Institute of Physics of the National Academy of Sciences of Ukraine
Taras Shevchenko National University of Kyiv
Ukrainian Physical Society

SPECTROSCOPY OF MOLECULES AND CRYSTALS

Book of Abstracts
of XXVI Galyna Puchkovska International School-Seminar

Dedicated to 90th birthday of Professor Galyna Puchkovska

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XXVI

Galyna Puchkovska International School-Seminar
Spectroscopy of Molecules and Crystals

22-25 September, 2024, Wojanow, Poland

Professor Galyna Puchkovska (June 22, 1934- September 29, 2010) is a famous Ukrainian scientists, physicist, Laureate of the State Prize of Ukraine, Honored Worker of Science and Technology of Ukraine, member of European Academy of Arts, Sciences and Humanities.
In 1973, Galyna Puchkovska initiated the all-Ukrainian School-Seminars "Spectroscopy of Molecules and Crystals" which since 1991 became an international one being among the first of such kind scientific meetings in Ukraine. In 2011, after professor Galyna Puchkovska's pass away, the International School- Seminar "Spectroscopy of Molecules and Crystals" was named in her honor. The ISSSMC conferences headed by professor Puchkovska were held for almost 35 years biennially in different cities of Ukraine, even in the most severe times for our country, and are still traditionally organized nowadays as a recognized world-wide meeting of spectroscopists from different research fields.

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In memoriam of professor Valeryi Yashchuk

TABLE OF CONTENT

Preface

In honor of Professor Galyna Puchkovska

The XXVIth Galyna Puchkovska International School-Seminar "Spectroscopy of Molecules and Crystals" (ISSSMC-2024) is held jointly with the XVIIth International Conference on Molecular Spectroscopy (XVIIth ICMS) on September 22-25, 2024, in Wojanow Palace, Poland.

Despite that we always consider live communication between participants as the most attractive feature of our conferences, this year we were forced to reduce the risks of traveling to Ukraine for the participants because of the ongoing terrible Russian invasion to Ukraine. Therefore we gladly accepted the kind offer of our Polish colleagues to organize ISSSMC-2024 together with the XVIIth International Conference on Molecular Spectroscopy.

This year's ISSSMC-2024 conference is dedicated to 90 years since the birthday of Professor professor Galyna Puchkovska Puchkovska (22.06.1934–29.09.2010), an outstanding Ukrainian scientist, laureate of the State Prize of Ukraine, and the Honored Worker of Ukraine in Science and Engineering. She was one of the world-famous specialists in the domains of molecular spectroscopy, solid state physics, and phase transformations in crystals with hydrogen bonds.

During many years of her scientific activity, the research interests of professor Galyna Puchkovska were related to various aspects of solid-state physics, molecular physics, spectroscopy of molecules and crystals, liquid crystals, and disordered molecular systems. A considerable achievement of professor Galyna Puchkovska was an experimental study of surface polaritons in anisotropic crystals of alkaline iodates, zinc oxide, and beryllium oxide. The surface polaritos dispersion branches were determined for the first time for bulk crystals, as well as thin films on various substrates and ceramics, which was important for various applications.

In 1984, for her works related to the research and development of new generation of infrared pyroelectric detectors, professor Galyna Puchkovska was awarded the State Prize of Ukraine in Science and Engineering.

Professor Galyna Puchkovska was the first who proposed to use the Davydov splitting phenomenon in the vibrational spectra for the analysis of phase transitions in the crystals of long-chain aliphatic compounds. In particular, she found a correlation between the magnitude of Davydov splitting of sensitive IR absorption bands and the crystal lattice parameters, which made it possible to prove the existence of rotational crystalline phases in the crystals of n-paraffins and carboxylic acids. Her other research works on crystals with hydrogen bonds are highly recognized. Professor Galyna Puchkovska is also known for her pioneer works in the filed of liquid crystals and LC nanocomposites, which revealed the role of conformational changes in liquid crystal molecules and the nanoparticles effect on the LC mesogenic properties and phase transitions.

In 2006, for the cycle of works “Polymorphic and quantum effects in molecular crystals”, professor Galyna Puchkovska was awarded the Antonina Prykhot’ko Prize of the NASU. In 2008, by a decree of the President of Ukraine, she was awarded the honorary title of the Honored Worker of Ukraine in Science and Engineering.

Professor Galyna Puchkovska was one of the first scientists at the Institute of Physics of the NASU, whose scientific achievements have found practical application. In particular, she proposed to apply the IR spectroscopy for the analysis of oil-lubricating materials produced at some Ukrainian oil refinery, which was then widely used to improve their performance for automotive industry.

Professor Galyna Puchkovska was highly recognized among the scientific community. In 1998, she received the Soros' Associate Professor honorary title. In 2001, for her outstanding achievements in science she was elected a member of the European Academy of Arts and Humanity (Paris, France). In 2004, a special issue of the Journal of Molecular Structure was dedicated to professor Galyna Puchkovska on occasion of her 70th birthday [J. Mol. Struct. 2004, 708, 1–210].

Professor Galyna Puchkovska was a uniquely heartfelt person. Communicating with her was always full of warmth and sincerity, and, despite her academic titles and high recognition, she was always enthusiastic about taking part in informal meetings and social events. She was always surrounded by her grateful students, interesting people, colleagues and friends.

In 1973, on her incentive and with her active participation, the all-Ukrainian (which have later become International) School-Seminars “Spectroscopy of Molecules and Crystals” were initiated. For more than 35 years (!), professor Galyna Puchkovska headed this meetings, being the unchanged president of the organizing committee of this unique scientific forum. She was not only the founder, but also the great friend and the soul of these conferences!

In 2011, after Galyna’s pass away, the International School-Seminar “Spectroscopy of Molecules and Crystals” was named in her honor. With active participation of the Institute of Physics of the NASU, Taras Shevchenko National University of Kyiv and Ukrainian Physical Society as the conference organizers, with its more than 50 year history, Galyna Puchkovska International School-Seminar "Spectroscopy of Molecules and Crystals" remains one of the oldest international scientific forums in Ukraine.

Many well-known Ukrainian specialists in the field of theoretical and experimental spectroscopy have lectured at the ISSSMC conferences, and many famous scientists from Poland, Lithuania, USA, France, Germany, Spain, Sweden, Romania, Uzbekistan, Turkey, Israel, and other countries have presented their brilliant reports at the School-Seminar in different years. Such involvement of outstanding Ukrainian and foreign scientists, as well as scientific youth, including gifted and talented children from the National Center “Minor Academy of Sciences of Ukraine”, contributes to the development of advanced scientific spectroscopic methods, the establishment of international scientific relations, and the growth of the authority of Ukrainian scientists in the world.

We do much hope that the next XXVIIth Galyna Puchkovska International School-Seminar "Spectroscopy of Molecules and Crystals" will be held in an ordinary format in peaceful beautiful Ukraine with a lot of participants from all over the globe!

Stay with Ukraine! Be brave like Ukraine! Glory to Ukraine!

Organizing Committee ISSSMC-2024

INVITED LECTURES

IGP-1	**Linear photophysics, fast vibronic relaxations and two-photon absorption properties of new coumarin derivatives** *M.V. Bondar*
IGP-2	**Solid-state NMR of phosphate based functional materials** *V. Klimavicius*
IGP-3	**Induced and spontaneous nanostructuring in liquid crystal colloidal systems for display and sensor applications** *L.N. Lisetskii*
IGP-4	**Molecular machines powered by electronic excitation** *A. Demchenko*
IGP-5	**ROS-regulating nanomaterials** *S. Yefimova*
IGP-6	**Luminophores for luminescent solar concentrators** *G. Rudko*
IGP-7	**Phases transition phenomena in highly sensitive luminescence nanothermometry** *M. Drozd*
IGP-8	**Triplet-triplet annihilation mechanism of intrinsic charge-carrier generation in neat organic semiconductors** *A. Kadashchuk*
IGP-9	**Heat capacity of molecular crystals with different types of disorder** *A. Krivchikov*
IGP-10	**War-derived air pollution based on carbon-containing smoke nanoparticles with Fe and Cu metal compounds: physical chemical property, and neurotoxicity risk assessment** *G. Dovbeshko*
IGP-11	**Optical Dielectric Spectroscopy Associated with Plasmonic Resonance in LC Nanocomposites with Gold Nanoparticles** *S. Bugaychuk*
IGP-12	**Making 10 nm nano-holes for trapping light by mixing monolayers of gold and silver nanoparticles** *T. Mykytyuk*

IPG-1

Linear photophysics, fast vibronic relaxations and two-photon absorption properties of new coumarin derivatives

G. Klishevich[1], N. Bashmakova[2], Y. Shaydyuk[1], A. Dmytruk[1], I. Kuziv[3], M. Bondar[1]

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Linear photophysical and photochemical properties, fast vibronic relaxations, and two-photon absorption (2PA) efficiency of new coumarin derivatives, methyl 4-[2-(7-methoxy-2-oxo-chromen-3-yl)thiazol-4-yl]butanoate (**1**) and methyl 4-[4-[2-(7-methoxy -2-oxo-chromen-3-yl)thiazol-4yl]phenoxy]butanoate (**2**), were comprehensively analyzed using stationary and time-resolved spectroscopic techniques. The steady-state one-photon absorption, fluorescence emission, and excitation anisotropy spectra, as well as 3D fluorescence maps of 3-hetarylcoumarins **1** and **2** were obtained at room temperature in solvents of different polarities. The nature of large Stokes shifts (~4000 - 6000 cm^{-1}), specific solvatochromic behavior, weak electronic $\pi \rightarrow \pi^*$ transitions, and adherence to Kasha's rule were revealed. The photochemical stability of **1** and **2** was explored quantitatively, and values of photodecomposition quantum yields, on the order of ~10^{-4}, were determined. A femtosecond transient absorption pump–probe technique was used for the investigation of fast vibronic relaxation and excited-state absorption processes in **1** and **2**, while the possibility of efficient optical gain was shown for **1** in acetonitrile. The degenerate 2PA spectra of **1** and **2** were measured by an open aperture z-scan method, and the maximum 2PA cross-sections of ~ 300 GM were obtained.

Acknowledgment

This work was supported by the grant of the National Research Foundation of Ukraine within the framework of the Project 2022.01/0011 "Innovative photonic technologies of bio-medical direction for the post-war reconstruction of Ukraine".

IPG-2

Solid-state NMR of phosphate based functional materials

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Solid-state NMR is a powerful experimental technique which is based on the detection of transitions between nuclear energy levels which appear at strong magnetic fields. In combination with magic angle spinning (MAS) and various pulse sequences solid-state NMR provides information on various aspects of studied systems at molecular level such as chemical surroundings, connectivities, internuclear distances, quadrupolar parameters, etc. All this makes solid-state NMR an excellent technique for studying functional materials based on phosphates specifically designed for bone engineering, light/sensing technologies or energy storing devices.

The presentation is planned to fit the scientific interests of wider audience; therefore, will cover several aspects of NMR. For the audience which does not represent NMR community a brief introduction to solid-state NMR will be given. It will cover basic concepts of NMR and experimental methods widely used in materials research. Afterwards, applications of solid-state NMR for studying phosphate based inorganic functional materials will be presented.

As examples of NMR applications for studying materials for bone engineering, light/sensing technologies our current research on calcium phosphates and halophosphates will be covered. Applications of ^{1}H, ^{31}P, ^{35}Cl, MAS and wideline NMR employing 1D and 2D techniques will be presented. Particular emphasis will be given on the potential of 2D techniques and quadrupolar NMR.

What is more our recent *ex-situ* ^{23}Na, ^{31}P, ^{13}C and ^{47,49}Ti MAS NMR results for studying NASICON based electrode materials will be presented. The potential of solid-state NMR for detecting the charge-discharge degradation products formed on the electrode-electrolyte interface will be highlighted.

Acknowledgment

Funding Research Council of Lithuanian (S-MIP-23-47) is gratefully acknowledged.

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IPG-3

Induced and spontaneous nanostructuring in liquid crystal colloidal systems for display and sensor applications

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Alongside with synthesis of more and more complicated organic substances with anisometric molecules forming various liquid crystalline (LC) phases in the application-suitable temperature range, more and more attention is paid to improving the LC functional properties by introducing various nanoparticles (NP). In many cases, the mechanism involves additional NP-induced nanostructuring in the LC system. On the other hand, similar nanostructuring features can emerge when certain organic substances introduced into the LC system as non-mesogenic dopants (NMD) lead to formation of various aggregates, associates and complexes due to specific intermolecular interactions.

In this presentation, an attempt is made to generalize the experience of more than forty years with such LC systems, adding a review of the newest results to substantiate the proposed generalizations. The LC system analyzed include nematics doped with carbon nanotubes, laponite platelets, metal oxide and ferroelectric NPs, as well as specific organic substances (quercetin, salicylaldoxime, luminophores forming J-aggregates, etc.). The presence of the enhanced LC ordering is checked by comparative studies of these LC systems under similar conditions, with analysis of DSC and temperature-dependent optical transmission as the primary methods.

The emerging features can give rise to various practical applications, including both improvement of electrooptical characteristics for displays and new approaches to chemical and biological sensors, e,g., detectors of absorbed vapors.

IPG-4

Molecular machines powered by electronic excitation

A. Demchenko

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Molecular machines are the systems that operate in thermodynamically nonequilibrium conditions and can perform long-lasting mechanical work of high periodicity by using external source of energy. They can perform specific and directed in space translocation of molecular species and ions. Though the Nobel Prize of 2017 for their development was awarded in chemistry, many basic problems in their physics that involve thermodynamic irreversibility, kinetic asymmetry as well as the role of random thermal fluctuations and of dissipation of energy have to be resolved. The key problem is to make the machine work periodic but microscopically irreversible. The source of energy can be not only the coupled chemical reaction but also photophysical process in organic fluorophores performing excited-state electron and proton transfer. Here the light quanta can operate as molecular machines for directed translocation of ions. They can provide not only triggering and powering these "piston" actions by coupled photochemical reactions but also spectroscopic observations of their elementary steps in time and energy domains. This allows unique possibilities for researchers that were realized in our recent work on light-driven translocation of anions [1]. We demonstrated that the electrostatic force generated in excited-state coupled electron transfer and coupled proton transfer reaction can transfer anions directionally with ultrafast rate and measured the kinetics of this process. Thus, molecular machines can be of simplest design and the light-generated reactions can supply the molecular machines the energy for their indefinitely lasting cycles. These cycles can be recorded in time domain using the time-resolved spectroscopic techniques [2].

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IPG-5

ROS-regulating nanomaterials

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Reactive Oxygen Species (ROS) are redox-active species containing oxygen, such as superoxide ($O_2^{\bullet -}$), hydroxyl radical ($\cdot OH$), hydrogen peroxide (H_2O_2), and singlet oxygen ($^1O_2$), playing a key role in cell functionality [1]. Healthy cells produce ROS for such cell functions as cellular signaling and growth, synthesis of various biological compounds, blood pressure modulation, and immune system control [1]. To address the ROS balance control, cells have developed a complete antioxidant system, which includes enzymatic (SOD, catalase, peroxidases, reductases) and non-enzymatic (vitamins C, E, and A, glutathione, etc.) components, which convert ROS excess into O_2 or H_2O [1]. When the action of cell antioxidants becomes depleted, the level of ROS increases causing oxidative stress through the oxidation of lipids (lipid peroxidation), protein and DNA damage, etc. It is now generally accepted that the oxidative stress caused by imbalance in ROS production and scavenging is closely related to a broad spectrum of diseases including cancer [1] as well as aging [3]. Recently it has been revealed that some nanomaterials such as metal oxide nanoparticles can act as ROS scavengers or ROS inductors that causes the development of a new trend in nanomedicine – ROS regulating nanomaterials. In the report, state-of-the-art of ROS regulating nanomaterials will be presented.

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IPG-6

Luminophores for luminescent solar concentrators

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The war in Ukraine demonstrated the vulnerability of the energy supply system with centralized power supply. Moreover, it showed that the country must not rely on imported gas and oil, and also highlighted the danger of using nuclear plants. Under these circumstances solar energy gains the acute attention especially because of possibility to decentralize energy production. However, using of traditional solar cells in Ukraine encounters a problem of rather low amount of sunny days thus there is a demand for the devices capable of operating under diffuse illumination.

Recently luminescent solar concentrators (LSCs) have received a lot of attention as an effective addition to solar cells. The main reason is expectation of increasing efficiency of electricity generating as well as realization of building-integrated photovoltaics.

A typical LSC device consists of a transparent wave guide (usually a polymer) with embedded luminophore (either molecules or nanoparticles), the edges of the wave guide being coupled with solar cells. The operating principle of LSCs is as follows: luminophore absorbs incident sunlight and then re-emits the photons of down-shifted frequency, which are transported via the waveguide to solar cells where the light energy is converted to electricity.

The key issue for LSC efficiency is a highly luminescent material that absorbs most of the solar radiation and demonstrates close to unity quantum yield. Other requirements of ideal luminophores are: little or even zero overlap between absorption and emission spectra, high stability, “green” synthesis, low cost, etc.

In the present report we analyze “pros and cons” of various liminophores. The manifold of the already studied luminophores can be subdivided onto three main groups. These are organic dyes, quantum dots and lanthanide ions.

Organic dyes are attractive due to their high quantum yield and good solubility in polymer matrices. However, the absorption of these species covers only a little fraction of solar spectrum because they have a narrow absorption bands in visible and UV regions. One more important drawback is the well-known instability of organic dyes under the UV illumination.

Quantum dots are at present very actively studied as alternative luminophores for LSCs. One of the most attractive features of these species is controllability of their absorption and emission spectra by synthetic conditions. Easy wet synthesis procedures as well as good stability as compared with other luminophores can also be listed as the strong side of their application.

Rare earth ions are known for their high efficiency of luminescence, broad absorption bands, large Stokes shift and narrow emission bands, so, they are also good candidates for LSCs applications. However, lanthanides are not abundant and, hence, rather expensive.

Some novel types of luminophores for LSCs, which demonstrated promising performances, are also discussed.

IPG-7

Phases transition phenomena in highly sensitive luminescence nanothermometry

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Temperature and its precise quantification have been of interest to mankind for millennia. Currently, more accurate and faster new devices to measure temperature are proposed. In opposite to conventional thermometers, such as mercury-based, thermocouples or semiconductor detectors a new approach called luminescent thermometry is proposed. In these devices, the phase transition phenomena play a key role. These kinds of microthermometers can be utilized in many technical devices, especially in medicine in tumour and cancer diagnosis.

Phase transition-based thermometers are widely known for their remarkable sensitivity to temperature changes. Due to the host material's stoichiometry, these devices exhibit a narrow temperature range. This limits the applicability of optical sensors utilizing structural phase transitions.

Based on some examples the new materials for luminescent thermometry will be discussed. The main objective of this lecture will be to focus on the phase transition phenomena investigated by differential scanning calorimetry (DSC). The mechanism of observed phase transition will be explained using Raman spectroscopy measured at low temperatures. The symmetry principles with relationship selection rules will be used to explain observed changes in experimental spectra.

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IPG-8

Heat capacity of molecular crystals with different types of disorder

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The physics of disordered solids poses a persistent challenge, particularly regarding the characterization of their low-temperature anomalies in thermal properties. Extensive experimental data, encompassing heat capacity and thermal conductivity measurements, has been amassed, accompanied by numerous hypotheses and theoretical frameworks aimed at elucidating the dynamics of disordered solids [1]. This report presents experimental evidence about the uniform low-temperature heat capacity of both ordered and disordered solids [2-4]. The investigation seeks to identify universal characteristics of the $C(T)/T^3$ hump, characterized by its maximum value ($[C(T)/T^3]_{max}$) and the corresponding temperature (T_{max}), across a broad spectrum of complex solids. Special consideration is given to the presumed curve, potentially stemming from the intricate structural features of these solids. Notably, the quantities $[C(T)/T^3]_{max}$ and the Debye temperature, in conjunction with T_{max}, collectively form a distinctive set for solid characterization. Strong correlations between these parameters and a universally applicable scaling dependence have been established. These correlations facilitate the observation of excess low-temperature heat capacity phenomena in both ordered crystals and disordered solids. The emerging insights suggest a close relationship between the origin of the boson peak in glasses and the presence of a hump in $C(T)/T^3$ observed in complex crystals, where an avoided crossing between acoustical and optical branches in the dispersion law occurs.

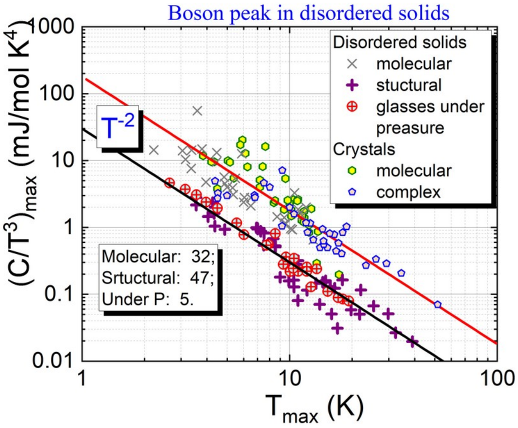

Fig. 1 illustrates the temperature correlation between the maximum value of the $C(T)/T^3$ hump and its corresponding temperature, T_{max}. The depicted inverse quadratic dependence serves as a manifestation of the avoided crossing phenomenon between low-lying acoustical and optical branches in the dispersion law of the crystal.

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IPG-9

Triplet-triplet annihilation mechanism of intrinsic charge-carrier generation in neat organic semiconductors

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Triplet–triplet annihilation upconversion (TTA-UC) in organic semiconductors (typically involving a two-component system) offers the advantages of low excitation power with incoherent light source compared to other photon upconversion techniques, such as multiphoton excitation, excited state absorption and energy transfer upconversion. The TTA-UC is becoming a hot topic of interest for various photonic applications, particularly in the field of organic solar cells since it potentially allows to enhance the efficiency of photovoltaic devices. It is also viewed as an alternative triplet harvesting mechanism in organic light-emitting diode (OLED) devices, which might potentially solve the “efficiency roll-off” problem associated with these devices. In addition, it has shown great potential in the fields of photodynamic therapy and photocatalytic production of solar fuels.

