size, shape, composition and number of layers[1]. In presented research tungsten disulphide dispersions with high population of single and few layers were prepared by LPE method. High quality of the 2D structures was verified with use of techniques like TEM, AFM UV-Vis, Raman Spectroscopy. Applying earlier developed size selection procedure, narrow lateral size distribution of WS2 nanosheets in liquid dispersions was achieved. Further, monolayer enrichment procedure was demonstrated to successfully enrich liquid exfoliated WS2 dispersions in monolayers, resulting with WS2 monolayer contents of about 75%[2]. Although Liquid Exfoliated 2D materials exhibit a wide range of desirable for applications properties, there is a significant drawback associated with them being dispersed in a liquid. For many applications such as transistors, it is required that the materials must be in a solid form. That is challenging without quenching the optical properties. Therefore, transfer from liquid to the solid state became undoubtedly important in nowadays research. The presented study will discuss preparation of highly homogenous, smooth and transparent WS2 films in the polymer matrix, which will surely open doors for future electronics devices fabrication.

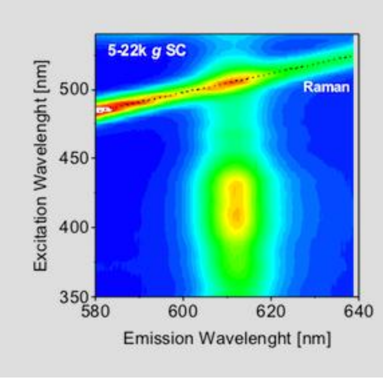

Figure 1: Photoluminescence Excitation-Emission map of WS2 in PMMA matrix.

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The influence of atmospheric factors on the electrical properties of organic light emitting diodes tested by impedance spectroscopy method

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The paper presents the results of tests carried out using impedance spectroscopy in organic light emitting diodes (OLED), in which the anode was indium tin oxide (ITO) coated with a thin layer of poly (3,4-ethylenedioxythiophene) composite: poly (2-styrene sulfonate) (PEDOT:PSS). The active compound was a commercially available compound called super yellow[1] emitting yellow light, made of a thin layer of calcium (Ca) coated with an aluminium layer (Al). The investigations for OLEDs, in which the semiconductor layer was isolated from the influence of atmospheric factors were performed. The similar tests were carried out for the same diodes exposed to oxygen and air humidity

A significant reduction in the luminance of the OLED diode as a result of diffusion of oxygen molecules (or water) to the super yellow layer was observed. Nyquist graphs show the evolution of the studied system during exposure of the semiconductor layer to atmospheric conditions (Figure 1).

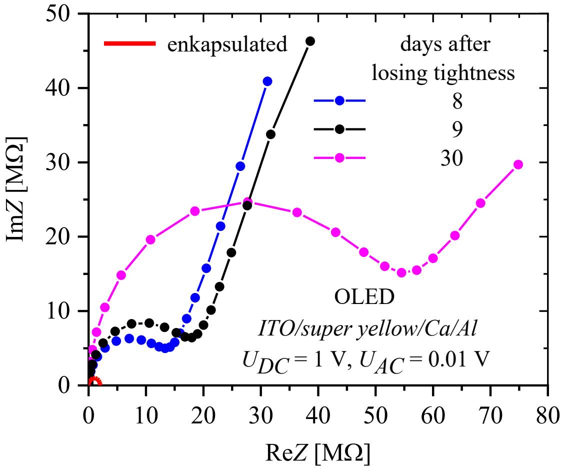

Figure 1. Evolution of the Nyquist graphs for studied OLED system.

Charge transfer resistance, double layer capacitance, Warburg constant and other parameters were determined and represented as a function of the applied potential. Analysis of charge transfer resistance as a function of potential allowed an estimation of standard redox rate constants for the compounds' oxidation and reduction processes.

This work was partially supported by The National Science Centre (Poland) under grant(2016/21/B/ST5/00984).

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Comparison of solution – processed organic field-effect transistors on rigid and flexible parylene C substrates

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Over the past years organic electronics have attracted attention due to advantages over traditional inorganic technology. One of the largest advantages of organic electronics is the possibility to create flexible devices, where traditional silicon is replaced by conjugated molecules or polymers [1].