In the present work [1] we demonstrate another intriguing application of TTA-UC as a predominant mechanism of intrinsic charge carrier generation in a neat self-TTA heavy-atom-free annihilator medium. We show the triplet fusion can promote the energy up-conversion in a carbazole-based organic semiconductor enabling thereby the autoionization of a high-energy neutral excited state upon excitation within the lowest-energy singlet exciton state. Our findings challenge established beliefs by revealing efficient charge-carrier generation via TTA upon excitation near the absorption edge. Photocurrent measurements together with optical spectroscopy and spin-sensitive techniques (light-induced ESR) support this model of bimolecular charge generation. This work highlights unconventional mechanisms in organic semiconductors, relevant beyond OLEDs, but also for long-persistent luminescence, organic photovoltaics, and potentially for photocatalytic water splitting.

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IPG-10

War-derived air pollution based on carbon-containing smoke nanoparticles with Fe and Cu metal compounds: physical chemical property, and neurotoxicity risk assessment

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The air pollution based on carbon nanoparticles with heavy metals is a significant health hazard. Now, the impact of such pollution is increased due to the explosions and fires caused by the war in Ukraine. Due to the artillery shelling and missile attacks, a large amount of smoke enters the atmosphere bearing copper, iron, sulphur, carbon particles, remains of organic molecules. Toxic effect of such particles can be significantly increased due to the formation of different complex nanohybrids in the atmosphere [1,2].

Here a modelling of such nanohybrids and their characterization with FTIR, Raman, UV-Vis spectroscopy, optical and electron microscopy (TEM), photoluminescence spectroscopy, dynamic light scattering (DLS) and elemental analysis were done. According to TEM and DLS studies, the size of nanoparticles increases with the addition of Fe and Cu ions. FTIR spectra of wood smoke display the absorption bands originating from the wood combustion products, lignin etc oxidation products. One of the most toxic components of the wood and plastic burning smoke are aldehydes, benzopyrene, polycyclic aromatic, hydrocarbons, various solid particles, as well as heavy metal ions. The neurotoxic effects associated with the formation of the nanohybrids comprising carbon particles, metal ions, remains of organic molecules are discussed.

Funding/ Acknowledgement
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IPG-11

Optical Dielectric Spectroscopy Associated with Plasmonic Resonance in LC Nanocomposites with Gold Nanoparticles

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Liquid crystal nanocomposites with Au nanoparticles (NPs) embedded into the cell volume have attracted great interest in the last decades [1]. The main feature of such nanocomposites is the excitation of surface plasmon resonance (SPR) in gold NPs under the exposure to light [2]. Particularly, in LC-nanocomposites with Au NPs, localized SPR leads to confinement effects for LC molecules surrounded near the NPs. It is expected that these additional mechanisms will improve many properties of LC materials required for modern application, such as accelerating the switching time under the action of electric voltage (or light), increasing the magnitude of optical response, and conversion of the frequency of acting laser beams. In LC-nanocomposites with Au NPs, dynamic grating recording and study of nonlinear optical properties have also been considered [3]. However, numerous theoretical and experimental studies have confirmed that a great drawback of such nanocomposites is the significant heating of the samples due to the strong light absorption on the SPR [2-3]. Thus, the thermal effect become dominant and drowns out all other useful mechanisms.

We examine dielectric spectroscopic properties of LC-nanocomposites with Au NPs [4-5]. We consider a statistical model applicable to such materials, combining the properties of anisotropic liquid and metallic NPs of small size. One of the main point of such a model is the proper accounting of the local field factor conditioned by the NPs. Exposure to light leads to a change in the complex dielectric permittivity of the whole nanocomposite. We consider the influence of SPR depending on the wavelength of the exciting laser radiation. Our results show that useful effects associated with a significant change of the refractive index can be acieved under very restrictive conditions: depending on the volume fraction of NPs and the wavelength of the acting laser beam.

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IPG-12

Making 10 nm nano-holes for trapping light by mixing monolayers of gold and silver nanoparticles

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Control over the trapping and propagation of light is a key research area in modern optics and physics. Localization and controlled management of light fluxes on scales that are comparable to the wavelength opens the way for the creation of nanoscale fast-acting devices, such as nanoantennas, biosensors, nanolasers, and others. In this work, we present a technique to make precision 10nm nano-holes for trapping light by admixing gold and silver nanoparticles through directed assembly.

The aim of the work is to create nanocavities, and study them using dark field scattering. Individual 80-100nm nanoparticles are placed on top of large-area self-assembled nanoparticle monolayers (MLAgg) of 10nm metal nanoparticles placed on a mirror (Fig. 1). To create this, we self-assemble colloidal MLAggs of 10 nm mixed gold and silver nanoparticles on a gold surface and dissolve out the silver nanoparticles. This allows robust and uniform construction of the MLAgg spacer film with controlled density of holes in it. Inside the sandwich between the large AuNP and the gold surface (known as a NanoParticle-on-Mirror or NPoM construct), these MLAggs form electromagnetic hot spots which can become conductive bridges under external control. The combination of extreme confinement, holes, and MLAgg, strongly influence the scattering spectra.

The dark field scattering spectra of many hundreds of the individual 100 nm nanoparticles on the surface of the colloidal MLAgg are measured, and tracked while irradiating with a laser. Dark field scattering spectra of individual nanoparticles have different shapes, maximum scattering wavelengths, numbers of peaks, and show red or blue shifts during laser irradiation. Comparison to stable dielectric spacers shows these effects are due to the restructuring of the self-assembling MLAgg, such as size and position of holes, as well as reshaping of the 100 nm nanoparticle facet. This dynamic optical spectroscopy thus enables a detailed reconstruction of the sculpting at the 1-10nm scale inside such extreme optical resonators, which can be used for sensing applications.

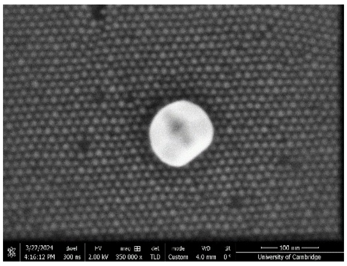

Fig. 1. SEM image of individual 100 nm nanoparticle on top of large-area self-assembled 10 nm nanoparticle monolayer.

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The Ukrainian Academic Support Scheme from University of Cambridge, ERC PICOFORCE Project G103192.

ORAL PRESENTATIONS

OGP-1 **Vibrational and Imaging Markers of Circulating Metastatic Cells Based on the Lewis Lung Carcinoma Cell Line**
O. Gnatyuk, D. Kolesnyk, A. Nikolenko, S. Karachim, S. Hnatyuk, T. Voitsitskyi, G. Solyanik, G. Dovbeshko

OGP-2 **Effect of Tin and Tin-Carbon Dopants on Physicochemical Properties and Photocatalytic Behavior of TiO_2 in Hydrogen Production Reaction**
E. Manuilov, V. Shymanovska, N. Shcherban, G. Korzhak, V. Permyakov, T. Khalyavka

OGP-3 **Soliton Mediated Long-Range Electron Transport in Donor—Alpha-Helix-Acceptor Systems**
L. Brizhik

OGP-4 **Nonlinear Optical Properties of Azo-Naphthols with a Pyridine Nitrogen Atom: Theoretical and Experimental Study**
V. Ovdenko, A. Ronkovych, A. Labunets, D. Komarenko, O. Kachkovsky, V. Gayvoronsky

OGP-5 **WS_2 and MoS_2 2D Nanoparticles as Inducers of Changes in Liposome Formation and Spectroscopic Properties**
G. Monastyrskyi, O. Gnatyuk, I. Gubareni, G. Levchenko, A. Nikolenko, M. Olenchuk, A. Tolochko, G. Dovbeshko

OGP-6 **Luminescence Mechanisms in Oxide Glass-Ceramic Composites: Insights from Electronic Structure Calculations**
Yu. Hizhnyi, V. Chornii, V. Borysiyk, S. Nedilko, Ya. Zhydachevskyy

OGP-7 **Spectral Properties of Two Pyrrolopyridine Derivatives Synthesized from Citric Acid and Urea**
N. Bashmakova, I. Klyuyev, M. Bondar, G. Klishevich, A. Dmytruk, W. Kasprzyk, T. Świergosz

OGP-8 **Electronic Structure and UV-Vis Spectroscopy of Mesoionic Compounds**
M. Kyrpa, S. Kovalenko, V. Ivanov

OGP-9 **Noncovalent Complexes Of Dimethyl Sulfoxide With Anticancer Thioderivatives Of Purine Nucleobases: Model Mass Spectrometry And Quantum Chemical Study On Molecular Mechanisms Of Transmembrane Drug Delivery Facilitation**
V. Pashynska, S. Stepanian, M. Kosevich, A. Gömöry, L. Drahos, L. Adamowicz

OGP-10 **Variation of Donor/Acceptor Substituents in Azo-Azomethine Containing Polymer Composites to Control NLO Response Under CW and Pulsed Laser Excitation**
V. Gayvoronsky, A. Ronkovych, A. Labunets, D. Komarenko, V. Ovdenko

OPG-1

Vibrational and imaging markers of circulating metastatic cells based on the Lewis lung carcinoma cell line

O. Gnatyuk[1], **D. Kolesnyk**[2], **A. Nikolenko**[3], **S. Karachim**[4], **S. Hnatyuk**[1], **T. Voitsitskyi**[1], **G. Solyanik**[2], **G. Dovbeshko**[1]

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It is known that metastasis in oncological diseases remains one of the main reasons for negative prognosis regarding treatment. That is why the determination of the biophysical and biochemical characteristics of circulating metastatic cells can give us a new concept for antimetastatic therapy. In this study the FT-IR spectral features of Lewis lung carcinoma tumour cells grown under different conditions - adhesive and de-adhesive manner - were investigated. An effective model for the study of circulating metastatic cells has been proposed, which consists in the cultivation of the tumour cells in a de-adhesive manner. Such a model can be also used for the study of antimetastatic drugs. We have registered changes in the FT-IR and Raman spectra of the studied cells in the region of CH stretching and bend vibrations which can be associated with structural rearrangements in the cell membrane, as well as changes in the intensity and position of the stretching of PO_2- and C-O, OH groups and Amid 1 vibrations bands which correlate with a proliferative activity of the cells and membrane transformation. CARS and confocal imaging of the LLC cells under different stimuli and their analysis of cytoplasm state on the basis of RGB confocal microscopy data as well as a correlation with cytofluorometric method were discussed also.

Acknowledgment

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OPG-2

Effect of tin and tin-carbon dopants on physicochemical properties and photocatalytic behavior of TiO_2 in hydrogen production reaction

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Modification of TiO_2 by coupling with other semiconductors is significant way to engineer its band gap, particle size, specific surface area, crystallinity, and optical properties [1]. In the present research, tin-doped (Sn/TiO_2) and tin-carbon-co-doped ($Sn/C/TiO_2$) titanium dioxide was synthesized by modified sol-gel method and characterized by XRD, TEM/SEM/EDX, Brunauer–Emmett–Teller and Barret–Joiner–Halenda methods, FT-IR, and UV-vis diffuse reflection spectroscopy.

It has been found that TiO_2 doping with Sn leads to the formation of a three-phase compound consisting of anatase (TiO_2), rutile (TiO_2), and tetragonal rutile-structured SnO_2. Co-doping of TiO_2 with Sn and C promotes the two-phase TiO_2 formation containing anatase and rutile structures. The relative phase content of rutile, anatase and SnO_2 depends on the quantity of dopants. The growth of Sn content leads to increasing of crystallite size, mean pore volume and pore radius and decreased specific surface area of the samples. Co-doped $Sn/C/TiO_2$ demonstrate a decreased pore volume and radius of pores along with increased specific surface.

The prepared photocatalysts exhibit good performance in photoproduction of hydrogen under UV illumination with ethanol as a sacrificial agent. The results have shown that the modified TiO_2 exhibited a two-fold increase in photocatalytic activity over the pristine TiO_2. The most active appeared SnO_2/TiO_2 containing 2.29% at. Sn, as well as co-doped $SnO_2/C/TiO_2$ with Sn and C content of ~1% at. The improved photocatalytic performance of Sn/TiO_2 is mostly connected with a formation of heterojunctions SnO_2-anatase-rutile which promote charge transport, decrease the recombination rate of photoinduced electron–hole pair thus extending the charge carriers lifetime. The enhanced photocatalytic activity of SnO_2/TiO_2 and $SnO_2/C/TiO_2$ can be also attributed to their increased specific surface area. The prepared new photocatalysts can be considered as favorable cost-effective candidates for hydrogen economy.

Acknowledgment

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OPG-3

Soliton mediated long-range electron transport in donor--alpha-helix--acceptor systems

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It is well known that in one-dimensional molecular chains the long-range electron transport is provided by Davydov solitons [1]. Such solitons are the bound states of a quasiparticle and local deformation of the chain formed due to the electron-lattice interaction. Here the results are reported on the study of the long-range electron and energy transfer mediated by solitons formed in an α-helix three-spine polypeptide chain [2] coupled to donor and acceptor molecules at opposite ends. It is proven that there exists the broad interval of the parameters for which an electron initially located on the donor, tunnels onto the chain where it forms a soliton-like state, which then travels to the opposite end, where it is captured by the acceptor. It is shown that the efficiency of the electron transport from the donor to the acceptor can reach 90% (see Fig.1). It is also shown that for polypeptide parameter values this process is stable at physiological temperatures.

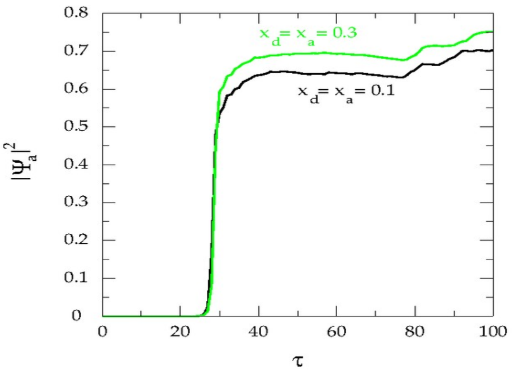

Fig. 1 Probability of electron presence on the acceptor molecule as function of time for two values of the coupling constant.

These results explain highly efficient long-range donor-accepor electron transport in redox reactions in photosynthesis and cellular respiration in biological systems, and in donor-acceptor systems mediated by various types of long molecular chains, widely used in modern microelectronics and nanotechnologies [3,4].

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OPG-4

Nonlinear optical properties of azo-naphthols with a pyridine nitrogen atom: theoretical and experimental study

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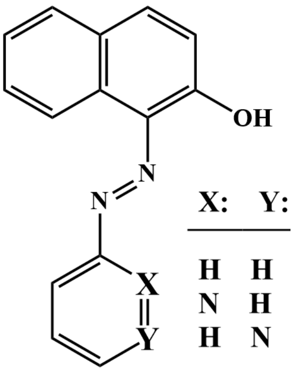
Azo compounds are gaining increasing interest among scientists studying photosensitive materials for optoelectronics, information recording and storage, nonlinear optics. This is due to significant changes in the optical characteristics of materials under the action of light, caused by reversible *trans-cis-trans* isomerization, which leads to conformational transformations in the structure. The more well-known azo molecules are those in which the 4,4-position to the azo bond contains substituents with pronounced electron donor and acceptor properties for effective electron density transfer (the so-called push-pull systems). Moving substituents to a different position or replacing a substituent with a heterocyclic moiety greatly expands the possibilities for developing new materials.



Scheme 1. Structure of azo dyes

In this work, a series of azo-naphthols (Sudan 1 and two of its analogues with a pyridine nitrogen atom in the 2- (PAN-2) and 3-positions (PAN-3), Scheme 1) were studied in the form of thin PMMA polymer films with 1% wt. dopant, as well as using quantum chemical modeling methods. Calculation of the static first hyperpolarizabilities β_{tot} values showed a fundamental difference in the responses of Sudan 1 in comparison with pyridine-containing molecules. With *trans-cis* isomerization of Sudan 1, the value of β_{tot} increases by 1.6 times, while for PAN-2/PAN-3 it decreases by 2.5/3.8 times respectively. The highest absolute value of β_{tot} was shown by PAN-2.

It is also shown that the first transition is forbidden in the *trans* form, but allowed in the *cis* form, which may be a key factor in explaining multiphoton processes.

NLO response efficiency *via* CW laser beam self-action effects manifestation in thin films has been studied at wavelength 532 nm. All thin films demonstrated self-focusing effect at the initial stage of the experiment ($I \sim 25$ W/cm^2) and opposite sign for laser excitation $I \sim 50$ W/cm^2. Sudan 1 and PAN-2, have shown self-defocusing effect ($\mathrm{Re}(\chi^{(3)}) = -(3.8/3.9)\cdot 10^{-3}$ esu), meanwhile PAN-3 demonstrated self-focusing one with similar efficiency $\mathrm{Re}(\chi^{(3)}) = 3.1\cdot 10^{-3}$ esu. We suggest that in the PAN-2 molecule with the pyridine nitrogen at the 2-position is conjugated with an azo bond, while in Sudan 1 and the PAN-3 analog it is not, that opens up a possibility to control the magnitude and sign of the materials` refractive NLO response.

WS_2 and MoS_2 2D nanoparticles as inducers of changes in liposome formation and spectroscopic properties

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Liposomes are excellent model structures for studying the properties and functions of cell membranes. To form single-component liposomes, 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) was used. Liposomes were formed in an aqueous medium through three cycles of shock freezing and thawing, followed by ultrasonic treatment. Two types of liposomes were prepared: 1) nanoparticles were added to the lipid stock solution, forming liposomes with nanoparticles inside; 2) nanoparticles were added to the formed liposomes, resulting in complexes with nanoparticles on the outside.

To investigate the impact of 2D nanoparticles, methods of dynamic light scattering and microscopy were used to determine the size of liposomes, along with Raman and IR spectroscopy and luminescence analysis.

WS_2 and MoS_2 nanoparticles differently affect the formation of liposomes, as WS_2 can oxidize in an aqueous medium and become less active. Analysis of IR spectra shows changes in the region of phosphate molecular group vibrations, manifested by the redistribution of contributions from symmetric and antisymmetric $(PO_2)^-$ vibrations. Quenching of luminescence is observed in liposomes with nanoparticles compared to pure liposomes. In the luminescence spectra of liposomes with nanoparticles, two characteristic bands are observed, which are redistributed differently for various nanoparticles under different excitation wavelengths.

The luminescent properties differed between liposomes with encapsulated nanoparticles and those with nanoparticles on their surface. The formation of liposomes involving 2D MoS_2 and 2D-WS_2 nanoparticles occurs through distinct mechanisms and exhibits different spectral properties. Consequently, the enhancement of the optical signals from liposomes, with 2D-WS_2 nanoparticles differs greatly from the same systems with 2D-MoS_2 nanoparticles. The mechanism of the liposomes interactions with the nanoparticles and formation bonds are studied.

Acknowledgement
O. Gnatyuk acknowledges the Academy of Finland mobility project Decision number 358103 for financial support and G. Dovbeshko acknowledges Academy of Finland mobility project Decision number 359463; M. Olenchuk acknowledges NRFU project No 2021.01/0229 “Biophysical characteristics of circulating metastatic cells as potential targets of antimetastatic therapy”.

OPG-6

Luminescence mechanisms in oxide glass-ceramic composites: insights from electronic structure calculations

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Glass-ceramic composites, in which oxide micro/nanocrystals are incorporated into the oxide-glass matrix, are intensively studied at present as perspective materials for a wide range of practical applications [1]. The properties of such composites are largely determined by interphases regions, which have atomic structure and chemical composition intermediate between the crystalline and glass components. For this reason, formation of the electronic and optical properties of glass-ceramic composites is difficult to understand without knowledge of the electronic structure and related optical characteristics of interphase regions. The atomic structure of interphases can be obtained in calculations by molecular dynamics (MD) methods. Further application of the electronic structure calculations allows to obtain the most important micro- and macro-characteristics of the interphase layers and thus to explain the experimentally observed properties of glass-ceramic composites.

This report presents results of complex computational and experimental studies of the atomic and electronic structures of luminescent oxide glass-ceramic composite materials. Three different types of glass-ceramic composited are considered: a) $KBi(MoO_4)_2$ crystal @ K_2O-P_2O_5-MoO_3-Bi_2O_3 glass b) $K_2Bi(PO_4)(WO_4)$ crystal @ K_2O-P_2O_5-WO_3-V_2O_5 glass; c) $LaVO_4$ crystal @ Li_2O-V_2O_5-B_2O_3 glass. The atomic structures of interphase regions were calculated by MD methods. The electronic structure calculations were performed in the DFT approximation using the band-periodic plane wave pseudopotential method. The excited electronic states and optical spectra of possible centers of luminescence of glass-ceramic composite materials are calculated using the Time-Dependent Density Functional Theory (TD-DFT) within molecular cluster approach.

Obtained computational results are compared with experimental data on structural analysis, optical and luminescence spectroscopy. A relationship between atomic and electronic structures of interface (interphases) layers and optical characteristics of studied composites is analyzed. The possibility of tuning of the optical properties of studied oxide glass-ceramic composite materials is examined. The mechanisms of luminescence and excitation energy transfer in oxide glass-ceramics of different types are clarified.