This work focuses on the fabrication and investigation of flexible organic field-effect transistors (OFETs) based on parylene C as substrate and dielectric [2]. 6,13-Bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene) is used as an organic semiconductor, and solution-processed by three different methods: drop-casting, spin-coating and zone-casting. The diverse film morphologies of the semiconductor layers influence in different manner the charge carrier transport in bended OFETs. The transistors are firstly processed on rigid auxiliary substrates and lifted-off by means of a scotch tape. Thereby, the transistor is placed into a free window of the tape to create a free-standing device (Figure 1). No difference in device performance was observed before and after the lift-off process. Further bending studies, under small angles, did not reveal any influence on the charge carrier transport for all investigated film morphologies (large, oriented in random direction crystallites, small crystallites and large, long, linearly oriented crystallites).

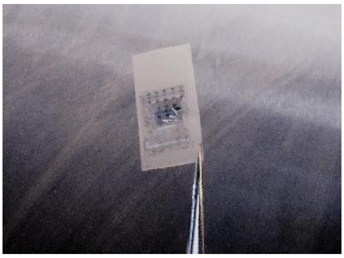

Figure 1. A free-standing OFET lifted-off from a rigid glass substrate by using scotch tape.

This work is supported by the National Science Centre UMO2015/18/E/ST3/00322.

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Bending of C8-BTBT based field-effect transistors

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Organic field-effect transistors (OFETs) have been widely studied because of their unique potential to enable applications such as low cost, flexible or stretchable electronic devices. The possible applications are wide, from flexible consumer electronics to medical applications [1]. In last decades, great progress was made reducing device size and increasing the charge carrier mobility. Several new organic semiconductors attracted attention such as 2,7-dioctyl[1]benzothieno[3,2b][1]benzothiophene (C8-BTBT) with charge mobilities exceeding 10 [$\mathrm{cm^2/(V\cdot s)}$] for solution processed, flexible devices [2]. Despite many research groups exploring the bending stability of flexible OFETs, until today no unified benchmark bending tests for OFETs were developed.

In this work, we present a quantified bending test of a series of transistors based on C8-BTBT deposited from solution and by thermal evaporation with various device architectures. The transistor parameters were measured before, during and after bending down to bending radius of 2 mm. The experiment was conducted on a home-build bending test setup. The transistors were bent on a stiffer support polymer foil, allowing concave and convex bending. Both solution processed and sublimed films were prepared on a Parylene-C dielectric layer, which was also exploited to encapsulate the active layer. The total thickness of the entire devices ranged from 2 μm to 10 μm. A series of C8-BTBT transistors was prepared with a symmetric geometry of the dielectric/support and encapsulation layers in order to test the neutral-zone bending in OFETs.

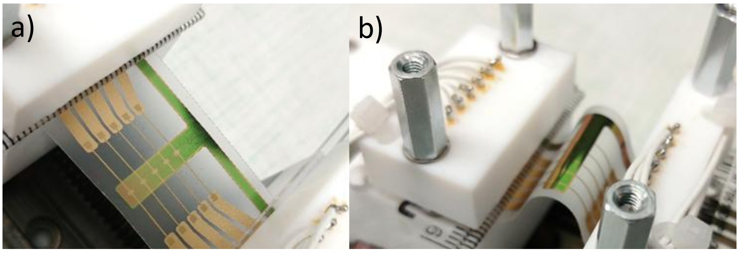

Figure 1: Bending test of a five transistor sample based on C8-BTBT active layers a) flat sample before bending and b) bent transistor in the home-build bending setup.

This work is supported by the National Science Centre UMO2015/18/E/ST3/00322

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Efficient materials for photonics – azopyridine derivatives with a hydroxyl group

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Efficient materials, in which light can induce reversible changes in physicochemical properties, are continuously search for due to possible applications in photonics. In this work, photochromic phenomena of azopyridine derivatives in three different organic solvents was described. The studied compounds differed in the position of the nitrogen atom in the pyridine ring and the way of substitution of the hydroxyl group in the aromatic ring **(Fig. 1)**. Photochromic reaction yields and the rate constants (k) of the thermally driven *cis-trans* isomerization were determined **(Fig. 2)**.

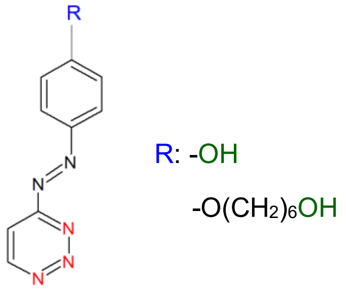

Fig. 1. Chemical structure of the studied azopyridine derivatives; R corresponds to the respective

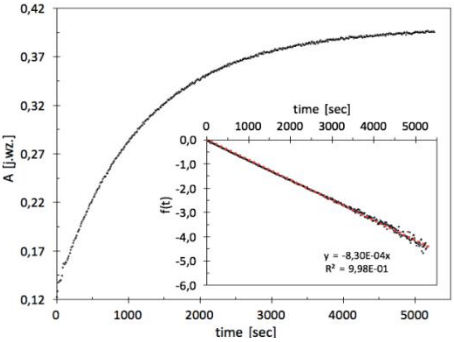

Fig. 2. Changes in the absorbance at wavelength that corresponds to the maximum of the absorption band. The inset shows the way of determination of the rate constant of thermal back reaction, where $f(t) = ln\frac{A_t - A_\infty}{A_0 - A_\infty} = -kt$.

It has been shown that the chemical modification of the structure significantly affects the parameters of photochromic reaction. The influence of the polarity of the solvent on the course of the isomerization process was investigated. The results of the study were compared with those already reported in the literature [1-3]. The analysis of the results allows to select materials that can be used in the optical information recording, e.g. as photonic memories.

The work was partially financed from the funds of the Faculty of Chemistry of Wroclaw University of Science and Technology. This work was financially supported by the National Science Centre, Poland 2014/15/B/ST8/00115.

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Employing TADF dopant for performance enhancement in solution processed phosphorescent OLEDs

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Relatively new approach of performance enhancement was applied in case of phosphorescent organic light-emitting diodes (OLEDs). Adachi's group in 2014 proposed application of thermally activated delayed fluorescence (TADF) type material, as an assistant dopant, in a host-guest system[1]. However, most of studies is related to the usage of a fluorescent material, as a target emitter. Therefore, operation of TADF sensitizer in the system of 'matrix–>TADF–>phosphorescent emitter', was checked.

Up to date, the most efficient blue TADF OLEDs were obtained with 10-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-10H-spiro[acridine-9,9'-fluorene] (SpiroAC-TRZ) [2] [3]. Therefore, this compound was selected as the assistant dopant. Whereas, for the matrix, commonly known, poly(*N*-vinylcarbazole) (PVK) was applied. Mostly due to its good emission overlap with TADF absorption and perfect film forming properties. Additionally, high singlet and triplet energies force efficient exciton energy transfer to the dopant.

First of all, mixtures of the host with the TADF were checked, in wide range of concentration. In the next step, new β-ketoiminate Ir complex was added to the system. Results were compared, for OLEDs based on PVK + Ir complex, with those obtained for SpiroAC-TRZ addition into the emissive system. TADF assistance lowered turn-on voltage, raised brightness, stabilized flowing current and increased current efficiency, by approximately 4 times. Furthermore, electroluminescence, in both cases, totally occurred from the Ir complex, that confirms appropriate materials adjustment. Additionally, lifetime measurements, in regime of constant current, revealed largely improved device stability.

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Synthesis and Electrical Properties of Polymeric Materials Crosslinked by Metal-Ligand Coordination

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Intensive development of flexible printed electronics and miniaturization of devices determine production of new materials with well-defined electrical parameters, and very good mechanical properties. These requirements can be fulfilled by creation and characterization of fully stretchable dielectric materials with enhanced self-healing properties.

The main scope of this work is synthesis of dielectric polymers cross-linked by metal-ligand coordination and investigation of their electrical properties with reference to various metal-ligand cross-linkers used.

Preparation of dielectric polymers with metal-ligand coordination was done by a two-step synthesis. First, bipyridine (bpy) moiety was incorporated into polydimethylsiloxane (PDMS) chain by coupling reaction. Then, the obtained bpy-PDMS system was mixed with a required amount of transition metal salt to initiate the crosslinking process [1] [2]. Proton nuclear magnetic resonance (^{1}H NMR) was used to monitor the structure of bpy-PDMS conjugate. UV-Vis spectroscopy was used to check metal ion‑bpy complexation. Electrical measurements were performed by broadband dielectric spectroscopy (BDS), which gave correlation between structure of materials and their electrical properties.

Extended knowledge about the synthesis and electrical properties of polymeric materials crosslinked by metal-ligand coordination can give more information about chemistry aspects and possible industrial applications of such a type of materials.

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Controlling the crystal organization of the C8-BTBT organic semiconductor film to improve the charge transfer properties and morphology based on the film thickness and substrate speed relation

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Organic semiconductors have attracted enormous attention in the last few decades due to the improvement in the performance of the electronic devices based on these materials. Especially, small molecules have been used as an active layer in the field-effect transistors (FETs) is one of the main potential application.[1]

In this study, the thickness dependence of the organic semiconductor solution (C8-BTBT as OSC – Tetrahydrofuran as solvent) due to substrate speed and its effect on the microstructure, morphology and charge transfer properties have been investigated.