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OPG-7

Spectral Properties of Two Pyrrolopyridine Derivatives Synthesized from Citric Acid and Urea

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The spectral-luminescence properties of 4-hydroxy-7-[(2,5-dioxopyrrolidin-3-yl)methyl]-1H-pyrrolo[3,4-c]pyridine-1,3,6(2H,5H)-trione (**1**) and 3-(4-hydroxy-1,3,6-trioxo-2,3,5,6-tetrahydro-1H-pyrrolo[3,4-c]pyridin-7-yl)-2,6-dioxopiperidine-4-carboxamide (**2**) obtained under the syntheses of carbon-based nanodots were investigated in liquid solutions by the steady-state and time-resolved femtosecond techniques. The main linear photophysical and photochemical characteristics of **1** and **2** were obtained in methanol and distilled water at room temperature, including steady-state absorption, fluorescence, and excitation anisotropy spectra, 3D fluorescence maps, fluorescence lifetimes, and photodecomposition quantum yields. The nature of large Stokes shifts (~ 5000 cm^{-1}), specific solvatochromism, aggregation effects, no violations of the Kahsa's rule, and weak velocities of radiative transitions were revealed. The transient absorption kinetic curves for **1** and **2** in water were measured with femtosecond pump-probe setup and the effective light amplification of the probe beam was shown in the fluorescence spectral range.

Linear one-photon absorption spectra exhibited structureless shape, weak absorption efficiency ($\varepsilon_{max} \approx (3\text{-}7)\cdot 10^{-3}$ M^{-1} cm^{-1}), no dependence on solvent polarity and strong H-aggregation effects in MeOH. The excitation anisotropy spectrum revealed the only one electronic transition $S_0 \rightarrow S_1$ in the main long wavelength absorption band and small angle ($\alpha \approx 24\text{-}29°$) between the absorption and emission transition dipoles. Fluorescence emission processes were characterized by a single exponential decay with a lifetime of 5-11 ns and quantum yields ~ 30-60%. The level of photochemical stability of **1** and **2** was around $\varphi_{ph} \approx 10^{-3}$, which is acceptable for practical use. Potential ability of light amplification for **1** and **2** in water was confirmed from the femtosecond transient absorption kinetics in the fluorescence spectral range.

Complex studies of the steady-state and time-resolved spectral-luminescence properties of new pyrrolpyridine derivatives obtained from the synthesis of carbon nanodots are a promising step in the development of new specific functional materials for various applications.

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OPG-8

Electronic structure and UV-Vis spectroscopy of mesoionic compounds

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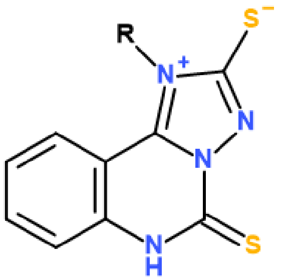
Mesoionic compounds (MC) are dipolar molecules in which both positive and negative charges are delocalized. The structures of MC cannot be presented in the form of classical covalent structures and require the introduction of integer charges on atoms. Currently, the classification of mesoionic compounds is based on the origin of π-electrons contributed by the atoms of a five-membered ring within an 8π-electron conjugated system. Our previous research indicates that this classification is partially supported by the QTAIM, quantum theory of atoms in molecules.

MC attract significant research interest in spectroscopy, nonlinear optics, and medicinal chemistry. The high dipole moments and polarizabilities of MC suggest a broad spectrum of intriguing physicochemical properties, notably pronounced solvatochromism, which was the primary focus of this study.

We considered a number of structures, assuming a simultaneous experimental investigation and computational descriptions. Among the studied structures, in particular, structures with an exocyclic Sulfur atom are presented (Fig. 1) [1].



R = Et, Bn, Ph

Fig. 1 Structures under consideration.

Time-dependent density functional theory (TDDFT) calculations were performed and various approaches were used to characterize solvatochromic properties of studied substances. Different DFT functionals, as well as approaches for accounting of environment effects, were tested. Among the latter were the Linear Response Theory, State-Specific Theory, and the «Solvation Model Density» methodologies. The most effective approaches for adequate description of spectral properties were identified.

For example, the structure with R = Et is characterized by the following hypsochromic shifts in the absorption band, attributed to the HOMO-LUMO transition: 0.22 eV (experiment), 0.16 eV (B3LYP/cc-pVTZ) and 0.15 eV (M062x/cc-pVTZ).

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OPG-9

Noncovalent complexes of dimethyl sulfoxide with anticancer thioderivatives of purine nucleobases: model mass spectrometry and quantum chemical study on molecular mechanisms of transmembrane drug delivery facilitation

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The development of new prospective drug delivery approaches is a topical study area in modern biomedical research, including molecular spectroscopy investigations. Special drug delivery methods and supramolecular systems are applied to enhance the drug`s therapeutic effect by facilitating the targeted transportation of medication molecules into cells. This facilitation of transmembrane drug transfer is specifically significant for lipid-insoluble medicines, as well as certain anticancer agents and antibiotics with high toxicity. One effective way to enhance the transmembrane delivery of drug molecules is by using membrane penetration facilitating agents that form noncovalent complexes with the drug molecules to be delivered.

In the current combined mass spectrometry and quantum chemical study, we have investigated the intermolecular interactions between the molecules of selected anticancer thioderivatives of nucleobases and the drug delivery facilitating agent dimethyl sulfoxide (DMSO). DMSO is well known as a transmembrane and transdermal drugs penetration enhancer. Formation of stable noncovalent complexes of DMSO with 6-thiopurine and 2-thioadenine in the polar solvent methanol was revealed by the electrospray ionization mass spectrometry (ESI MS) probing. The complexes are similar to the noncovalent clusters of DMSO with the molecules of a number of antibiotics, formation of which was demonstrated in our previous study [1]. To evaluate the structure and energetic parameters of the observed in the ESI MS experiments noncovalent complexes of DMSO with the anticancer drugs, the quantum chemical calculations was performed using the DFT method. We also used the Polarizable Continuum Model (PCM) approach to estimate the influence of the solvent on the structures and the interaction energies of the complexes. The results of the calculations confirmed the noncovalent complexes stability and provided information regarding the optimal geometry of such complexes. The outcomes of the study on the formation of stable noncovalent intermolecular complexes between the anticancer thioderivatives of nucleobases and the delivery facilitating molecules such as DMSO contribute to the elucidation of the molecular mechanisms underlying drug delivery processes, with a particular focus on delivery of fat insoluble or toxic drugs.

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OPG-10

Variation of donor/acceptor substituents in azo-azomethine containing polymer composites to control NLO response under CW and pulsed laser excitation

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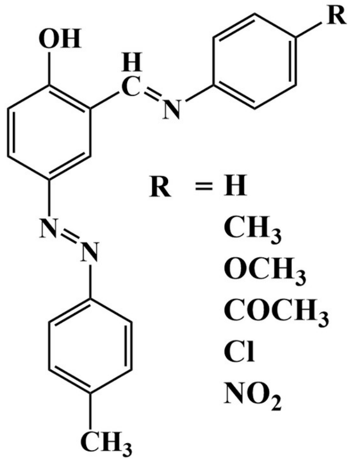
The development of new smart polymeric materials based on photosensitive molecules with different donor-acceptor substituents for the realization of push-pull systems has recently found a lot of interest among scientists in chemistry and physics. The most popular are systems based on azobenzene, containing–N=N– bonds capable of photoinduced reversible *trans→cis→trans* isomerization, which leads to a change in the dipole moment and redistribution of the electron density of the system. Structurally similar, but having a different photosensitivity, the azomethine fragment, corporalized into one conjugated system with an azo one, is a promising material for nonlinear optical polymer smart materials.



Scheme 1. Structure of azo-azomethines

Within the framework of the proposed approach, a series of azo-azomethine compounds with variations of substituents` donor-acceptor properties were synthesized (Scheme 1). Study of thin polymer films with 1% wt. of azo-azomethines was carried out within CW and ps range pulsed laser excitation at wavelengths 532 and 1064 nm. In CW mode (532 nm) it was shown that electron-donating substituents in the *para*-position to the imino-group contribute to additive photoinduced refractive index variation $\Delta n > 0$ with pronounced self-focusing effect manifestation (Re $(\chi|(3))$ ~ 10^{-3} esu), while electron-acceptor substitutes (-NO_2) – to self-defocusing one $\Delta n < 0$). UV mercury lamp (exposition of the films promotes self-focusing effect manifestation, even turning on self- focusing response for -NO_2 substituted azo-azomethine dye due to UV irradiation.

Under pulsed excitation at 532 nm a similar trend persists: molecule with electron-acceptor exhibits self-defocusing, while electron-donating and unsubstituted molecules – self-focusing effect manifestation. It was established linear dependence between second-order hyperpolarizabilities at 532 nm for single pulsed excitation mode of as prepared dyes and for CW one of the preliminary UV exposed dyes molecules. It means that subjecting azo-azomethine dyes to ps single pulses irradiation provides transfer of individual molecules into an excited state, as with prolonged exposure to UV radiation. We suggest that molecular NLO response is determined by readout of the dyes' polarizabilities in excited states *via* photoinduced isomerization for both excitation regimes.

POSTERS

PGP-1 **The effect of protein structure on optical absorption spectra of oxyhemoglobin: QM/MM study**
T. Afanasieva, V. Prokhorets, S. Mamilov

PGP-2 **TD-DFT computational studies of the optical properties of luminescence centers in Bi-containing glass-ceramics**
V. Borysiuk, A. Oliynyk, Yu. Hizhnyi, S. Nedilko, Ya. Zhydachevskyy

---

PGP-3 **Effect of (Ba/Sr)titanate nanoparticles on optical and dielectric properties of microcrystalline cellulose**
V. Chornii, V. Boyko, M. Lazarenko, S. Nedilko

PGP-4 **Plasmonic enhancement of Raman scattering of multilayer HfS_2 by metal nanoparticles**
O. Datsenko, S. Golovynskyi, M. Usman, I. Golovynska

PGP-5 **Spectroscopic studies of polymorphism in 4-methylphenol**
J. Baran, N. Davydova, M. Drozd, V. Reznichenko

PGP-6 **Effect of Argon Environment on Vibrational Spectra of Ethanol**
I. Doroshenko, M. Onuk, A. Nekboev, B. Kuyliev

PGP-7 **Interaction of new pyrrolo[2,3-*d*]pyrimidine-based telomerase inhibitor with G-quadruplex DNA**
V. Negrutska, V. Trots, L. Muzychka, I. Yaremchuk, O. Smolii, I. Dubey

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PGP-8 **Boron-oxygen interaction in boron-doped Czochralski grown silicon**
A. Duvanskii, L. Khirunenko, M. Sosnin, N. Abrosimov

PGP-9 **Molecular interactions and thermal properties of dye-doped polyurethane resins**
T. Bezrodna, V. Nesprava, O. Roshchin, O. Antonenko, L. Kosyanchuk, T. Gavrilko, J. Baran, M. Drozd

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PGP-10 **Determination and refinement of the value of the Urbach energy and the optical band gap based on the long-wavelength absorption edge spectra of C_{60} and C_{70} fullerene films of different thicknesses.**
M. Gorishnyi

PGP-11 **Induced smectic ordering and blue phase formation in mixtures of cyanobiphenyls and cholesterol esters**
I. Gvozdovskyy, N. Kasian, L. Lisetski

PGP-12 **Study of LIPSS replicas for surface enhanced spectroscopy**
Ye. Hrabovskyi, N. Berezovska, I. Dmytruk, A. Dmytruk

PGP-13 **Spectral markers and morphological features of diabetic foot ulcer tissues**
T. Isokov, L. Yanitskaya, S. Verevka, O. Gnatyuk, T. Voitsitskyi, G. Dovbeshko

PGP-14 **Experimental and Quantum Chemistry Investigations of Nitrazine Yellow Absorption Spectra on Organosilica Surfaces**
V. Ivanov, I. Khristenko

PGP-15 **Spectral investigations of 60S bioglass modified with La and Y ions**
V. Karbivskyy, N. Kurgan, I. Sukhenko, V. Zaika, O. Puz'ko

PGP-16 **Sub-THz emission by IR-active shear phonons in** $\mathbf{K}\boldsymbol{Re}(\mathbf{MoO_4})_2$
D. Kamenskyi, K. Vasin, L. Prodan, K. Kutko, V. Khrustalyov, S. Pavlov, and H.-W. Hübers

PGP-17 **Investigation of Intermolecular Interactions in Various Solutions of Aniline Using Raman Spectroscopy and DFT Calculations**
A. Jumabaev, H. Hushvaktov, I. Doroshenko, U. Holikulov, B. Khudaykulov

PGP-18 **Low temperature secondary ion mass spectrometric study of mixtures of primary alcohols**
M. Kosevich, V. Shelkovsky, O. Boryak, V. Orlov, A. Gömöry, K. Vekey

PGP-19 **Photoluminescence of PCBM fullerene derivative confined in mesoporous glasses**
A. Kostetskyi, Yu. Piryatinski, A. Verbitsky, P. Lutsyk, A. Rozhin

PGP-20 **Interaction of methyl uracil with polyethylene glycol**
I. Doroshenko, D. Kostsiukevych, A. Lesiuk, M. Kulish, O. Dmytrenko, L. Davtyan, A. Drozdova

PGP-21 **Spectral Properties of Indole Derivatives as Parts of New π-Electron-Containing Drugs**
V. Kudrya, A. Naumenko, N. Tkach, O. Karpenko

PGP-22 **Crystal structure disorder in ultra-small quantum dots**
I. Kupchak, D. Korbutyak

PGP-23 **Reversible photoisomerization and photoinduced birefringence in main-chain azobenzene poly(arylene ether) films**
Yu. Kurioz, I. Tkachenko, R. Kravchuk, D. Litoshenko, V. Shevchenko, V. Nazarenko

PGP-24 **Photo- and electrically-induced alignment of liquid crystals and colloids by Pigment Red 176 nanoparticles**
Yu. Kurioz, O. Buluy, S. Kredentser and J. Parka

PGP-25	**Investigation of Photochemical Transformations in Solutions of Organic and Inorganic Compounds with Silver Ions** *T. Zashivailo, V. Kushnirenko*
PGP-26	**Enhancement of the nematic ordering in cyanobiphenyl 5CB doped with salicylidenealdoxime due to supramolecular nanostructuring** *P. Vashchenko, S. Minenko, K. Vus, M. Cherniakova, K. Belikov, L. Lisetski*
PGP-27	**Quantum Chemical Study OF structural Changes of some triazenes, azo-compounds** *I. Maga*
PGP-28	**Hydrogen Peroxide Detection Using Reversible Luminescent CeO_{2-x} and $CeO_{2-x}:Eu^{3+}$ Nanocrystals** *P. Maksimchuk, Ye. Neuhodov, K. Hubenko, A. Onishchenko, N. Kavok, G. Dudetskaya, Yu. Kot, S. Yefimova, V. Seminko*
PGP-29	**Oxidation of tin telluride films in an oxygen atmosphere** *T. Mazur, M. Mazur*
PGP-30	**Peculiarities of electron structure and photo-electrophysical properties of new carbazole derivatives** *O. Navozenko, M. Losytskyy, O. Bezvikonnyi, D. Gudeika, D. Volyniuk, M. Stanitska, E.U. Rashid, J.V. Grazulevicius*
PGP-31	**Manifestations of interphase interactions in $Ca_3Eu_2(BO_3)_4$@$mLi_2O–nB_2O_3–pV_2O_5$ glassceramics** *S. Nedilko, V. Chornii, V. Scherbatskyy, V. Scheludko, O. Gomenyuk, A. Shekhovtsov, M. Kosmyna*
PGP-32	**Experimental and Theoretical Studies of Intermolecular Interactions in Benzophenone and its Solutions** *A. Norkulov, H. Hushvaktov, A. Absanov, B. Khudaykulov, I. Norbutaeva*
PGP-33	**Biological affinity of aromatic amino acids in intermolecular π-stacking interaction** *N. Obernikhina, O. Navozenko, A. Naumenko, O. Kachkovsky, V. Brovarets*

PGP-34 **Mechanical Spectroscopy of SiO_2, nanocomposites of multiwalled carbon nanotubes and polymers**
A. Onanko, D. Charnyi, Y. Onanko, O. Dmytrenko, M. Kulish, T. Pinchuk-Rugal, M. Yatsiuk, E. Matselyuk, S. Marysyk, A. Gaponov, L. Kurochka, P. Ilyin

PGP-35 **Electro-Optical Properties of Hybrid LC Materials Containing Photo-Controlled Inorganic-Organic Interface**
S. Bugaychuk, Yu. Kurioz, A. Gridyakina, J. Parka, L. Fedorenko, A. Evtukh, S. Kredentser, V. Pinchuk, P. Onyfrijevs

PGP-36 **Stable Cyanine Dye J-aggregates with Plasmon Enhanced Fluorescence**
P. Pisklova, O. Sorokin, I. Bespalova, S. Yefimova, J.-N. Heidkamp, T. Korn, S. Lochbrunner

PGP-37 **Electron transport through degenerate electron level in single-molecular junction in the presence of electron-vibrational coupling and attractive electron-electron correlations**
E. Ponezha

PGP-38 **Interaction of ibuprofen with polyethylene glycol**
I. Doroshenko, T. Rudenok, A. Lesiuk, M. Kulish, O. Dmytrenko, L. Davtyan, A. Drozdova

PGP-39 **Spectroscopic changes resulting from binding of $TMPyP^{4+}$ and $TMPyP^{3+}$ porphyrins to *ds*-polynucleotides**
O. Ryazanova

PGP-40 **Clusteroluminescence: Properties, Chirality and Applications**
T. Sakhno, A. Semenov, Y. Sakhno, S. Kuchmiy

PGP-41 **Vibrational structure of absorption spectrum of 2,5-bis(2-benzoxazolyl)hydroquinone**
Y. Syetov, Ye. Kyrpa

PGP-42 **Three-Layer Optical Sensor "Prism–Metal–Water Suspension of Inclusions" Based on Surface Plasmon Resonance**
A. Suprun, L. Shmeleva

PGP-43 **Spectral markers and morphological features of supratentorial gliomas tissues from patients of different ages**
A. Shmeleva, V. Rosumenko, T. Malysheva, O. Chernenko, A. Rosumenko, O. Gnatyuk, S. Karakhim, G. Dovbeshko

PGP-44 **Introducing the microscopic distribution of particles for the quantum optical averages**
A. Sizhuk

PGP-45 **Features of the silver nanoparticles formation in a photopolymer under uniform lighting**
T. Smirnova, V. Hryn, D. Klymchuk, Y. Akimov

PGP-46 **Investigation of Relaxation Processes and Phase Transition in the Polyethylene glycol 400 Using IR Spectra in a Wide Temperature Range**
A. Sobchuk, D. Andrusenko, V. Shevchenko, S. Alekseev, K. Yablochkova, R. Dinzhos, F. Ublekov, P. Tuleshkov, E. Lysenkov, M. Lazarenko, O. Alekseev, M.M. Lazarenko

PGP-47 **Internal photoeffect and other photoelectric and spectral properties of film compositions based on oligo-9-anthracenyl glycidyl ether doped with anionic polymethine dye**
S. Studzinsky, H. Solodukha

PGP-48 **Spectral-luminescent, photoelectric and information properties of new photosensitive compositions based on some methacrylic azo polymers doped by organic dyes with different ionicity**
S. Studzinsky, I. Savchenko, O. Ishchenko, H. Solodukha, M. Chuprina, V. Smokal, O. Nadtoka, O. Mokryns'ka, V. Kravchenko

PGP-49 **Electro- and photoelectric properties of new photosensitive thin film structures based on anionic σ-complexes**
S. Studzinsky, A. Siniugina

PGP-50 **The features of information and photoelectric properties of new effective polarization-sensitive holographic recording media based on azo-containing oligosilsesquioxanes**
S. Studzinsky, M. Gumenna, V. Shevchenko, V. Pavlov, H. Solodukha

PGP-51 **Synthesis and optical properties of new azobenzene-containing side-chain fluorinated poy(arylene ether)**
I. Tkachenko, Yu. Kurioz, R. Kravchuk, D. Litoshenko, V. Nazarenko, V. Shevchenko

PGP-52 **Study of influence of TiO_2 nanoparticles on the thermal stability of native DNA**
E. Usenko, A. Glamazda, V. Valeev, V. Karachevtsev

PGP-53 **Thermal Processes Induced by Chemical Reactions in Defects of Silicon Films**
V.M. Yashchuk, I. Lebedyeva , O. Vashchilina

PGP-54 **Investigation of multilayer samples of porous silicon with periodic structure by spectroscopic ellipsometry**
T. Veremeichyk, O. Makarenko, V. Shevchenko, S. Ivanchuk

PGP-55 **Universal force field minimization for predicting secondary structure changes in proteins due to post-translational modifications**
T. Voitsitskyi, O. Gnatyuk, F. Naeimaeirouhani, O. Skorokhod, G. Dovbeshko, G. Gilardi

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PGP-56 **Temperature evolution of Raman spectra and nature of phase transitions in $CuInP_2S_6$ and $Ag_{0.1}Cu_{0.9}InP_2S_6$ crystals**
A. Kohutych, M. Medulych, V. Hryts, V. Liubachko, Yu. Vysochanskii

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PGP-57 **IR and Raman spectra of Ukrainian beers: machine learning exploratory study**
K. Yablochkova, D. Daniliuk, A. Yezhola

PGP-58 **Features of stimulated Raman scattering of a laser dye mixture in media with multiple elastic scattering of light**
V.P. Yashchuk, O. Komyshan, S. Zelensky, E. Tikhonov

PGP-59 **Anionic polyacrylamide/gold nanoparticles/temoporfin hybrid nanosystem as a promising third-generation anticancer photodynamic therapy system**
O. Yeshchenko, P. Khort, O. Fedotov, V. Chumachenko, P. Virych,
H.S. Warren, B.W. Booth, V. Bliznyuk, N. Kutsevol

PGP-60 **Raman Non-Coincidence Effects of C=O Stretching Modes of Ethyl, Buthyl, and Amyl Acetates Probed by Polarized Raman Spectroscopy**
A. Jumabaev, I. Doroshenko, A. Absanov, U. Holikulov, Sh. Yormatov

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PGP-61 **Spectral and Photoelectric Properties of Ionic Liquid Crystals Tuned by Nanoparticles**
D. Zhulai, N. Boichuk, D. Pustovyi, V. Chekubasheva, O. Kovalchuk,

Y. Garbovskiy, G. Klimusheva, T. Mirnaya, and S. Vitusevich

PGP-62 **Influence of athermal microwave action on PL spectra SiC/por-SiC/Dy_2O_3 structures**
O. Okhrimenko, Yu. Bacherikov, O. Kolomys, V. Strelchuk

PGP-1

The effect of protein structure on optical absorption spectra of oxyhemoglobin: QM/MM study

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We present the results of the detailed study of the optical absorption spectra of oxyhemoglobin in R (relaxed) and T (tense) states.

The optical properties of oxyhemoglobin are explored because of its use in biomedical applications such as photodynamic phototherapy. UV-VIS spectroscopy and ab initio calculations are widely used to clarify the mechanisms of laser-induced photodissociation. It is known that the photodissociation of oxyhemoglobin involves structural changes in the protein. However, the difference between the α and β subunits of R and T states has been neglected in the theoretical models.

This work mainly aimed to compare the optical absorption spectra of α and β subunits of the oxyhemoglobin in R and T states.

We explore the effect of protein structure as well as solvation effect on optical absorption spectra of oxyhemoglobin using a hybrid quantum mechanical-molecular mechanical (QM/MM) method and embedded clusters - SIMOMM (Surface Integrated Molecular Orbital Molecular Mechanics) with GAMESS/TINKER software [1,2]. Density functional theory method and all-electron 6-31G(p,d) basis set with p, d polarization functions were used for the QM region. The MM region was described using the MM3 force field for the protein atoms. Solvent effects are included using the polarizable continuum model (PCM) in a water solvent.

First, we obtained optimized structures for α and β subunits of the hemoglobin in T and R states in vacuum and solvent. Then, we calculated electronic excitation spectra for α and β subunits of oxyhemoglobin in R and T states. Optical absorption spectra were obtained from the first 30 vertical singlet-singlet $S_0 \rightarrow S_n$ transitions, and the first 30 singlet-triplet excitations $S_0 \rightarrow T_n$ are also considered.

The protein environment induces a larger redshift of the Soret band in the β subunit than in the α subunit. Additionally, the Soret band of the isolated oxyheme is blue-shifted relative to those of both the α and β subunits. Solvation significantly redshifts the Soret band for the α and β subunits and the Q-bands for the β subunit.

Furthermore, we have examined singlet-triplet excited states up to 1300 nm. No significant spectral features were observed between 900 and 1200 nm in the singlet-singlet spectra. In contrast, singlet-triplet transitions can be responsible for spectral features within the 800-1000 nm range.

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PGP-2

TD-DFT computational studies of the optical properties of luminescence centers in Bi-containing glass-ceramics

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Theoretical modeling of the electronic structure of interphases in heterostructure composites is powerful tool in elaboration of novel technologically perspective optical materials [1]. This report presents results of the excited electronic states and optical spectra calculations of molybdate groups MoO_4 and Bi ions, which are currently considered as possible centers of luminescence of glass-ceramic composite material "$KBi(MoO_4)_2$ crystal@phosphate-molybdate glass of K_2O-P_2O_5-MoO_3-Bi_2O_3 system". The atomic and electronic structures of the crystal, glass and interphase layers of composites were obtained in using molecular dynamics [2] and band-periodic DFT methods [3].

The calculations were carried out at the Time-Dependent Density Functional Theory (TD-DFT) within molecular cluster approach. The geometry-optimized calculations were carried out using Gaussian software package [4]. Excited electronic states of molybdate groups MoO_4 or Bi ions in crystal, glass and interphase layers were calculated using the two-level ONIOM-2 approach. The quantum mechanical (QM) region comprised the atoms of molybdate groups MoO_4 or Bi ions, while the mechanical (MM) region comprised all atoms of crystal, glass and interphase layers. The electronic embedding was used in order to take into account electrostatic interaction between the QM and MM regions, i.e., the atoms of the QM region were treated by TD-DFT calculations, while the atoms of the MM region were treated as partial charges contributing to the quantum-mechanical Hamiltonian.

Calculations were carried out for 10 structures of glass and interphases regions of the composite and then averaged to obtain statistically valuable results. The excited states of the MoO_4 groups and Bi ions in $KBi(MoO_4)_2$ crystal were also calculated using the same approach, method and approximations. The results of the calculations indicate that the optical absorption spectra of bismuth atoms and molybdate groups exhibit significant differences in various regions of the composite material.

Results on the optical spectra for three different components of composite material (crystal, glass and interphase) are compared with experimental data in order to outline the properties inherent to each component. T+he origin of intrinsic luminescence in phosphate-molybdate glass-ceramics is discussed.

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PGP-3

Effect of (Ba/Sr)titanate nanoparticles on optical and dielectric properties of microcrystalline cellulose

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Flexible paper electronics has been considered as perspective branch of modern technology [1]. Cellulose in its various forms can be the backbone of the flexible devices technology that provides many advantages in respect to common semiconductor-based devices, e.g., low cost, eco-friendliness, bio-degradability, etc. Currently, a cellulose (paper) has been considered mainly as a substrate for printing of electric circuits with conventional or 3D printing. Additives (fillers) to cellulose substrate, such as dielectric or conductive materials, affect its physical properties and, consequently, an operation of paper-based devices. Unfortunately, the mechanisms of the interaction between cellulose materials and fillers are insufficiently studied so far.

Our study deals with optical and dielectric properties of microcrystalline cellulose (MCC) incorporated with $BaTiO_3$ and $SrTiO_3$ oxide nanoparticles. The samples were prepared by "dry" method – simultaneous grinding of the commercial MCC with an oxide (0, 10, 20 and 40% of cellulose mass) in agate mortar. The obtained fine powders were pressed at $2.0 \cdot 10^7$ Pa into tablets used for all the experiments except measurements of light diffuse reflection. The analysis of diffuse reflection spectra has shown that band gap values for MCC@$BaTiO_3$ and MCC@$SrTiO_3$ are almost the same as for grinded pure MCC. It was found from optical microscopy that obtained tablets have smooth surfaces without any notable agglomeration of oxide nanoparticles. The photoluminescence of the cellulose host vanished if $BaTiO_3$ or $SrTiO_3$ content increased in composites. Intensive lines of Eu^{3+} or Pr^{3+} f - f emission have been observed in the case of the MCC@$BaTiO_3$:Eu and MCC@$BaTiO_3$:Pr composites. So, the total of the photoluminescence intensity increased as a result of the Eu^{3+} or Pr^{3+} ions luminescence addition to cellulose-related emission. Thermogravimetrical analysis showed that $BaTiO_3$ or $SrTiO_3$ fillers decrease content of "free" and "bounded" moisture in MCC (e.g. 20% of $BaTiO_3$ adding to MCC decreases total moisture content from 4.8 to 2.3 %). A decrease in the moisture amount with an increase in oxide nanoparticles content has been also found by dielectric relaxation measurements. Due to an interaction between oxide particles and water molecules in hydrate shell of cellulose the activation energy of relaxations increases if compare to the case of "unfilled" cellulose. Therefore, it is possible to control the electrical properties of MCC@oxide by changing the concentration of the $BaTiO_3$ and $SrTiO_3$ nanoparticles.

Acknowledgment

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PGP-4

Plasmonic enhancement of Raman scattering of multilayer HfS_2 by metal nanoparticles

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Effect of spherical and nonspherical metal nanoparticles (NPs) on the Raman scattering of multilayer thick HfS_2 was studied. 2D-HfS_2 flakes were decorated with Ag and Au NPs of different shapes and sizes by drop-casting. A few-fold increase in the HfS_2 Raman modes was observed after the decoration (Fig. 1a). This is attributed to a plasmonic effect related to an enhancement of the electric fields of excitation and scattered quanta near the NPs. The effect depends on the absorption of the light in HfS_2 and NPs (Fig. 1b).

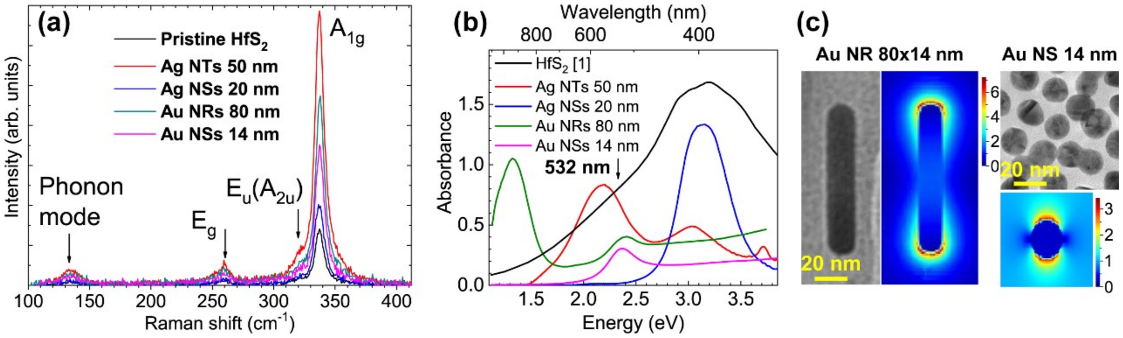

Fig. 1 (a) Raman spectra of a pristine HfS_2 flake and flakes decorated with different metal NPs. (b) Absorption spectra of few-layer HfS_2 [1] and the used NPs. (c) SEM images of the Au nanorods and nanospheres as well as the electric field distributions calculated in their vicinity under the excitation of 532 nm (vertical light polarization).

The excitation (532 nm) and scattered light is effectively absorbed both in the 2D-HfS_2 and Au nanorods and nanospheres as well as and Ag nanotriangles within their plasmonic absorption modes. Withal, it is out of the effective absorption range of the Ag nanospheres, thus their effect on Raman modes in Fig. 1a is minimal. The enhancement of the HfS_2 Raman modes is higher in a contact to non-spherical NPs. This is related to enhanced electric fields induced by the excitation quanta near their tips (Fig. 1c) [2, 3].

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PGP-5

Spectroscopic studies of polymorphism in 4-methylphenol

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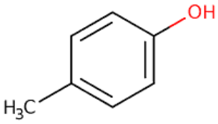
4-methylphenol (*p*-cresol) is an organic compound with the formula $CH_3C_6H_4(OH)$. It is widely used in the production of antioxidants, disinfectants and pharmaceuticals [1].



The molecule structure of 4-methylphenol has a methyl group (CH_3) which is located far from the hydroxyl group (OH) at *para*-position. The hydroxyl groups (OH) are involved in the formation of an intermolecular hydrogen bonding.

Polymorphic crystalline phases of 4-methylphenol were investigated earlier using the X-ray diffraction and DSC methods [2]. It has been shown that 4-methylphenol can exist in two polymorphic forms: stable phase (form I) and metastable phase (form II) whose melting temperatures are 309.2 and 307.9 K, correspondingly. The existence of polymorphic forms in 4-methylphenol provides a unique opportunity to study structure-property relationships, since the differences in the vibrational properties between the polymorphs must be due to differences in structure.

The aim of this work is to study polymorphism in 4-methylphenol using FT-IR spectroscopy and differential scanning calorimetry (DSC). We have demonstrated experimental evidence of the existence of a third polymorphic form of *p*-cresol in addition to the already known two forms [2]. The metastable phase III melts at 302.9 K. For the first time we have received the FT-IR spectra of the stable and two metastable phases of *p*-cresol and their temperature dependences in the range 300 - 12 K. To our knowledge, no vibrational spectral studies of *p*-cresol polymorphs have been reported so far. A computer with an OPUS operating system was used to collect and process the data. V. Balachandran et al. [3] have reported a detailed interpretation of the infrared spectra of 4-methylphenol molecule. In the present paper the assignments of the observed bands were all based on these analyses. The obtained FT-IR spectra showed significant differences in the position and shape of the bands related to the stretching vibrations ν(OH) and ν(CC); as well as the bands related to the aromatic C-H out-of-plane γ(CH) and in-plane β(CH) bending vibrations, and methyl group bending $\beta(CH_3)$ and rocking $\omega(CH_3)$ vibrations, when passing from one polymorph to another.

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PGP-6

Effect of Argon Environment on Vibrational Spectra of Ethanol

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Ethanol as one of monohydric alcohols in the liquid state can be considered as a partially ordered system. Partial order in liquid alcohols is due to the formation of hydrogen-bonded molecular associates (clusters). Spectroscopic methods for studying the structure and properties of liquids allow one to obtain only generalized information averaged over the volume, but do not make it possible to study individual molecules or their small associates. The way out of this situation is to use the matrix isolation method, the essence of which is that the molecules under study are frozen in a matrix formed by an inert gas (most often argon) at low temperatures (about 10 K) [1]. One of the main advantages of the matrix isolation method is the absence of interaction of the matrix with objects isolated in it, however, in numerous experimental studies, a weak influence of the matrix is observed, which manifests itself in a slight (up to several percent) shift of the spectral bands compared to the spectra of the gas phase [2, 3].

Geometry optimization of ethanol monomer and trimer in vacuum, as well as in ethanol and argon environments, was performed using methods of quantum-chemical simulation (DFT, B3LYP/cc-pVTZ level of theory). It is shown that the influence of the environment on the structure of ethanol molecules consists in an increase in the length of C–H and O–H bonds. The calculated frequencies of IR absorption bands for three different environments show that the effect of the environment is manifested as a red shift of the corresponding spectral bands.

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PGP-7

Interaction of new pyrrolo[2,3-*d*]pyrimidine-based telomerase inhibitor with G-quadruplex DNA

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Telomerase, the enzyme performing the synthesis of telomeric DNA, is active in a majority (85-90%) of tumor cells, in contrast to normal somatic cells. Its inhibitors are promising anticancer drugs. Single-stranded guanine-rich telomeric DNA sequences can fold into specific four-stranded structures, G-quadruplexes (G4), formed by the stacks of guanine quartets stabilized by metal ions. Small molecules able to bind and stabilize G4s inhibit the telomerase and demonstrate the antitumor activity. G4 ligands typically contain large heteroaromatic cores with cationic or basic side chains.

We have developed a series of potential enzyme inhibitors based on pyrrolo[2,3-*d*]pyrimidine annelated with pyrazine ring and containing strongly basic tertiary amine groups protonated under physiological conditions. A number of compounds were found to inhibit the telomerase *in vitro* at low micromolar concentrations. Here we studied the interaction of the active inhibitor **1** (Fig. 1, IC_{50} 18.6 μM) with G4 DNA. G4 structures were obtained by folding the Tel22 oligonucleotide d[AGGG(TTAGGG)$_3$], a fragment of human telomeric DNA. Tel22 formed the quadruplexes of parallel and antiparallel topology in the presence of K^+ and Na^+ ions, respectively. The interaction of **1** with G4s was studied by UV-Vis spectroscopy. Its optical absorption in the region 320-400 nm decreases upon the addition ofG4s, suggesting π-π-electronic interactions of the ligand with G4 DNA and the formation of ligand-DNA complexes. Binding affinity of **1** was determined in UV titration experiments. The addition of increasing amounts of G4s to **1** resulted in concentration-dependent decrease of its absorption band intensity (Fig. 1).

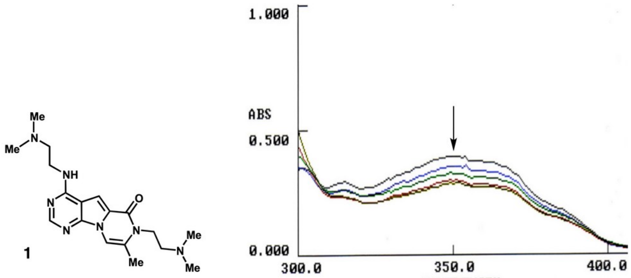

Fig. 1. UV-Vis spectra of the inhibitor **1** (50 μM) in the presence of various concentrations of parallel quadruplex Tel22 (0-50 μM). 10 mM Tris-HCl buffer, 100 mM KCl, pH 7.5; the arrow indicates the increase of quadruplex DNA concentration.

Binding constants were obtained from absorption *vs*. concentration plots by the classic Skatchard method. The ligand binds to G4 DNA with K_b values of 5.7×10^5 and 3.1×10^5 M^{-1} for parallel and antiparallel quadruplex, respectively. Thus, **1** shows high affinity to G4 DNA, with more efficient binding to the parallel G4. Its interaction with G4 structures of telomeric DNA may be the molecular basis for telomerase inhibition.

PGP-8

Boron-oxygen interaction in boron-doped Czochralski grown silicon

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Until now, silicon remains to be a subject of active research because of its wide application in such areas as the conventional electronic industry, power electronics, the fabrication of solar cells, and quantum technology. Boron is the most commonly used impurity in modern micro- and nanoelectronics based on p-Si. Therefore, a detailed knowledge of the role of boron in the processes of defect formation in Si and devices made on its base is of importance. Of particular interest is the study of the interaction of boron with oxygen, which is a technological impurity in Si, is present in significant concentrations (up to 10^{18} cm^{-3} and higher) and is very active in defect formation processes. This paper presents new data on the electronic and vibrational properties of the boron-oxygen-related defect, which were obtained for a set of boron-doped Cz-Si samples with various levels of boron doping and with oxygen in a wide range of concentrations.

A new electrically active defect is revealed in Si:B samples. Additional linear absorption in the region of the intracenter absorption for boron is associated with the defect. The energy distance between the spectral lines is in good agreement with the predicted by the effective mass theory for acceptors of group III in Si. It testifies that the defect responsible for the detected lines has hydrogen-like properties. The defect associated with the line is identified as B_sO_{2i}* owing to the linear dependence of its formation efficiency on the boron content and the quadratic dependence on the oxygen concentration. The revealed absorption lines correspond to the intracenter transitions from the ground to the excited states of boron, which are shifted relative to the main transitions due to a deformation perturbation from two neighboring oxygen atoms. The defect is formed both during the growth of silicon and under the action of elevated temperatures. It is supposed, boron atom in the structure of revealed B_sO_{2i}* defect forms direct bonds with two neighbouring oxygen atoms.

It is found that at elevated temperatures the detected B_sO_{2i}* defect transforms into a new state, which is associated with the emergence of the additional absorption line in the range of intracenter transitions for boron. A strong correlation was registered between the increase in the intensity of new absorption component with the temperature and the decrease in the intensity of the line associated with the B_sO_{2i}*. It is suggested that the defect responsible for the detected line appears owing to the temperature-induced transformation of the local atomic configuration of the B_sO_{2i}* complex. The activation energy of the B_sO_{2i}* transformation into a new configuration is 2.59 eV.

The local vibrational modes are identified for both configurations of the B_sO_{2i}* complex.

The data obtained testify that the BO_2 defects with different structure and properties can be formed in Si and must be taken into account when developing Si:B-based devices because they can play an important role in charge carrier transfer and affect the optical and electrical parameters of the material.

PGP-9

Molecular interactions and thermal properties of dye-doped polyurethane resins

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Polyurethanes are extremely versatile polymers that are produced of a wide range of organic units that allows controllable modification of their properties. Due to their homogeneity and high optical transparency they are recently intensively studied as dye-doped media for the development of tunable solid-state dye laser. Though dyes could affects the polymer matrix, in particular, its mechanical and thermal stability, however, there are no detailed analysis on this matter in the literature so far.

In the present report we investigated two different sorts of resins, (i) aliphatic polyurethane (PU), which were synthesized by a two-stage polymerization process using toluene diisocyanate prepolymerised with polyoxypropylene glycol, with subsequent hardening by trimethylol propane; and (ii) well known polyurethane acrylate (PUA) obtained by radical photopolymerization of oligourethane acrylate and benzoin isobutyl ester mixture. The effect of xantene dyes, rhodamine 6G (R6G) and rhodamine B (RhB), on thermal properties of synthesized dye-doped PU and PUA has been investigated using the detailed TGA/DTG/DSC measurements. The analysis of TGA/DTA curves of the dye-doped polyurethane has shown that the introduction of dyes induces changes in the polymer thermal stability and degradation route. It appeared that incorporation of both R6G and RhB dyes into the polymers increased their thermal stability, the changes being more significant for the PU resin. Specifically, for dye-doped PU, in addition to the thermal stability growth by 30°C, the additional degradation stage with an onset at 254°C was observed that could be ascribed to the dye evaporation process. This finding is supported by FT-IR spectroscopy indicating that due to the dye solvation by polar groups of the polymer, effective molecular interaction between the dye molecules and the polymer occurs that results in significant changes in the polymer structure, in particular, flexible and rigid blocks cross-linking and their segregation. The PU-RhB demonstrates clearly improved thermal stability compared to PUA due to the formation of hydrogen-bond network which is absent in the dye-doped PUA. For both PU and PUA, the DSC analysis showed no phase transitions in the temperature range -100–+300°C confirming their amorphous structure.

This study demonstrates that xantene dyes impact on the thermal stability of polyuretane resins significantly depends on the polymer synthesis method (polycondensation reaction or radical polymerization) and the related type of the molecular interactions between the dye and the polymer functional groups.

Acknowledgment

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Determination and refinement of the value of the Urbach energy and the optical band gap based on the long-wavelength absorption edge spectra of C_{60} and C_{70} fullerene films of different thicknesses

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The long-wavelength edges of the spectra of the absorption coefficient $\alpha\ (E)$ of C_{60} and C_{70} fullerene films with a thickness of 20–5000 nm in the region of 1.4–2.5 eV were studied in detail. It was found that the Urbach energy E_u decreases from 59 to 35 meV as the thickness of the C_{60} films increases from 20 to 5000 nm, except for the ~1000 nm thick C_{60} film, for which E_u = 76 meV. For C_{60} films with a thickness of 20, 70, 900, and 5000 nm, a decrease in the value of E_u is observed with an increase in the film thickness. This may indicate a decrease in the concentration of defect states in the band gap and, accordingly, an increase in the degree of ordering of the structure of C_{60} films as their thickness increases. In C_{70} films with a thickness of 20, 160, 1000 and ~1000 nm, the value of E_u is 43, 107, 50 and 78 meV, respectively. The value of E_u of C_{70} films, unlike C_{60} films, varies randomly depending on their thickness.