The solution was deposited by using zone-casting deposition method.[2] The general trend in meniscus-guided coatings distinguished the film thickness-shearing speed relation into two distinct regimes in which the evaporative regime indicates that the increasing the shearing speed decreases the film thickness when the solvent evaporation speed is higher than the shearing speed and landeu-levich regime comes to exist at the moment where the film thickness starts increasing because more solution is pulled out and resulted film behind meniscus is wet. [3]

Furthermore, not just the film thickness but also the crystal organization of the OSC is strongly influenced by the transition of these two distinct regimes. Therefore, C8-BTBT crystallization on SiO_2 can be tuned intrinsically with better organization to transfer the charge-carriers based on the film thickness-substrate speed relation, as determined by atomic force microscopy (AFM), polarized optical microscopy (POM) and electrical characterization under the field-effect.

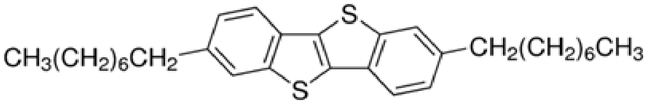

Figure 1. Molecular structure of C8-BTBT used as OSC.

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Synthesis, electrochemical and optical properties of new quinacridone derivatives

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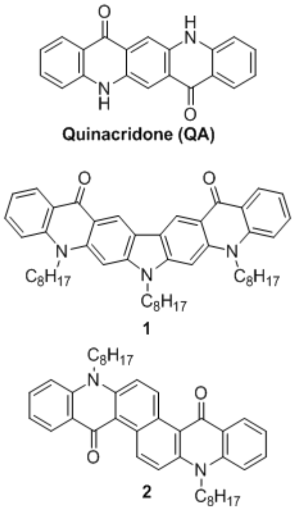
Quinacridone (**QA**) (**Scheme 1**) has recently attracted considerable attention as an organic semiconductor exhibiting interesting luminescent, transport and photovoltaic properties.

Here, we present synthesis of quinacridone derivatives allowing the incorporation of moieties other than phenylene ring into the central core of the molecule. Two new quinacridone derivatives with carbazole (**1**) and naphthalene (**2**) core (**Scheme 1**) were prepared and characterized by electrochemical and spectroscopic methods [1]. Modification of the conjugated core in **1** and **2** led to profound changes in their optical properties as compared to the case of *N,N'*-dioctylquinacridone. The compound **2** with the naphthalene central core is a very good emitter of fluorescence photons, much better than classical quinacridone. The synthesized new molecules are promising candidates for optoelectronics.



Scheme 1. Structures of quinacridone (**QA**) and its derivatives **1** and **2**

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Synthesis and characterization of palladium nanoparticles obtained from (bis)amino carboxylate complexes

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Stabilization of nanoparticles with ligands containing amino and carboxyl groups allows to obtain spherical nanoparticles with a narrow size distribution [1] [2]. Our work focused on understanding the mechanisms of formation of stable (bis) amino carboxylate complexes of palladium. Then, the obtained complexes were reduced by various methods: thermally and using the different silanes (e.g. 1,1,3,3-tetramethyldisiloxane).

Interactions of ligands with Pd^{2+} ions in the complex and interaction with the metallic surface of the nanoparticles were examined using various NMR and FTIR techniques. The thermal properties of alkylamine complexes with palladium acetate and palladium palmitate were also investigated using the DSC technique. These studies showed that in the synthesis of nanoparticles, the amines act as a solvent, reducer and ligand in the complex with the carboxylate and as the stabilizer of nanoparticles.

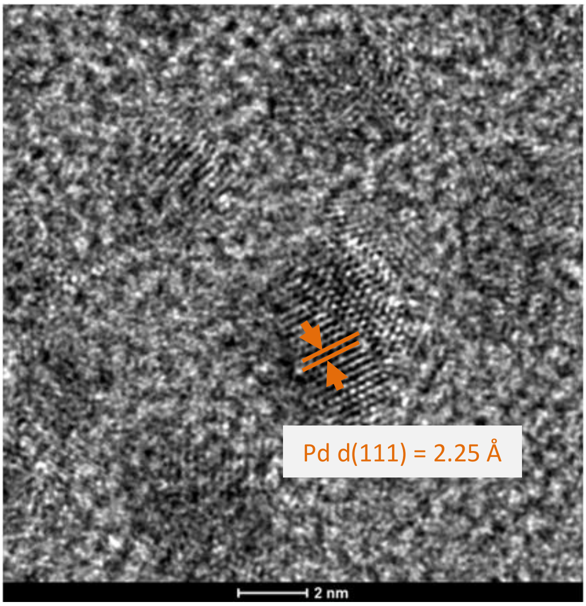

Figure 1. HRTEM of PdNPs obtained from $Pd(OAc)_2$_2HDA complex at 140 °C.