The value of the optical band gap E_g of indirect electronic transitions of C_{60} and C_{70} films was determined by extrapolating the linear least squares fit of $(\alpha * E)^{0.5}$ (Tauc), $(\alpha/E)^{0.5}$ (Cody) and $(\alpha)^{0.5}$ (classical method) to zero ("$(\alpha * E)^{0.5}$, $(\alpha/E)^{0.5}$ and $(\alpha)^{0.5}$ versus E" plots, respectively). For C_{60} and C_{70} films, the largest, intermediate, and smallest values of the E_g were obtained by Tauc-, classical-, and Cody methods, respectively. The $<E_g>$ value is numerically equal to the average of the E_g values obtained for the three methods. It practically coincides with the value of E_g determined by the classical method. For C_{60} and C_{70} films with a thickness of 20 nm, $<E_g>$ is 1.699 and 1.678 eV, respectively.

The long-wavelength edge spectra $\alpha\ (E)$ of C_{60} and C_{70} films were approximated by exponential lines in accordance with the equation:

$$\alpha(E) = <\alpha_0> \exp\left(\frac{E - <E_g>}{E_u}\right) \qquad (1)$$

The average values of the parameter $<\alpha_0>$ were estimated. The value of $<\alpha_0>$ is greater for C_{70} films. It is due to the stronger absorption of C_{70} compared to that of C_{60}. For example, the value of $<a_0>$ for C_{60} and C_{70} films with a thickness of 20 nm is 163.38 and 302.52 cm^{-1}, respectively. It was established that approximated exponentials lines coincide with the long-wavelength spectra $\alpha\ (E)$ of C_{60} and C_{70} films in the range of photon energies $\{E_1;\ E_2\}$. The approximated exponential lines pass below and above the spectra of $\alpha\ (E)$, at $E < E_1$ and $E > E_2$, respectively.

PGP-11

Induced smectic ordering and blue phase formation in mixtures of cyanobiphenyls and cholesterol esters

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It has been found that in mixtures of nematic E7 and smectogenic cholesteryl oleyl carbonate (COC), the S_A-N^* transition temperature is substantially (by ~20 K) increased at E7 concentrations around ~40% as compared with pure COC. Within the same concentration range, the isotropic transition is preceded by formation of blue phase, with its maximum width of ~3.5 K clearly correlated to the increased thermal stability of the S_A phase. With other cholesterol esters or cyanobiphenyls (cholesteryl nonanoate, 5CB), this effect was either much weaker or not observed. No enhancement of smectic phase was observed when E7 was replaced by CB7CB with two cyanobiphenyl moieties. Selective reflection (SR) spectra were measured in all three temperature regions, with unwinding of the cholesteric helix on cooling towards S_A phase and characteristic SR changes in the blue phase. In the latter case, the measured λ_{max} values were dependent both on the helical twisting power in the cholesteric phase and on the lattice size and orientation in the blue phase.

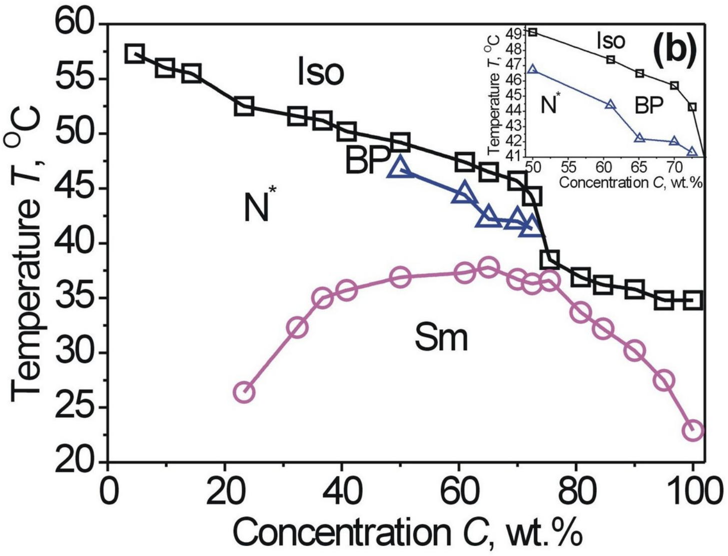

Fig. 1. Phase transitions in the mixture of nematic E7 and cholestery oleyl carbonate (COC) as function of COC concentration

PGP-12

Study of LIPSS replicas for surface enhanced spectroscopy

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Formation of laser induced periodic surface structures (LIPSS) was first reported in 1965. This phenomenon of formation of periodic surface micro- and nano-relief on solid materials under powerful laser irradiation has been studied ever since.[1] It invokes interest both as a surface functionalization tool and as a manifestation of complex processes of light-matter interaction. Nevertheless, there is no unambiguous and universal theory of this process.[2]

In this work, we report our results of application of basic metalworking techniques to the task of creating LIPSS replicas. Laser structured hard metals (steel, tungsten, molybdenum) were used as pressing dies (molds) to create an imprinted nanostructure on soft metals (copper, argentum) by a straightforward mechanical pressing. Mold and sample foils were placed between gauge blocks (Johansson gauges) and pressed for around 30 seconds in a small manual hydraulic press. Resulting surface structures and molds before and after pressing were investigated by SEM and AFM. Quasiperiodic surface structures were obtained, though their relief depth is smaller than on initial structures. Surface structure of mold did not receive noticeable damage in the process after a few repetitions. To our best knowledge, this has not been previously reported in literature. This approach is interesting for several reasons. LIPSS is naturally a field built around application of lasers, and most researchers have corresponding skills and mindset. It may be useful for some practical applications, like structuring of large surface areas with reproducible patterns, to use different methods, like pressing (stamping) or mold casting. Obtaining surface structures with morphologies similar to LIPSS but created in a different way can although be beneficial for LIPSS research.

One of possible applications of LIPSS on plasmonically active metals is as components of surface enhancement spectroscopy substrates. To evaluate properties of such structures for SERS, Raman spectra of test substance (Rhodamine 6G) on smooth, laser structured and mechanically structured surfaces were obtained.

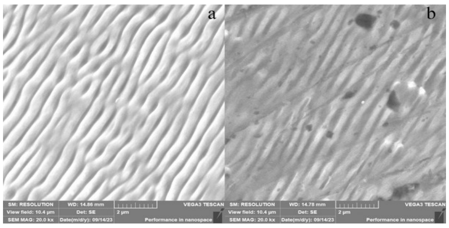

Fig. 1 a) LIPSS on molybdenum; b) imprinted structure on copper.

Acknowledgment

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PGP-13

Spectral markers and morphological features of diabetic foot ulcer tissues

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Metabolic disorders are an integral part of the development of diabetes mellitus. One of the most severe complications of diabetes is diabetic foot, which is characterised by the formation of necrotic sores. As a result, local accumulation of tissue breakdown products, secondary toxins, complications and progression of the disease. The aim of the study was to experimentally test the hypothesis of the formation and accumulation of β-structured protein aggregates in diabetic foot tissues. The formation of β-structured protein aggregates promotes their non-enzymatic glycosylation, which in turn promotes aggregation. Thus, there is a positive connection between the individual links of the pathological process. Breaking this link is a prerequisite for effective treatment.

The study investigated samples of surgical material of pathological tissues of the diabetic foot with fixation in a 10% formaldehyde solution. The samples were taken in accordance with the provisions of bioethics with the consent of the patients. The structure of the studied histological samples was assessed with Congo red staining by Puchtler-Mayer. To register the infrared absorption spectra, the tissues were washed from formaldehyde and dried on the working surface of the ATR attachment in the cuvette chamber of the Tensor 27 FTIR spectrometer.

The results of the optical image analysis indicate the presence of β-structured protein aggregates, which was confirmed by IR spectroscopy. However, such structures may not be amyloid fibrils, but instead be linked to aggregates of a different type. In addition, unique IR markers of necrotic tissues in the absorption region of stretching vibrations of C=O and C-O molecular groups were registered, and a 2.5-fold increase in the intensity of the CH stretching bands was observed compared to OH. The obtained data raises the question of the necessary methodological approaches to prevent sores progression and require further research to develop effective therapeutic strategies.

PGP-14

Experimental and Quantum Chemistry Investigations of Nitrazine Yellow Absorption Spectra on Organosilica Surfaces

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The modern impetus in the development of the chemistry of organic dyes is associated with the use of the latter in electronic devices, laser technology, linear and nonlinear optics, ion sensors, and biomedical analysis. The importance of the functions performed by dyes contributed to the emergence of the term "functional" dye. An example of a functional dye is Nitrazine Yellow (3-[(2,4-dinitrophenyl)azo]-4-hydroxy-disodium salt, NY), which exhibits halochromic and thermochromic properties, is photoacoustically sensitive, and allows non-invasive measurement of acidity in clear and cloudy environments. The ability of NY to change color in solution is due to the presence of azo-hydrazone tautomerism and deprotonation of the system in an alkaline environment (Fig. 1, left, A-C). Characterization of molecular shapes and understanding of the mechanism of tautomerism is crucial for controlling the properties of the molecule depending on the polarity and acidity of the environment. Studying the state of NY on the surface of modified silicas (Fig. 1, right, D) will allow to identify the influence of the matrix on the halochromic properties of the dye upon its incorporation into the silica matrix environment. In the present study, we perform an experimental and theoretical investigation of the environmental effects impacting the absorption spectra of NY.

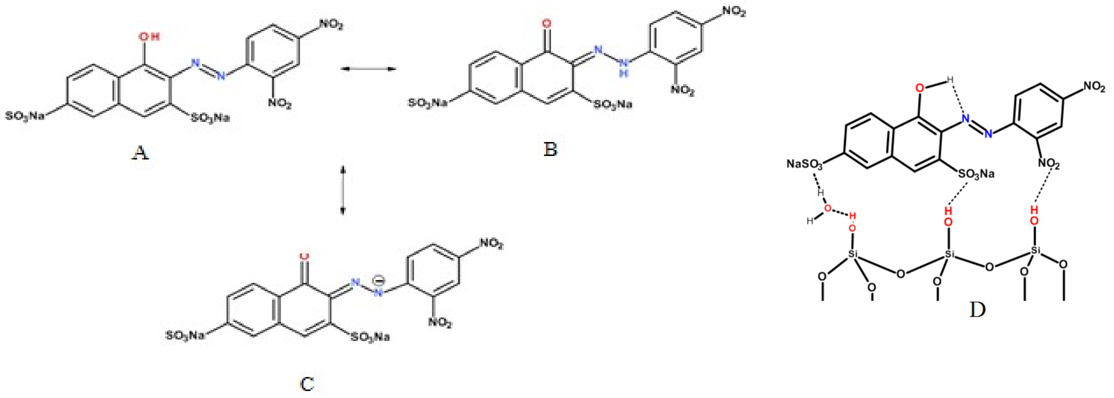

Fig. 1 NY forms (left) and NY on the silica surface (right).

For this purpose, we conducted time-dependent density functional theory (TDDFT) calculations, employing a variety of methodologies based on polarization continuum model to evaluate environmental effects on the studied systems (including Linear Response, State-Specific, and Solvation Model Density approaches). Through this comprehensive analysis, we have identified the most effective theoretical approaches to accurately describe the spectral properties of NY in various environmental situations.

PGP-15

Spectral investigations of 60S bioglass modified with La and Y ions

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Bioactive glasses, which are mainly made of silica with the addition of other oxides, have a higher ability to stimulate bone regeneration compared to other types of bioactive materials [1]. 60S glass, which has a chemical composition (mol%) of 60% SiO_2, 36% CaO, 4%P_2O_5, has shown favorable characteristics for bone regeneration and bone defect repair [2]. This work presents the results of studies of the electronic structure of the 60S bioglass (4% P_2O_5, 36% CaO and 60% SiO_2) by the FTIR method when it is doped with La^{3+} and Y^{3+} ions in different proportions (La (4%), Y (4%) and La (2%) + Y (2%)). The data obtained are compared with those for a typical 45S5 glass (Fig.1).

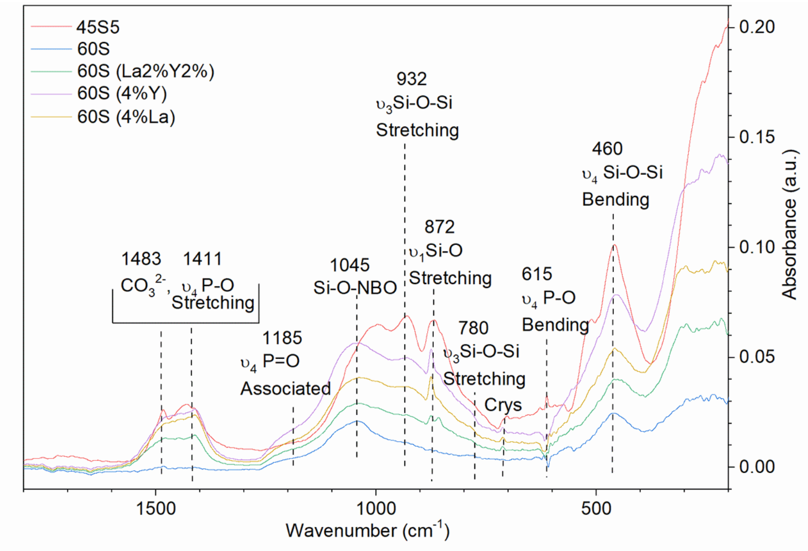

Fig. 1. FTIR absorbance spectra of studied bioglasses.

The bands at 460 cm^{-1}, 780 cm^{-1}, 872 cm^{-1}, and 900-1100 cm^{-1} are characteristic of the silica mesh and reflect the bending vibrations of Si-O-Si bridge bonds in SiO_4 tetrahedra, which have four oxygen atoms bonded to four Si neighbors. The vibration bands at 780 and 900-1100 cm^{-1} correspond to symmetric and asymmetric stretching vibrations of Si-O-Si.

A wide absorption band in the range of 1400-1500 cm^{-1} corresponds to the vibrations of non-bridging PO_2 in $P_2O_4^{-3}$ groups, as well as unbound CO_3^{2-} groups (formed from CO_2 during synthesis). It was established that the modification of 60S bioglass leads to an increase in the symmetry of functional groups, in particular oxygen tetrahedra, which, in turn, causes a change in the strength of Ca-O, Si-O, and P-O ionic bonds of the silica network.

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PGP-16

Sub-THz emission by IR-active shear phonons in K*Re*(MoO$_4$)$_2$

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Last decades significant achievement in the Time-Domain Terahertz Spectroscopy (THz-TDS) boost interest to THz research and its application. Despite progress in many aspects of Terahertz technology, generation of the monochromatic THz radiation remains a challenging task. Here we report the experimental observation of the re-emission of monochromatic sub-THz radiation by coherent optical phonons in double molybdates K*Re*(MoO$_4$)$_2$ single-crystals (where *Re* = Y, Lu, Tm, Dy, Er) using THz-TDS method. Layered structure of these compounds leads to infrared-active share lattice vibrations with energies below 3.7 meV [1], which corresponds to the frequencies below 900 GHz where solid state monochromatic radiation sources are rare.

Our results for KY(MoO$_4$)$_2$ are summarized in the Fig.1. Coherent infrared-active optical phonons are excited by broadband THz pulse and re-emit monochromatic sub-THz radiation with the decay time τ = 33 picoseconds (Fig.1, c,d). Such slow decay is an exception for the oscillators in solids with frequencies below 1 THz. Long coherent emission allows for the detection of more than 50 periods of radiation with frequencies of 568 GHz for $E^{\omega}\|a$. A similar sub-THz re-emission is observed for other compounds of the studied series. Thus, these unique characteristics together with the chemical durability of K*Re*(MoO$_4$)$_2$ suggest a variety of possible applications in THz laser technology.

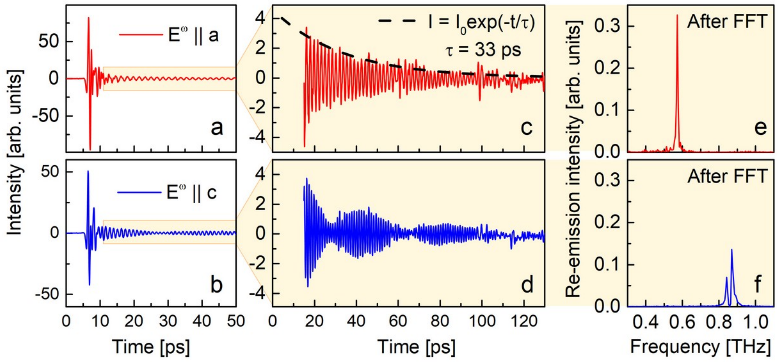

Fig.1. (a,b) The waveforms of THz pulses passed the sample (for the case of 80 μm thick sample plate at *T* = 4 K). (c,d) Zoomed waveforms of re-emission tails. (e,f) The re-emission intensity (after FFT post-processing). The spectra obtained at polarizations $E^{\omega}\|a$ and $E^{\omega}\|c$ denoted by red and blue colors respectively.

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PGP-17

Investigation of Intermolecular Interactions in Various Solutions of Aniline Using Raman Spectroscopy and DFT Calculations

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The study of the nature of weak intermolecular interactions has been quite interesting in recent years because they play a significant role in determining the physicochemical properties of molecular structures in a condensed medium [1]. Aniline is a simple amine representative of aromatic ring substances, and N-H vibration gives good results in the study of hydrogen bonding [2]. This work utilized Raman spectroscopy to investigate the effect of water/ethanol/chloroform on aniline vibrational modes. The intermolecular interactions of aniline and water/ethanol/chloroform molecules were investigated using the DFT approach using the B3LYP/6-311++G(d,p) basis set. The effect of various solvent concentrations on the N-H, C-H stretching, and C-H breathing vibrations of aniline was investigated. The Raman spectra of aniline-water, aniline-ethanol, and aniline-chloroform complexes were simulated. NBO analysis was performed to examine the mechanism of intermolecular and intramolecular charge transfer. MEP, HUMO-LUMO gap energy, and other electronic properties are described. Interactions at important connection points were studied by applying topological (AIM, NCI, RDG, ELF, and LOL) analyses.

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PGP-18

Low temperature secondary ion mass spectrometric study of mixtures of primary alcohols

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Cooling of volatile primary alcohols permits their mass spectrometric study in the liquid state by means of low temperature (LT) fast atom bombardment (FAB) and secondary ion mass spectrometry (SIMS). Earlier we applied LT FAB/SIMS to individual alcohols methanol (Me) and ethanol (Et) [1, 2], as well as propanol (Pr) and butanol. Sputtering of sets of clusters both in the positive and negative ion modes, such as $Me_n{\bullet}H^+$, $Et_n{\bullet}H^+$, $[Me_n\text{-}H]^-$, $[Et_n\text{-}H]^-$ (n up to 30), was observed. In the present communication we report on LT SIMS study of binary (methanol:ethanol) and triple (methanol:ethanol:propanol) mixtures. Reference data show that the volatility of primary alcohols decreases in the row Me>Et>Pr, which permits observation of fractioning of alcohols on the heating of the liquid mixture. Indeed, on gradual increase of the temperature of the liquid mixtures (starting from 135 K) the related changes in mass spectral pattern were observed. Mixed clusters incorporating molecules of all alcohols present in a sample are recorded right after the melting of initially solid frozen samples. In the case of binary methanol: ethanol mixture a variety of mixed clusters $Me_n{\bullet}Et_m{\bullet}H^+$ was gradually substituted by the ethanol-dominated clusters (m>n) in the course of methanol evaporation, finishing with pure ethanol $Et_n{\bullet}H^+$ cluster set. In the case of triple methanol:ethanol:propanol mixture, sets of $Me_n{\bullet}Et_m{\bullet}Pr_k{\bullet}H^+$ clusters with varied n:m:k ratios were recorded at the stage of appearance of the liquid phase. However, the most abundant sets contained mainly methanol and ethanol components: $Me{\bullet}Et_n{\bullet}H^+$, $Me_2{\bullet}Et_n{\bullet}H^+$. Evaporation of methanol on temperature increase led to redistribution of abundances in favour of $Et_n{\bullet}H^+$ clusters and suppression of methanol-containing clusters. On further temperature increase evaporation of ethanol led to liquid enrichment by less volatile propanol, reflected in the growth of $Et_m{\bullet}Pr{\bullet}H^+$, $Et_m{\bullet}Pr_2{\bullet}H^+$ sets. Thus, it is possible to monitor fractionation of alcohol mixtures under low temperature and low pressure conditions by means of LT SIMS. The data obtained may be useful for model studies of space-related systems.

Experimental details: a drop of alcohols of about 5 μL was frozen down to liquid nitrogen temperature on steel sample holder and subjected to spontaneous thawing in the ion source. Secondary ions were produced due to sample sputtering by Cs^+ ions of 15 keV energy. The spectra were recorded in the 10-1000 Da mass range at a rate of 5 seconds per scan.

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PGP-19

Photoluminescence of PCBM fullerene derivative confined in mesoporous glasses

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This work is dedicated to the study of photoelectronic properties of electron-accepting material, a fullerene derivative - [6,6]-phenyl-C61-butyric acid methyl ester (PCBM). Early we have been investigated the photoluminescence (PL) spectra of PCBM in various organic solvents [1].

The novelty of this work is that the linear spectral properties of this molecule were investigated, including absorption, steady-state PL spectra, kinetic decay curves and lifetimes in acetonitrile, toluene, PMMA; as well as in polystyrene matrix and in porous sodium borosilicate glasses with a pore diameter from 1 to 44 nm at excitation wavelengths λ_{ex} = 255, 337.1, 325, 405, and 532 nm.

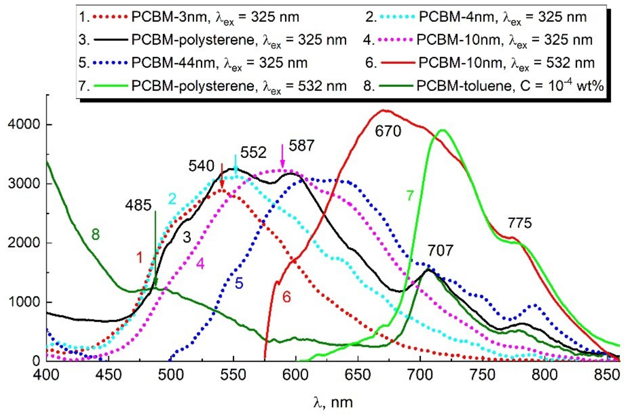

Fig. 1 PL spectra of PCBM in porous glass, d = 3 nm (1, dotted), 4 nm (2, dotted), in polystyrene (3, solid), 10 nm (4, dotted), 44 nm (5, dotted), in toluene (8, solid) at λ_{ex} = 325 nm; and in porous glass, d = 10 nm (6, solid) and in polystyrene (7, solid) at λ_{ex} = 532 nm; T = 296 K.

In this figure in the region of 500–600 nm we have bands which corresponds to CT excitons, when PCBM molecules confined in porous glass and in the polystyrene matrix are aggregated. When reducing the diameter of pores band maxima are blue shifted comparatively to PCBM in polystyrene. This effect is especially observed for pore diameters less than 10 nm. It's proof of existence the quantum size effect of PCBM molecules confined in mesoporous glasses, which form nanocrystallites in the pores in the region of CT excitons emission.

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PGP-20

Interaction of methyl uracil with polyethylene glycol

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Methyl uracil is widely used for treatment of complicated, poorly healing wounds; radiation and trophic ulcers (including patients with diabetic angiopathy, ulcers in weakened patients with significant immunosuppression); burns and other skin damage. The drug has a photoprotective effect in patients with photodermatosis. So, it can be used as a component of application drugs for treatment of skin wounds of various etiologies, restoration of damaged biotissues, rapid and effective wound healing. Such drugs can be developed on the basis of polymer composites with the addition of anti-inflammatory, antiseptic, antimicrobial, anesthetic medicines. Thus, it is important to investigate the interaction of methyl uracil with polyethylene glycol – a polymer which can be used as the base of the composite.

Quantum chemical calculations of the structure and IR spectra of methyl uracil were performed. The calculation results were compared with the experimentally registered spectra of methyl uracil. FTIR spectra of pure methyl uracil and polyethylene glycol (PEG 400) as well as their solutions with different concentrations were registered and analysed. The obtained results of IR spectroscopy of a mixture of polyethylene glycol and methyl uracil at different concentrations indicate the potential for controlled release of the medicine in pharmaceutical formulations with a polyethylene glycol matrix. This can contribute to the creation of new dosage forms that provide a constant and controlled release of the active substance, which can improve the effectiveness of therapy and the convenience of use for patients.

Acknowledgement

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PGP-21

Spectral Properties of Indole Derivatives as Parts of New π-Electron-Containing Drugs

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The majority of Indole derivatives are the class of biologically active pi-electron-containing compounds that possess broad "spectrum" of bio-medical activities. For example, Tryptophan is a well-known π-electron-containing amino acid, the structure unit of high-molecular proteins that together with DNA/RNA are the smallest building blocks of any living creature. Tryptanthrin is a naturally occurring yellow alkaloid, that can easy bind to telomeric G4 DNA and stabilize it. Due to this unique feature Tryptanthrin possesses anti-pathogenic, anticancer, anti-inflammatory, etc activities [1,2]. At the moment scientists paid their attention on the investigations of optical absorption and fluorescence of this class compounds mainly at room temperature [2]. We have an experience in the investigations of such class of compounds [3], and now our study is aimed at the comparative spectral-optics investigations (mainly at low temperatures) of Indole (Ind), Tryptophan (Trp), Tryptanthrin (Try) and Indoloquinazoline (IQX).

Comparative spectral investigations of optical absorption (at room temperature), fluorescence (at room temperature and $T = 78$ K) and phosphorescence (at $T = 78$ K) of solutions of Ind, Trp, Try and IQX (in different solvents) under different excitation wavelengths were carried out. The positions of the first excited singlet (S_1) and triplet (T_1) energy levels of these compounds were obtained. The effect of solvents on spectral properties of the investigated compounds is fixed. It is shown that the main centre of optical absorption, fluorescence and phosphorescence of Trp is Ind pi-electron system. Optical absorption spectra of Try and IQX are complex, but they contain the band associated with absorption of Ind pi-electron system. In fluorescence (under both temperatures) and phosphorescence of Try two optical centers have been fixed, one of them is associated with emission of Ind-segment of Try pi-electron system. In contrast to Try, in fluorescence (under both temperatures) and phosphorescence of IQX only one optical center has been fixed, it is not emission of Ind pi-electron system.

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PGP-22

Crystal structure disorder in ultra-small quantum dots

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Semiconductor Quantum dots (QDs) are significant for medical applications, such as contrast agents in magnetic resonance imaging, as materials for targeted drug delivery to diseased cells [1], *etc*. However, their most straightforward application lies in light-emitting devices. Due to the spatial confinement effect, QDs offer the unique ability to alter the band gap, enabling a wide range of exciton luminescence spectra with high quantum yield. As the size of QDs decreases, the surface-to-volume ratio increases rapidly, resulting in abrupt changes in optical spectra due to the activation of additional luminescence channels. This effect is especially pronounced in ultra-small QDs of the size less than 2 nm with a specific number of atoms (magic numbers), characterized by sharp light absorption and predominantly surface luminescence [2].

In this work, we investigate the impact of crystal structure disordering on the electronic and optical properties of ultrasmall A_2B_6 quantum dots. The characteristics of quasiparticles (electron, hole, and phonon) were calculated using the effective mass approximation based on the local atomic structure of the QD, determined by the density functional method. The calculations were performed on model atomic clusters $(CdX)_n$, where n ranges from 9 to 98 and X is Te or S, passivated by effective fragments of the thiol-glycolic acid molecule. Our results show that for larger clusters, the atomic structure is mostly homogeneous, but the near-surface layer exhibits significant reorganization of chemical bonds, which can strongly influence quasiparticle characteristics mainly due to changes in the electron (hole) wavefunction localization. Surface passivation partially mitigates this effect in CdS clusters due to the formation of natural Cd-S bonds with sulfur atoms from the thiol-glycolic acid molecule, but it remains significant for CdTe clusters. For smaller clusters, the entire crystal structure is highly disordered even with passivated surfaces, which significantly affects their optical properties, though this effect is somewhat weaker in the case of CdS clusters.

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PGP-23

Reversible photoisomerization and photoinduced birefringence in main-chain azobenzene poly(arylene ether) films

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Polymer materials containing azobenzenes as optically active groups have attracted significant attention due to their possible use in the efficient reversible light-responsive devices. In this work, four fluorinated poly(arylene ether) (FPAE) copolymers and one FPAE homopolymer were synthesized by polymerization of combinations of *bis*-azo-based monomer, decafluorobipheny and resorcinol. The copolymers are identified as Azo-FPAE with suffixes, -10, -30, -50, and 70, which refer to the initial molar amount of azomonomer whereas the homopolymer referred to as Azo-FPAE-100. The success of the synthesis of the Azo-FPAE polymers is confirmed with ^{1}H NMR, ^{19}F NMR, FTIR and Raman spectroscopy techniques.

The combination of *meta*-isomeric units, flexible ether groups, and non-coplanar units of octafluorobiphenylene within macromolecular chains results in polymers with exceptional solubility and film-forming capabilities, along with high thermostability (up to 440°C and beyond). In these polymers the *trans-cis-trans* photoisomerization of azobenzene switches occurs both in the solution and in the solid state (Fig. 1a and 1b, Azo-FPAE-100 shown as an example). As well, they also exhibit the remarkable ability of its azobenzene fragments to orient under light illumination (Fig. 1c).

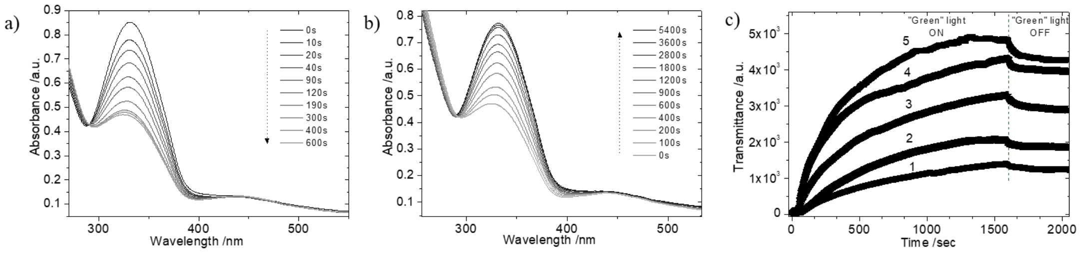

Fig. 1 a) *Trans-cis* photoisomerization (λ = 365 nm, 3-4 mW) and b) *cis-trans* photoisomerization (deuterium lamp, λ = 275 ± 25 nm, 8-12 mW) for Azo-FPAE-100 thin film. c) Kinetics curves for the buildup and relaxation of birefringence (λ = 532 nm, P ~10 mW) in Azo-FPAE-10 (1), Azo-FPAE-30 (2), Azo-FPAE-50 (3), Azo-FPAE-70 (4), and Azo-FPAE-100 (5) films.

This research shows the potential of the developed main-chain azobenzene polymers in advancing smart, light-driven materials (the reconfigurable photonic elements, optical switching, signal processing, laser technology, and actuation).

Acknowledgments

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PGP-24

Photo- and electrically-induced alignment of liquid crystals and colloids by Pigment Red 176 nanoparticles

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The dispersions of Pigment Red 176 nanorods in liquid crystals and dodecane [1,2] were fabricated and their elecro-optical properties have been studied. We report the investigation of the light transmittance as a function of applied voltage, frequency, concentration of pigment and geometry of the electrodes in the cells. The birefringence and dichroism induced by a.c. field were investigated within a high frequency range from 10 kHz to terra hertz ranges. The obtained results clearly show a great potential of dispersions of Pigment Red 176 nanoparticles for their applications in advanced optical and nonlinear optical devices.

Acknowledgments
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PGP-25

Investigation of Photochemical Transformations in Solutions of Organic and Inorganic Compounds with Silver Ions

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Investigation of photochemical transformations in solutions activated with silver promotes an elucidation of various physical processes that occur in such systems. In present work, the photochemical transformations in organic ($C_3H_8O_3$, C_2H_5OH, CH_3OH) and inorganic (H_2SO_4 , $HClO_4$, Na_2SO_3 , Na_2SO_4) aqueous solutions with an admixture of silver are studied taking into account the photoactivity of the Ag^+ ion.

While investigating the photochemical transformations in above-mentioned solutions activated by silver ions (10^{-5} – 10^{-1} mol/l), the absorption, photoluminescence (PL) and PL excitation spectra of the solutions were measured. The solutions involved do not luminesce at room temperature but at 150–180K they strongly emit under UV irradiation. The spectra under observation are conditioned by an electron transition between energy levels of the Ag^+ ion which are deformed due to the interaction with the environment.

At room temperature, in such solutions under irradiation by the light with the spectral distribution that meets the absorption region of the Ag^+ ion, the photochemical transformations occur, resulting in the transformations of Ag^+ ions in an insoluble Ag^0 association. The rate of photochemical transformations from the Ag^+ ions to the Ag^0 satisfactorily correlates with the energy values of electron detachment from solvent and with the maximum peak positions of absorption bands for given solvents in the aqueous solutions. Under irradiation with the visible light, the photochemical transformations in such systems ran rather slowly, during several months. Under storing in the dark over a long period of time, the solutions under observation did not lose their own luminescent properties. During measuring the absorption spectra of the solutions, the photochemical transformations ran very slowly and therefore those did not influence the experiment.

The study photochemical processes which occur in the solutions with silver complexes allowed us to elucidate the influence of media on the impurity Ag^+ ion and to determine a number of medium parameters that describe their properties.

PGP-26

Enhancement of the nematic ordering in cyanobiphenyl 5CB doped with salicylidenealdoxime due to supramolecular nanostructuring

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It has been found that salicylaldoxime (SA), added to nematic 5CB as a non-mesogenic dopant (NMD), increased the isotropic transition temperature T_i up to SA concentrations of ~4 mass %, with the nematic liquid crystal (LC) phase persisting up to ~30 mass % of the dopant (Fig.1). FTIR studies and quantum-chemical calculations suggested formation of weak charge-transfer 5CB-SA complexes. Such interactions could hinder 5CB dimerization, resulting in clusters of higher local anisotropy due to steric factors ensuring the optimum molecular packing. The 5CB+SA phases were studied by DSC, optical microscopy, and by the analysis of optical transmission at wavelengths outside the absorption bands as function of temperature close to the isotropic phase transition. To single out the molecular structure features responsible for the nematic ordering, studies under similar conditions were carried out with a mixture of cholesterol esters M5 as a LC matrix and *l*-menthol as an NMD capable of forming a deep eutectic with SA. The calorimetry and spectroscopy data obtained with the corresponding ternary systems (including changes in selective reflection of M5) were interpreted in terms of quasi-binary systems of interacting components in the allegedly indifferent solvent. The obtained results show that doping a nematic system with purposely selected NMDs can substantially affect their mesomorphic and optical properties, making this approach an alternative to introduction of nanoparticles to LC systems.

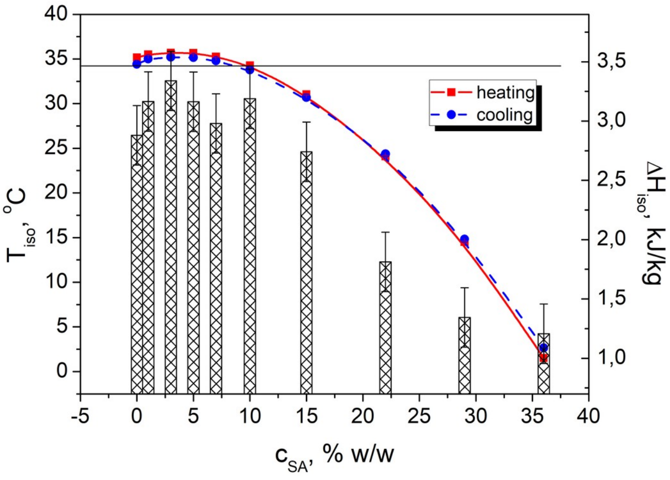

Fig. 1. Nematic to isotropic transition temperature and enthalpy of 5CB doped with SA (Mettler DSC 1).

PGP-27

Quantum Chemical Study of Structural Changes of Some Triazenes Azo- Compounds

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The complexes of molecules of triazenes with solvent molecules were regarded. It was demonstrated that at change from free molecules to the intermolecular complexes with molecules of polar solvents (two molecules of water or one molecule of acetonitryl or formamide) the difference in energy of common and izo-phorm of triazens somewhat increases. The same situation was observed in calculation of continual model PCM. The mechanism of transformation of common form of triazenes into izo-form in water medium is proposed. It suggests synchronic exchange by the hydrogen atoms between molecules of triazones and water [1].

Spatial structure and energetic characteristics of the molecules of azo- and bis-azocompounds p-H_2N-C_6H_3(R)-N=N-C_6H_4-NO_2 and O_2N-C_6H_4-N=N-C_6H_3(R)-NH-N=N-C_6H_4-NO_2 (with izo-forms including), where R – H, o- and p-CH_3 were estimaded. Possible content of solvate complexes of these compounds with molecules of solvents, produced due to hydrogen bounds with polar groups was regarded. It was estimated that hydratic envelope of the molecules of azocompounds consists of six molecules of water. The influence of the amounts of solvent molecules in complex and their spatial structure on energetic stability was studied.

Electronic absorption spectra of the azo- , bis-azocompounds and triazenes were calculated by the method of configurational interaction with taking into account only one-electronic exiting. The spectral shifts caused by solvent molecules were estimated.

The spatial structure and relative energetic stability of diazo-cations R-C_6H_4-N(+)≡N, and NH(+)(-C_6H_4-NO_2)(R-C_6H_4-N=N-)(O_2N-C_6H_4-N=N-), which are able to act as intermediates into reaction R-C_6H_4-NH-N=N-C_6H_4-NO_2 + O_2N-C_6H_4-N(+)≡N → O_2N-C_6H_4-NH-N=N-C_6H_4-NO_2 + R-C_6H_4-N(+)≡N were investigated.

The study showed that creation of three-nuclear cation-intermediate in gas phase is energetically advantageous process and its disruption needs only small amounts of energy. The most strong bounds were observed between diazo- cathode ion and two molecules of water and between cation-intermediate and four molecules of water. It was found that solvatation could influence strongly on energetic of studied process.

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PGP-28

Hydrogen Peroxide Detection Using Reversible Luminescent CeO_{2-x} and $CeO_{2-x}:Eu^{3+}$ Nanocrystals

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Hydrogen peroxide (HP) is a prevalent industrial chemical used extensively for bleaching, cleaning, and disinfection. In biological systems, HP acts as a crucial signaling molecule and is involved in various enzymatic processes as a substrate or byproduct, such as those involving catalase, superoxide dismutase, and numerous oxidases and peroxidases [1, 2]. Thus, precise HP sensing is vital for monitoring its concentration in both industrial and biological contexts.

Traditional HP sensors based on dyes and enzymes often suffer from instability and irreversibility. In contrast, luminescent inorganic nanocrystals offer a promising alternative. Specifically, undoped (CeO_{2-x}) and Eu^{3+}-doped ($CeO_{2-x}:Eu^{3+}$) colloidal ceria nanocrystals facilitate HP detection through the reversible quenching of their luminescence bands at 590 nm (Eu^{3+}) and 430 nm (Ce^{3+}) [3]. Studying the quenching and recovery behavior of these luminescence bands during interactions with HP sheds light on the underlying mechanisms of HP detection by these nanoparticles.

CeO_{2-x} and $CeO_{2-x}:Eu^{3+}$ luminescent sensors demonstrate reversible detection capabilities, with their recovery rates significantly accelerated by increased temperature and continuous UV irradiation. However, the introduction of Eu^{3+} ions, while beneficial for luminescence properties, negatively impacts the catalase-like activity of CeO_{2-x} nanoparticles and diminishes their antioxidant efficacy. This trade-off must be considered when deploying these sensors in biological environments.

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PGP-29

Oxidation of tin telluride films in an oxygen atmosphere

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Tin telluride (SnTe) oxide films have wide applications in various industries such as electronics, optics and thermoelectricity due to their unique physical and chemical properties. One of the fundamental qualities of studying these materials is their behavior in an oxygen atmosphere, which describes the stability and duration of operation of devices based on them.

This study examines the main aspects of the oxidation processes of tin telluride films in an oxygen atmosphere. The main attention is paid to changes in the structure of films, their morphology and electrical characteristics [1]. Different oxidation conditions such as temperature, oxygen concentration and exposure time are analyzed to provide detailed insights into the behavior of SnTe in an oxidizing environment.

Of certain scientific and practical interest are works devoted to the study of changes in the chemical, phase composition and surface morphology of SnTe films during isochronous and isothermal annealing in an air atmosphere [2]. In this work, the oxidation of epitaxial SnTe films deposited from the gas phase on cleaved barium fluoride crystals (111) was studied using Auger electron spectroscopy, nuclear gamma resonance, X-ray diffraction and metallography [3]. SnTe films were subjected to isochronous (for 1 hour) annealing in air at $T = 300\text{-}850$ K.

A common pattern for all epitaxial films studied is that their initial surface is always saturated with oxygen. A further increase in the film annealing temperature causes an increase in the intensity of oxygen peaks in the Auger spectras [3]. This is direct evidence of an increase in the amount of oxygen on the surface of the films. In this case, the intensity of tin in the Auger spectras of SnTe remains almost unchanged. Consequently, tin is effectively oxidized at the initial stages of annealing, forming a stable oxide on the surface that prevents further progress of the process.

Oxidation processes are key to understanding changes in the properties of SnTe films under environmental influences. Oxidation can lead to the formation of oxide layers that affect the electrical conductivity, optical properties and stability of the material. Therefore, the study of oxidation mechanisms and their influence on the structure and properties of SnTe films is an urgent task of modern materials science.

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PGP-30

Peculiarities of electron structure and photo-electrophysical properties of new carbazole derivatives

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The design and creating of purely organic dyes which would exhibit the phenomenon of room temperature phosphorescence (RTP) efficiently in OLEDs has gained much attention due to their potential application in cheap illumination sources without using expensive rare-earth materials.

In this work, relationship between the electronic structure and photo-electrophysical properties of four new carbazole derivatives were studied. Interpretation of absorption and luminescence spectra of solutions and neat films at 293 K and 77 K has been performed using the quantum-chemical calculations. The equilibrium molecular geometry and electron structure of the dye molecules were obtained to gain further understanding of their molecular levels by the DFT method. Thin films were prepared by doping studied substances into Zeonex matrix with 0.5% of weight concentration and investigated under high vacuum at 298 K by using time-resolved and steady-state spectroscopic methods. The Zeonex polymer matrix provides a rigid molecular framework and suppresses any intermolecular interactions. Absence of interaction with oxygen molecules and strong reduction in the rate of non-radiative deactivation of excitation is important for the presence of RTP phenomenon. Investigated compounds are photostable as well as resistant to heating and cooling. Photoluminescence quantum yield values of investigated compounds in films are higher compared to those for solutions which points to the appearance of aggregation induced emission enhancement (AIE) phenomenon. Electrochemical properties of the studied compounds were evaluated by cyclic voltammetry and electron affinity values to characterize substances.

Suppression of the interactions with oxygen molecules in Zeonex matrix, ability to vary the region of absorption and emission, thermal and optical stability, increasing quantum yield due to AIE in thin films give possibility to expect that these compounds are promising candidates for applying in OLEDs.