The project "Synthesis and characterization of bimetallic nanoparticles obtained from (bis) amino carboxylate complexes of silver and palladium" was financed by the ***Centre of Molecular and Macromolecular Studies*** *PAS under a grant for young scientists*

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Role of polymer binder on the crystallization of organic semiconductors during meniscus guided coating

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Small molecule organic semiconductors (OSCs) suffer from their uncontrolled nucleation and growth during solution processing limiting their functionality in electronic devices. In this work, we focus on the role of polymer binder on the crystallization of conjugated small molecule OSCs for organic field-effect transistors. A small fraction of amorphous poly(methyl methacrylate) (PMMA) efficiently improves the crystallization of dip-coated small molecule OSCs, α,ω-dihexylquaterthiophene (DH4T) and diketopyrrolopyrrole-sexithiophene (DPP6T). The high charge carrier mobility originates from a continuous alignment of the crystalline films and stratified OSC and PMMA layers.[1]

During dip-coating of OSC:polymer blend, a high viscosity gradient is formed in the meniscus resulting from the polymer binder. In this way, the polymer binder facilitates the drag of small molecule OSCs and thus mass transport for film growth. Our findings demonstrate that a small fraction of a polymer binder during dip-coating efficiently balances the mass transport during dip-coating and improves the crystallization as well as the electronic properties of OSC films.

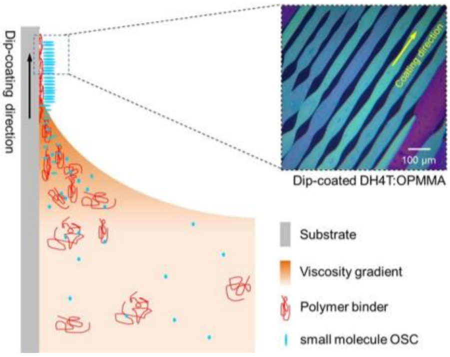

Figure 1: Schematic illustration of dip-coating of OSC:polymer blend.

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Salicylaldehyde azines exhibiting aggregation induced emission enhancement as fluorescent emitters for non-doped OLEDs

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Various luminescent materials have been studied for many years since their wide application potential in the field of organic electronics, especially in organic light-emitting diodes (OLEDs), transistors, organic lasers, as well as fluorescent sensors or probes. However, conventional luminophores have suffered from aggregation-caused quenching (ACQ) due to strong intermolecular p-p stacking when their molecules are aggregated. This results in significant decrease of luminescence thus prevention of this effect is needed. To that end, various approaches were employed. In field of OLEDs, aggregation is inhibited by so-called host-guest systems. Nevertheless, in numerous cases the aggregation can only be temporarily hampered to certain extents. The reason of this is that aggregate formation is a natural process for the luminogen molecules located in close proximity.

In sharp contrast to destructive ACQ, aggregation-induced emission (AIE) may be considered as a constructive effect. The AIE effect enables active utilization of the aggregation process, instead of passively working against it. AIE refers to the group of luminogenic materials which emission is poor once they are dissolved in good solvents but become significantly increased when molecules are clustered in poor solvent or solid state (for example thin layer) when aggregates are formed. In 2001, Tang et. al. at the Hong Kong University of Science and Technology have described this phenomenon for the first time. [1] They also proposed their the most possible working mechanism called "restriction of intramolecular rotation". Although that explanation was broaden recently to the "restriction of intramolecular motion" by taking into consideration the restriction of intramolecular vibration.

In this work, four compounds exhibiting AIE effect have been designed, synthesized and are under examination in terms of their utility as the emitters for non-doped OLEDs. This materials are non-emissive in a good organic solvent, eg. tetrahydrofuran (THF). When THF/water mixture with a fraction of water (fw) is lower than 60 vol%, weak or no fluorescence could be observed. Its fluorescence is turned on when fw reaches ca. 60 vol% and increasing upon increase of water fraction. Moreover, they exhibit strong emission in solid state (powder and thin layer). Nevertheless, film forming properties via spin coating method are not acceptable hence further work will be focused on improving the quality of deposited layers. It is a crucial step toward achieving solution processed OLED with these materials. Additionally, the effort will be put to fabricate OLED in which these AIE compounds are fabricated by a vacuum-deposited technique.

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