Acknowledgment

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PGP-31

Manifestations of interphase interactions in $Ca_3Eu_2(BO_3)_4$@$mLi_2O–nB_2O_3–pV_2O_5$ glassceramics

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Physical processes in composites determine the operation of almost all the main elements of modern micro- and nano-electronics, optoelectronics, laser technology, computer technologies, the Internet, and other communication media, without which, today, the existence of humanity is unthinkable. In the composite, it is customary to distinguish the matrix - this is the component whose contribution to the volume of the composite is the largest and, in addition, the space it occupies does not consist of separated parts. Another component of the composite is a filler (fillers, if there is more than one).

The simplest glass-ceramic (GC) can be considered a composite system that contains two phases: amorphous and crystalline. The interaction of components (phases) can play a significant role in the formation of macro-properties of GC. An intermediate region (interphase layer/interphase) is formed as a result of the interaction between the "pure" initial phases. The composition and structure of interphase do not correspond to the composition and structure of any of the initial phases.

Borate glasses are a technologically important class of materials used in various fields, and therefore representatives of this class of materials have been widely studied for the last decades. The lithium borate glass modified with vanadium oxide, V_2O_5: $mLi_2O–nB_2O_3–pV_2O_5$ was the matrix used in this work to elaborate SC and study the properties of the interphase. The glass net is formed by BO_3 and BO_4 groups, which are identified by their vibrations, in particular, in the IR absorption spectra. The various defects are luminescence centers of such glasses. Finely dispersed crystalline powder of the $Ca_3Eu_2(BO_3)_4$ oxide, where europium ions, Eu^{3+}, originate a luminescence, was used by us as a crystalline filler.

The purpose of our work was to determine the relationships between the characteristics of the material and its atomic and energy structure, the composition of the object under study, and the sizes of the particles/regions of the components. To achieve the goal, the method of luminescent probe was used, when the difference in the PL characteristics of the ions placed in the composite and its original components: matrix and the filler were detected. The XRD, FTIR, Raman scattering and diffuse reflection of light, as well as optical and electron microscopy methods, were used under study. As a result, some features specific to interphase layers were revealed.

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PGP-32

Experimental and Theoretical Studies of Intermolecular Interactions in Benzophenone and its Solutions

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Solvent plays a key role in diverse physico-chemical and biological processes. Therefore, understanding solute-solvent interactions at the molecular level of detail is of utmost importance [1].

In this work, biologically active benzophenone and its interactions with methanol and chloroform were investigated using vibrational spectroscopy (Raman) via C=O, C-H stretching and C-H breathing vibrational bands which involved in intermolecular interactions. The obtained experimental results show that in both solutions of benzophenone, a red shift was observed in the C=O stretching vibration band, and a blue shift was observed in the C-H stretching and ring breathing vibration bands. It was predicted that the reason for such shifts is H-bond formed by C=O and weak (non-classical) H-bond formed by C-H in benzophenone and solvents. Quantum chemical calculations, i.e. AIM, NCI and RDG, were performed to determine noncovalent interactions. It was confirmed that in the benzophenon-methanol and benzophenon-chloroform complexes there are weak H-bonds through the C=O group and mainly Van der Waals bonds are formed through the C-H group. By comparing the Raman frequencies and the calculated frequencies by PED analysis, agreement was observed[2]. Using the molecular electrostatic potential surface map, the charge distribution in benzophenone molecules was visualized and the charge-dependent parameters were determined. It was found that the parts of the negative electron potential for methanol moved from the carbonyl group of benzophenone to the carboxyl group of methanol, and for chloroform, the potential around the carbonyl group of benzophenone decreased. Through FMO analysis, electronic properties, thermodynamic and chemical parameters of benzophenone monomer, dimer and solvents, as well as parameters determined by HOMO and LUMO energy difference, were determined. When looking at the charge distribution in the formation of the complex through the Mulliken charge distribution analysis, it was observed that the atoms participating in the interaction changed more. Through electron localization function (ELF) and localized orbital locator (LOL) analyses, the chemical bonds and electron regions in the atomic and molecular systems of the titlle complexes were studied using colors differences.

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PGP-33

Biological affinity of aromatic amino acids in intermolecular π-stacking interaction

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Non-covalent intermolecular interactions are the basis of drug inhibition of a wide range of enzymes that contain amino acid residues phenylalanine and tryptophan with a developed π-conjugated system in their active sites. Previous studies have shown [1-2] that the stability of the complex between the amino acid residue of the enzymes enzymes and the π-conjugated system of the pharmacophore depends on their electron donation and the nature of the frontier molecular orbitals, which determine the type of electronic transitions, and therefore the nature of the intermolecular interaction.

Our spectral fluorescence study by titrating a solution of amino acids with a solution of thiochrome as a natural dye with a π-conjugated system under the same conditions and concentrations showed that the formation of a [π-π]-complex of thiochrome with tryptophan occurs more stably than with phenylalanine (Fig. 1).

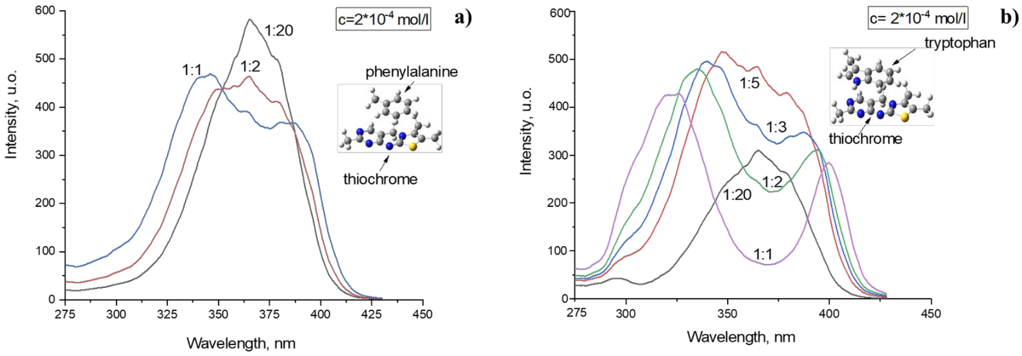

Fig. 1.

Fluorescence titration of a solution of amino acids phenylalanine (a) and tryptophan (b) with thiochrome dye.

Theoretical calculations show that the first electronic transition for both phenylalanine and tryptophan is $\pi \rightarrow \pi^*$, but its intensity is 6 times higher for tryptophan, both amino acid residues enter into π-stack intermolecular interactions, but with different energy (ΔE) complex formation. Biological affinity depends on the donor-acceptor properties of the bio-molecule, and was quantified by the φ_0 parameter: for tryptophan $\varphi_0 = 0.554$, for phenylalanine $\varphi_0 = 0.493$, that is, the tryptophan residue will form more stable intermolecular complexes: ΔE [π-π] complex with tryptophan is -13.6 kcal/mol, and ΔE [π-π] complex with phenylalanine is -9.2 kcal/mol. Such calculations agree well with spectral measurements.

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PGP-34

Mechanical Spectroscopy of SiO_2, nanocomposites of multiwalled carbon nanotubes and polymers

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X I am applying for **Bruker Customer Excellence Award** (see Award Guideline at icms.intibs.pl)

In this work mechanical spectroscopy of SiO_2, radiation and structural functionalized nanocomposites of multiwalled carbon nanotubes (MCNT) and polyethylene $(C_2H_4)_n$, polyvinylchloride $(C_2H_3Cl)_n$, polyamide $(NH(CH_2)_5CO)_n$ were researched. After stopping of laser radiation action of fusion solidification begun exactly from the surface, but the crater underbody is extended (molten) and created additional squeezing mechanical tension σ_i, that „pull" central part of crater surface [1].

The distribution diagrams of polarization vectors of quasilongitudinal velocity $V_{\|}$ $\vec{U},\vec{n}$ in SiO_2 is presented in Fig. 1. The value of mechanical spectroscopy, internal friction background Q^{-1}_0 after temperature, mechanical treatments describes the changes of the elastic stress σ_i fields in SiO_2, nanocomposite.

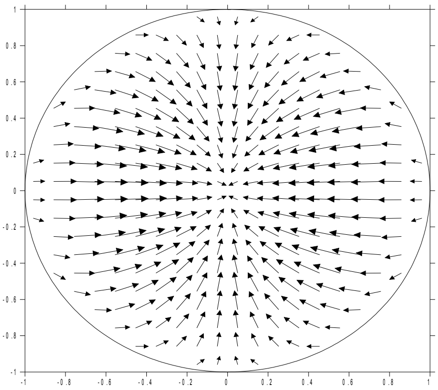

Fig. 1 The distribution diagrams of polarization vectors of quasilongitudinal velocity $V_{\|}$ $\vec{U},\vec{n}$ in SiO_2.

The crater fusion depth Δh at constant intensity I and laser irradiation time t is limited by the local heat-conducting and establishment of "time-equilibrium" distribution of temperature gradients ΔT perpendicular to the crater axis and along it.

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PGP-35

Electro-Optical Properties of Hybrid LC Materials Containing Photo-Controlled Inorganic-Organic Interface

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Hybrid liquid crystal (HLC) materials have been proposed by us recently [1-3]. Their feature is the inorganic-organic interface formed on the substrate of the HLC cell, where the inorganic side includes a pattern of nanoparticles (NPs). In our first investigations, we used the developed technique for fabrication of gold nano-island films by thermal annealing of solid Au film. In the meantime, we have proposed and are developing new promising techniques: (i) laser patterning and (ii) nanofragmentation of metal films by laser excitation of a pattern of superheated plasmons [4]. These new techniques provides more precise fabrication of metallic NPs with controllable size.

The electro-optical properties of HLCs strongly depend on the size and surface density of NPs in the inorganic-organic interface. Exposure to light leads to the excitation of surface plasmon resonance in the interface, the spectral range of which can span the visible or near-infrared ranges. We study a chain connection: the morphology of the layer of metallic NPs in the inorganic-organic interface – the spectral properties of HLCs containing such an interface owing to the excitation of surface plasmon resonance – the value of the nonlinear optical response and its speed, including their dependence on the applied voltage in the HLC. In the present work, we report on our latest achievements in this direction, both theoretical and experimental ones. The HLCs are perspective new materials for applications in high-speed electro-optical devices, including image processing.

Acknowledgment

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PGP-36

Stable Cyanine Dye J-aggregates with Plasmon Enhanced Fluorescence

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Molecular aggregates of cyanine dyes are low-dimensional molecular crystals that exhibit excitonic properties. Unlike larger crystals, the excitonic properties of J-aggregates can be manipulated with relative ease. These unique properties enable J-aggregates to be widely used in various fields, including photonics, sensors, photovoltaics, and biology. However, their stability and suitability for practical applications are critical considerations.

In polymer films, the fluorescence of J-aggregates is typically highly quenched. However, it can be enhanced through exciton-plasmon interactions, which occur due to the interaction of excitons with the local field of nanoparticles. The degree of plasmon enhancement is influenced by several factors, such as the chemical structure, size, and shape of the nanostructures, as well as the distance between the nanostructures and the fluorophore molecules.

In this study, the fluorescence of carbocyanine dye J-aggregates was enhanced by positioning them at a specific distance from a layer of gold nanoparticles. To further stabilize the J-aggregates, the samples were coated with a thin metal film composed of 20 nm of gold and 3 nm of titanium, applied using a thermal and electron beam evaporation system. The results demonstrated that all samples maintained stable fluorescence even after one month, indicating increased stability of the solid samples. This approach shows promise for the application of J-aggregates in photonic devices, particularly in thin-film configurations.

Acknowledgment

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PGP-37

Electron transport through degenerate electron level in single-molecular junction in the presence of electron-vibrational coupling and attractive electron-electron correlations

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Electron transport through a molecular junction consisted of a single molecule coupled to macroscopic leads is studied within the nonequilibrium Green's function method in the antiadiabatic regime. The molecule is modelled as a d-fold degenerated energy level with strong electron-vibron interaction (EVI) and attractive electron-electron correlations which lift the degeneracy. In the molecule the strength of the EVI may be significant that leads to the attractive character of the electron-electron interaction. It was shown that in the case of the attractive interaction, the dependence of the level occupation on the bias voltage becomes nonlinear and transport properties of the system are changed significantly. It was taken into account that due to the nonequilibrium distribution function of electrons in the molecule, the spectral function of the molecule becomes a function of the voltage and has to be calculated self-consistently.

We use the method of the transport spectroscopy which consists of calculating the differential conductance as a function of the bias and the gate voltages, that forms the 2D-map which is called the stability diagram. The current was calculated through each split levels and a stability diagram was built for each level. The method of transport spectroscopy made it possible to determine through which of the levels (both ground and excited) tunneling takes place depending on the applied voltages and to estimate the current through these levels.

It was shown that the EVI has a significant impact on the conductivity, that leads to pronounced sidebands in tunneling current caused by multivibron emissions leading to additional lines on the stability diagrams. It is also shown that the competition in the population of levels leads to the emergence of areas on the stability diagrams with the negative differential conductivity. With increasing power of the EVI, the areas with negative conductivity was observed also between the excited vibration lines. The reason is that the interaction limits the number of electrons that can be added to a level that leads to the competition between vibron levels associated with different orbits.

These results prove the significant influence of the EVI and electron-electron correlations on the electron tunnelling through molecular junctions. Understanding the physical processes of the transport through molecular devices is very important for their potential use as the next generation nano-scale building blocks of quantum computers.

The results of the work were published in the journal [1].

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PGP-38

Interaction of ibuprofen with polyethylene glycol

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Quantum chemical calculations of the structure and IR spectra of ibuprofen molecule were performed using various methods (HF, DFT, MP2). Several different conformers of ibuprofen were considered. The calculation results were compared with the experimentally registered spectra of ibuprofen. It is shown that MP2 method is the most appropriate for the description of the experimentally registered spectrum of ibuprofen. However, the positions of the maxima of the IR absorption bands in the calculated spectra of two different conformers of ibuprofen differ by only a few inverse centimeters, which makes it impossible to determine from the experimentally recorded spectrum which conformer is present in the sample under study.

FTIR spectra of pure ibuprofen and polyethylene glycol (PEG 400) as well as their solutions with different concentrations were registered and analyzed. The obtained results of IR spectroscopy of a mixture of polyethylene glycol and ibuprofen (at a concentration of 30%) indicate the potential for controlled release of ibuprofen in pharmaceutical formulations with a polyethylene glycol matrix. This can contribute to the creation of new dosage forms that provide a constant and controlled release of the active substance, which can improve the effectiveness of therapy and the convenience of use for patients.

Acknowledgment

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PGP-39

Spectroscopic changes resulting from binding of TMPyP^{4+} and TMPyP^{3+} porphyrins to *ds*-polynucleotides

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The porphyrins are macrocyclic compounds with unique spectroscopic and photophysical properties and a high biological activity. They are widely used as probes for the structure and dynamics of nucleic acids, as photosensitizers in anticancer photodynamic therapy, anti-viral and antimicrobial agents, as a carrier of antisense oligonucleotides for their delivery, stabilizers of G-quadruplexes. Dependence of the spectroscopic changes in the absorption and fluorescence spectra of TMPyP^{4+} and TMPyP^{3+} porphyrins (Fig. 1) resulting from their binding to double-stranded DNA (B-form) and RNA (A-form) polynucleotides, as well as to DNA:RNA hybrids (A-form) on the biopolymer base composition and spatial structure are summarized by comparing our [1, 2] and literature data. The porphyrins bind effectively to the biopolymers via two binding modes, which manifest themselves at low and high *P/D* ratios correspondingly. It was established that TMPyP^{4+} and TMPyP^{3+} discriminate between polynucleotide duplexes containing A:U (A:T) and G:C base pairs at low *P/D* ratios resulting in the porphyrin emission enhancement in the first case, and its quenching in the last case. It was shown that in contrast to TMPyP^{4+}, large bathochromic shift of the TMPyP^{3+} Soret band at high *P/D* is observed for all these polynucleotides regardless of their base composition and type of the helical structure. The features of the porphyrin aggregation at a near-stoichiometric in charge phosphate-to-dye ratio were analyzed.

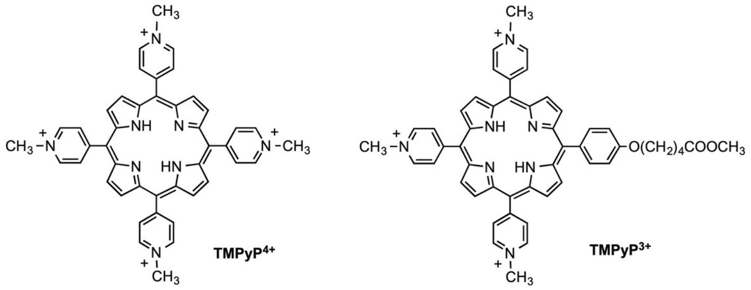

Fig. 1. Molecular structures of tetracationic TMPyP^{4+} and tricationic TMPyP^{3+} porphyrins.

Acknowledgment

Author acknowledges the National Academy of Sciences of Ukraine for the financial support (Grant No. 0123U100628); Wolfgang Pauli Institute (Vienna, Austria) for Pauli Postdoc research training scholarships "Data analysis in molecular biophysics" 2021/22 and 2023/2024; *Nanophotonics* journal, De Gruyter, Sciencewise Publishing, and the Optica Foundation for Ukraine Optics & Photonics Researcher Grant 2023.

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PGP-40

Clusteroluminescence: Properties, Chirality and Applications

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The current state of the art in the field of luminescent materials is related to a new phenomenon—clusteroluminescence. This phenomenon is due to the occurrence of end-to-end spatial conjugation, which is explained by the overlap of electronic orbitals of atoms in aggregates formed at high concentrations of substances in solutions or in the solid state. Clusteroluminescence is characteristic of a wide range of substances, including low molecular weight organic compounds of various classes, inorganic substances [1], polymers with heteroatoms [2], and some hybrid materials [3]. The practical applications of cluster luminogens are vast, including environmental protection, information security, optoelectronics in devices such as LEDs and displays, and medical applications for diagnosis and treatment as image markers [4]. Their unique optical properties make them valuable across these diverse fields. The chirality of amino acid residues plays a crucial role in the cluster luminescence of polypeptides [5]. Racemic polypeptides show significantly higher fluorescence intensity than enantiopure polypeptides both in bulk and in solution. Strong fluorescence intensity originates from the $n-\pi^*$ interaction in the space between the carbonyl groups of polypeptides. The insertion of amino acids with the opposite chirality disrupts the secondary structure of the α-helix of homochiral polypeptides, leading to the formation of a random helical structure. The flexibility of the random coils provides structural mobility for chain entanglement and cluster formation, indicating a stronger interaction between the carbonyl groups of the polypeptide chains. Such chirality-regulated cluster luminescence has been observed in various types of polypeptides, such as polylysine.The relationship between chirality and structure-property in cluster luminescent polymers can be widely used in many fields. The inclusion of amino acid residues with opposite chirality can be used to create proteins or peptides with strong fluorescence. Fluorescence spectroscopy provides detailed information about the relaxation, charge transfer, and energy transfer processes that occur after light absorption. If energy transduction is affected by spin selectivity in the chiral system, then the photoluminescence of the chromophore reflects the spin dependence of the transduction. It is known that the photoluminescence of nanoparticles attached to magnetized ferromagnetic substrates through chiral oligopeptides varies depending on the orientation of the external magnetic field. This is due to chirally induced spin selectivity [6].

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PGP-41

Vibrational structure of absorption spectrum of 2,5-bis(2-benzoxazolyl)hydroquinone

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An organic compound 2,5-bis(2-benzoxazolyl)hydroquinone (BBHQ) is extensively studied both experimentally and theoretically for several decades as a molecular system that undergoes excited state intramolecular proton transfer (ESIPT) [1,2]. Substances with ESIPT are considered to be suitable for lasing media [3]. Vibrational structure of the absorption bands of BBHQ is calculated for the transitions to the first and second excited states using the Franck-Condon approximation and harmonic model for vibrations. It is found that the use of normal modes calculated with the ωB97X-D3 density functional for the ground S_0 and two excited (S_1 and S_2) states provides good agreement with observed vibronic components in the spectrum. However, energy of the electronic transitions is overestimated by the calculations (Fig. 1). Changes in molecular geometry in the excited states and the normal modes demonstrating large intensity of transitions are discussed.

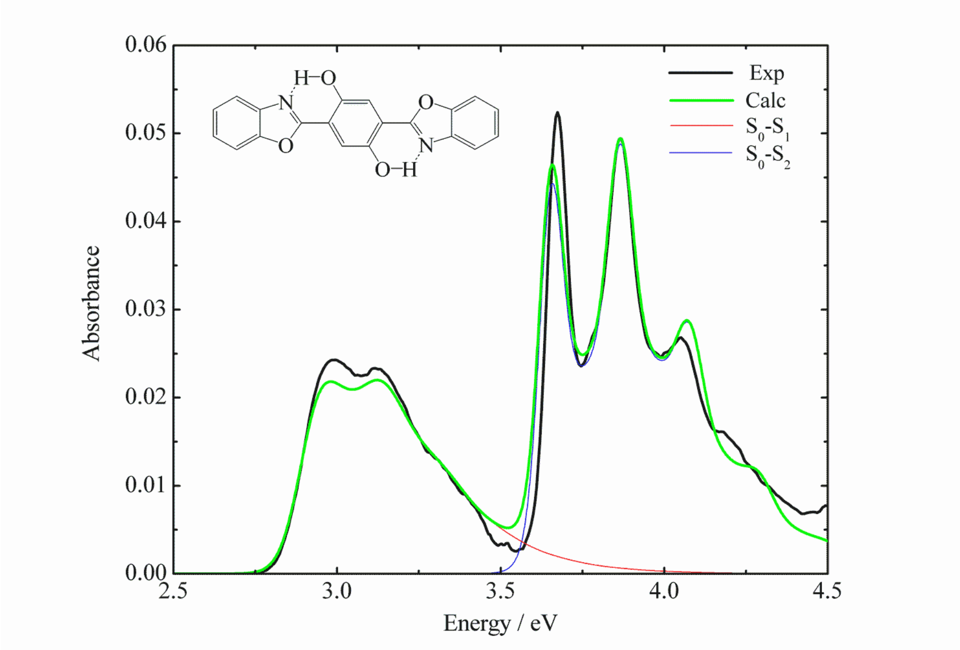

Fig. 1 Absorption spectrum of BBHQ dissolved in CCl_4 measured at room temperature (Exp) and modeled spectrum (Calc). Calculated energy of the S_0-S_1 transition is red-shifted by 0.2 eV, S_0-S_2 transition is red-shifted by 0.455 eV.

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PGP-42

Three-Layer Optical Sensor "Prism–Metal–Water Suspension of Inclusions" Based on Surface Plasmon Resonance

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An optical scheme of the Krechman type is considered, in which the receptor layer and the analyte layer do not exist separately, but represent a single receptor-analyte layer in the form of an aqueous suspension of micro inclusions. The presence of micro inclusions forms the effective dielectric constant of the suspension, different from the dielectric constant of the components (water and the dielectric constant of the inclusions). Surface plasmon resonance (SPR) consists in the possibility of determining the resonance wavelength and resonance angle of incidence from the minimum of the reflection coefficient and significantly depend on, in this case, the effective dielectric constant of the suspension. Therefore, in this study, the main attention was paid to the sign of the effective permittivity of the suspension, since the SPR exists only at its positive values.

The influence of two factors on the effective dielectric constant was investigated: the concentration of inclusions in the aqueous suspension and their dielectric constant. It is shown that for protein and nucleic inclusions, the effective dielectric constant cannot be negative for any concentrations, if the dielectric properties of the inclusions are considered "purely" real. But the dielectric constant of protein and nucleic acid molecules varies from –1 to ~2.5 depending on the length of the molecular chain. Therefore, a study was carried out of the influence of the dielectric constant of inclusions on the effective dielectric constant of the suspension for several actual concentration values. It has been confirmed that for protein and nucleic inclusions, in the case of their "purely" real dielectric properties, the effective dielectric permittivity of the suspension can only be positive and the SPR is realized at any concentration in the selected range (>10%).

It is also shown that for inclusions with a purely negative (< –1) dielectric constant, negative values of the effective dielectric constant of the suspension can also be realized.

PGP-43

Spectral markers and morphological features of supratentorial gliomas tissues from patients of different ages

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Oncological diseases of the brain are one of the most difficult in oncology because of the negative prognosis, their infiltrative growth and often resistance to commonly accepted treatment protocols. The purpose of this study was to establish the structural and molecular features of gliomas at various degrees of anaplasia and to identify possible correlations with the age of patients. Based on the obtained data, to determine the prognostic markers.

Bioptic material of gliomas of different degrees of anaplasia from 10 operated patients were studied in this work. The age of the patients ranged from 22 to 70 years. For IR spectroscopy, the samples were dried on the working surface of an ATP attachment. IR absorption spectra were registered on a Bruker INVENIO-R FT-IR spectrometer in the region from 3800 to 600 cm^{-1}. Histological preparations of the studied tissues stained with haematoxylin and iosin and iron haematoxylin were used for confocal microscopy. Confocal images were obtained on a Carl Zeiss LSM-510 META confocal microscope with Plan-Neofluar 40x/0.6 Korr objectives and a Zeiss AxioCam camera

A number of spectral features that can be defined as spectral markers of tumour tissues (gliomas) have been identified. Namely, the increasing contribution to the absorption of CH molecular groups, the presence of the C=O band in the 1740 cm^{-1} region, the pronounced asymmetry of the Amide I band with the contribution of different protein conformations in the absorption region of the PO_2^- molecular group.

The analysis of confocal images made it possible to reveal the morphological features of the studied samples and to conduct correlations with the data of IR spectroscopy. When analyzing the data, the peculiarities of the clinical course of patients with brain gliomas were taken into account.

PGP-44

Introducing the microscopic distribution of particles for the quantum optical averages

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In this work the representation of the quantum optical expressions for the absorption coefficient in terms of collisional integrals of the corresponding semi-classical kinetic equations is discussed. It was shown, that in certain approximation, the given gradient field of particle number distribution in the phase space (of coordinates and momentums) can determine the absorption properties of a system. The atom-photon and atom-atom collisions are formally represented here in the form of the corresponding items in the kinetic equation. The proposed approximation can be used to introduce the chronology of absorption/reemission and interatomic collision events in the system within an impact theory or a semi-classical evolution operator in the kinetic equation. The single-atom methods, such as the equation of motion for the one-particle population matrix, to find the number of quanta, imbibed by atoms or liberated into the environment per unit time, are not used here. The derived expression for the local absorption coefficient non-linearly depends on atomic density and initial intensity. It was found that the ability of the system to absorb or emit quanta can quantitatively be expressed through the semi-classical form of collision integrals (see details in [1]).

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PGP-45

Features of the silver nanoparticles formation in a photopolymer under uniform lighting

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Using a transmission electron microscope JEOL JEM-1230 the structure of a polymer film with silver nanoparticles (NPs), which are formed from a metal precursor during the polymerization of the photosensitive layer by uniform radiation, was studied. The starting composition includes a mixture of monomers, a radical polymerization initiator and a precursor. A liquid photosensitive layer was formed between glass substrates separated by 20 μm thick teflon spacers and was irradiated with a uniform beam of DPSS laser MBL-III-473 (λ = 473 nm, P = 20 mW) and UV radiation. Then the glass substrate treated with an anti-adhesive coating was removed.

To study the structure of the polymer layer film, slices perpendicular to the surface of the layer with a thickness of 40-50 nm and a height of 20-40 μm were made with help of Ultrotome III LKB 8800. The layers were placed on the microscope stage and scanned with an electron beam from the air/polymer interface to the polymer/glass interface. An example of such a structure is shown in Figure 1.

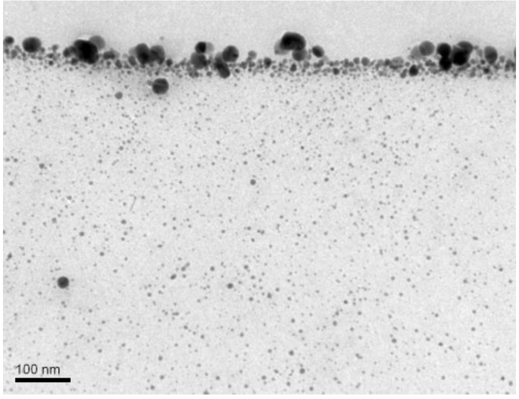

Fig.1. Structure of a film with Ag NPs near the air/polymer interface.

It was found that during polymerization, NPs are formed both at the air/polymer interface and at the polymer/substrate interface. The sizes of NPs at the boundary with air exceed their sizes at the boundary with glass. The average sizes of NPs in the bulk of the film are significantly smaller than at the boundaries. The sizes of NPs and their number decrease as the electron beam moves deeper into the film.

The mechanisms of NP formation at the boundaries and in the bulk of the polymer film are discussed. It has been suggested that the observed changes in the size and distribution of NPs are associated with the characteristics of microsyneresis of the precursor during layer polymerization.

PGP-46

Investigation of Relaxation Processes and Phase Transition in the Polyethylene glycol 400 Using IR Spectra in a Wide Temperature Range

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R. Dinzhos[2,3], **F. Ublekov**[3], **P. Tuleshkov**[3], **E. Lysenkov**[2], **M. Lazarenko**[4],
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Polyethylene glycol (PEG) and related compounds are widely used in a variety of spheres: from the polymer electrolytes, to thermal batteries, to pharmaceutical products. The properties of PEG are significantly affected by many factors, including the molecular weight, ambient conditions and the implementation processes. The thermal physical properties of PEG are affected by all of the above mentioned factors. For instance, the melting and crystallization processes of PEG differ at different rates of heating; the melting point of PEG can be anywhere from 1 to 66 ^{o}C depending on the molecular weight of the compound. The molecular weight of PEG also strongly affects its order of crystallinity. In a similar manner, the dielectric properties of PEG are strongly affected by the length of the macromolecule and its phase. At the same time the relaxation of PEG is influenced by the humidity of ambient conditions. According to N. Koizumi the relaxation time is the greatest for diethylene glycol, and somewhat smaller for higher homologues of this series. Such surprising property is discussed in terms of the elasticity of PEG chain, caused by the rotation of the chain's backbone about the C-O bonds, allowing for an independent orientation of hydroxyl groups at the ends of the molecular chains on higher polyethylene glycols.

Consequently, the present research aims to determine the mechanisms of thermal mobility in PEG molecules in relaxation processes. The object of this study is PEG 400, for which the specific role that the end groups play in relaxation processes can be analyzed separately, as opposed to higher polyethylene glycols. Our research methods include IR spectroscopy, differential scanning calorimetry, dielectric spectroscopy, and XRD. We demonstrate that, when heated, PEG 400 crystals undergo thermal and dielectric relaxation. We also discuss the mechanisms of the PEG 400 thermal mobility during relaxation processes as indicated by their IR spectra.

PGP-47

Internal photoeffect and other photoelectric and spectral properties of film compositions based on oligo-9-anthracenyl glycidyl ether doped with anionic polymethine dye

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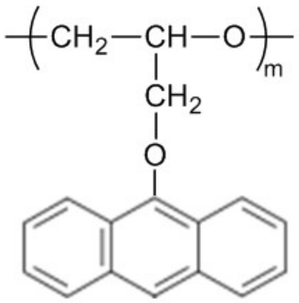
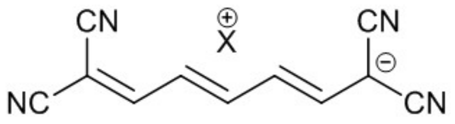
Thin film polymeric compositions based on oligo-9-anthracenyl glycidyl ether (OAGE) doped with anionic polymethine dyes (AD) were prepared both with low and with high concentrations of dopant. Their spectral luminescent, and photoelectrophysical properties were investigated.



OAGE



AD (X = NMe_4)

It is shown that the photoconductivity of such composites was rather unexpected effect since anionic polymethines usually induce n-type photoconductivity and there is no fragment in the OAGE structure capable of accepting a photo-excited electron from the AD chromophore. The absorption and luminescence spectra of these composites testify to the formation of contact ion-pair associates of AD molecules at its high concentration. Also unusual for semiconductor materials kinetics of the photocurrent growth and relaxation (photocurrent growth time is much longer than the time of its relaxation after the light is switched off) as well as effect of memory of preliminary illumination with light was observed in the studied composition films. Based on these data, the phenomenological kinetic model for internal photoeffect in the investigated composite films was suggested. Anomalous for semiconductor materials character of photocurrent kinetics was interpreted in terms of a photoinduced electron transfer from dye-anion to cation of dye molecule in the contact ion pairs, mediun polarity, photogenerated long-lived uncharged intermediate states (neutral radical pairs), media polarity-dependent mobility of the non-equilibrium charge carriers, and charge carriers mobility-dependent rates of the charge photogeneration and transport processes.

PGP-48

Electro- and photoelectric properties of new photosensitive thin film structures based on anionic σ-complexes

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The colored anionic sigma complexes – dinitro and trinitro**Studzinsky** substituted aromatic alkoxyl Meisenheimer complexes – were synthesized by the interaction of picryl chloride with corresponding sodium alcoholates. The novel photosensitive thin film structures based on these anionic sigma complexes and their composites with dielectric polymer matrices have been prepared. Their spectral, electric and photoelectrophysical properties have been investigated. All obtained thin film structures are characterized by a high level of ionic conductivity. It was shown, that all studied film structures exhibit photovoltaic effect and n-type photoconductivity under illumination by light from the long-wavelength edge of the synthesized anionic σ-complexes absorption region. The features of electrophysical, photophysical and photoelectric properties of the obtained thin film structures, as well as the possible nature of the photovoltaic effect and charge carriers photogeneration mechanisms are discussed. The respective phenomenological model for internal photoeffect and photovoltaic effect in the investigated thin film structures was proposed.

PGP-49

The features of information and photoelectric properties of new effective polarization-sensitive holographic recording media based on azo-containing oligosilsesquioxanes

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The novel thin film (~0,5-1 μm) polarization-sensitive reversible holographic recording media (HRM) based on newly synthesized polyhedral oligomeric silsesquioxanes (POSS), containing fragments of xanthene type or azo dyes, in particular Disperse Yellow 7 (POSS-DY7) in an organic shell have have been developed.

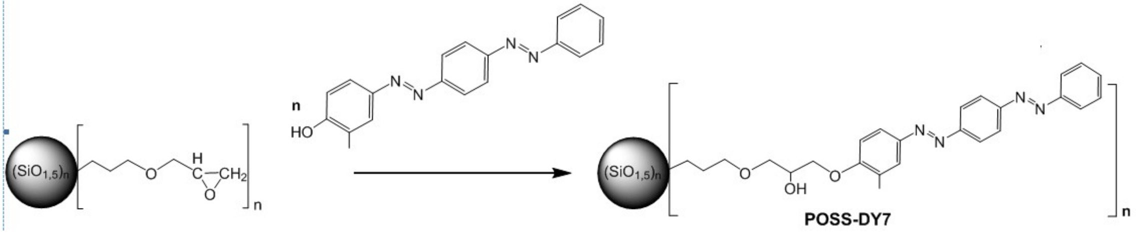

Fig. 1 Scheme of synthesis of POSS-DY7 (n = 8-13) (as an example).

Their spectral, photoelectrophysical, and information properties have been investigated. It was shown, that all studied thin film structures exhibit photoconductivity and photovoltaic effect under illumination by light from the dye-chromophores absorption region. The film structures informational characteristics measurements were carried out by using polarization holograms of a plane wave front recording method. In the films of HRM the holograms of the plane wave front were registered for parallel ($e_1||e_2$) and orthogonal ($e_1 \perp e_2$) orientations of polarization vectors of the object and reference light beams. The controlled parameter was the diffraction efficiency of the recorded planar-wavefront hologram determined in the –1 diffraction order. Figure 1 shows the reconstructed hologram of a planar wavefront image ($e_1||e_2$) recorded in the photosensitive film structure based on POSS-DY7 under sample illumination by green semiconductor laser (10 mW) irradiation. Hologram was recorded at a 1:1 intensity ratio of the reference to the object beam. The spatial frequency of hologram recording was ~ 250 mm^{-1}. The maximal attainable diffraction efficiency value for investigated HRM was ~ 4,5 %. The effect of "post-holographic recording" was revealed in the created HRM. The features of the spectral, photoelectric and information properties of the investigated recording media, as well as the possible nature of the photovoltaic effect, charge carriers photogeneration mechanisms, and dynamics of the recording and relaxation of the holographic gratings are discussed. The phenomenological model for holographic image recording mechanism in investigated HRM was proposed.

PGP-50

Spectral-luminescent, photoelectric and information properties of new photosensitive compositions based on some methacrylic azo polymers doped by organic dyes with different ionicity

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The novel photochromic thin film polymer compositions based on different methacrylic azo polymers doped by polymethine dyes with different ionicity have been prepared. Their spectral, photoelectric, and information properties have been investigated. The photoelectric properties of thin (~1 μm) polymeric composition films have been investigated by dynamic probe Kelvin method of surface electric potential measurement. It was shown, that studied oligomeric compositions films exhibit photovoltaic and photoconductivity effects under illumination by light from the long-wavelength edge of both corresponding azo-chromophores and polymethine dye-sensitizer absorption regions. The compositions films information characteristics measurements were carried out by using polarization phase holograms of a planar wavefront recording method. The controlled parameter was the diffraction efficiency of the recorded planar-wavefront hologram determined in the –1 diffraction order. Holograms were recorded under the sample illumination by green semiconductor laser (532 nm) irradiation at a 1:1 intensity ratio of the reference to the object beam. The spatial frequency of hologram recording was ~250 mm^{-1}. It was shown that the prepared photosensitive compositions can be used as holographic recording media for the polarization holography. The features of photoconductivity and holographic properties of the investigated film compositions, as well as the possible nature of observed photovoltaic effect are discussed.

PGP-51

Synthesis and optical properties of new azobenzene-containing side-chain fluorinated poy(arylene ether)

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Considerable attention is devoted to the preparation and performance of fluorinated poly(aryl ether)s (FPAEs) due to their high temperature resistance, stability, and low optical propagation loss. The structure of FPAEs with perfluoroaromatic fragments, especially biphenylene ones, provides opportunities for functionalization not only on non-fluorinated aromatic units but also on fluorinated aromatic fragments using nucleophilic agents. Therefore, FPAEs could hold promise for covalently attaching azo groups to their side chains, thus preventing chromophore aggregation and preserving their optical and electro-optical properties. The most attractive feature of azobenzene-containing side chain polymers is the large and reversible photoinduced birefringence, making them suitable for numerous applications in photonics and holographic storage.

Therefore, in this work, a new FPAE with azobenzene units in the side chains (FPAE-Azo), which has good solubility and film-forming capabilities, was obtained (Fig. 1a). The success of the synthesis of the FPAE-Azo is confirmed with ^{1}H and ^{19}F NMR as well as FTIR spectroscopy techniques.

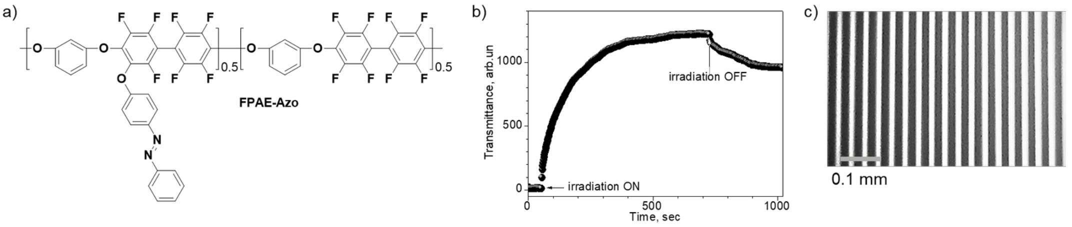

Fig. 1 a) Chemical structure of the obtained FPAE-Azo side-chain polymer; b) photoinduced birefringence curve for FPAE-Azo film as a function of the writing laser power (λ = 532 nm, P ~10 mW); c) photo of an FPAE-Azo diffraction grating with a resolution of 30 lines per millimeter.

UV irradiation induces E-to-Z photoisomerization of the synthesized material in both chloroform solution and solid state. Conversely, white light irradiation triggers the reverse Z-to-E isomerization in the film, highlighting the material's significant potential for reversible photo-switching. The birefringence intensity in the FPAE-Azo film increases upon exposure to polarized "green" light and eventually stabilizes at a constant value (Fig. 1b). After the light is turned off, a relaxation process occurs. The recording of a diffraction grating is also performed for the developed material (Fig. 1c).

Acknowledgments

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PGP-52

Study of influence of TiO_2 nanoparticles on the thermal stability of native DNA

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At the present, TiO_2 nanoparticles (NPs) are quite intensively used in environmental engineering, cosmetology, pharmaceuticals, and medicine [1]. But, despite the growing demand for these NPs in production and medicine, numerous works are currently appearing, indicating their possible negative impact on human health, as well as their genotoxicity [2].

The present work is devoted to the study of the thermostability of native DNA during binding to TiO_2 NPs at various concentrations under conditions close to physiological (0.1 M Na^+, pH 7) using thermal denaturation method.

The analysis of the DNA melting curves in the presence of TiO_2 NPs revealed a temperature range in which the light absorption of DNA decreases. We believe that the observed effect is explained by the unwound DNA regions that can bind to NPs and form a more ordered structure on the NP surface than double-stranded DNA at the initial moment. The injection of 2.5×10^{-5} M of TiO_2 NPs into DNA suspension leads to a decrease in the DNA melting temperature by ~ 6°C at pH 7. It is assumed that this effect is due to the predominant interaction of the nitrogenous bases of DNA with these NPs. It should be noted that in our previous studies performed at pH 5, slight changes in the melting temperature were observed in the entire studied range of TiO_2 concentrations [3]. The difference in the interaction of DNA to TiO_2 NPs at pH5 and 7 are discussed.

The results obtained in this study can be used to create various hygiene products, as well as in medicine and pharmacology.

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PGP-53

Thermal Processes Induced by Chemical Reactions in Defects of Silicon Films

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The Josephson effect [1], a physical phenomenon characterized by the flow of a superconducting current through a tunnel contact composed of two superconductors separated by a thin layer of dielectric or metal, is utilized to create detectors for weak magnetic field detection. In the fabrication of such detectors, cobalt is sputtered onto a heated silicon substrate. Technologists involved in manufacturing these bi-component films have encountered the issue of defect formation in the silicon substrate at the initial stages of the sputtering process [2].

Surface studies using microscopy have revealed that the defects manifest as molten droplets. A hypothesis was proposed to explain the observed phenomenon: a chemical reaction occurs between cobalt (Co) and silicon (Si) atoms within the cavities present in the silicon itself. These reactions would generate heat, leading to the formation of molten regions. These regions appear as droplets that move within the cavities where the reaction occurs, with silicon diffusing from the cavity walls. The mixture of Co and Si heats up to the melting temperature of the system, creating a Co-Si melt within the cavity (fig 1) [3].

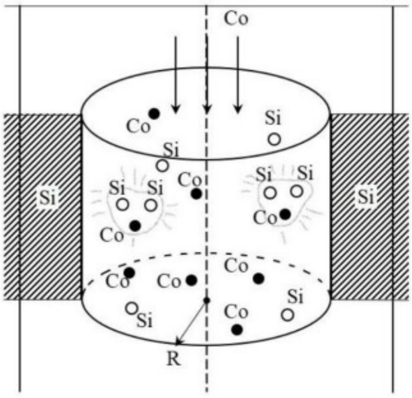

Fig. 1. Diagram of Co and Si atoms interaction in a cylindrical defect of the film.

This paper investigates processes corresponding to this hypothesis. A model is proposed for a cylindrical cavity in the silicon substrate where a reaction occurs between sputtered cobalt and silicon diffusing from the substrate through the cylinder walls. The problem formulation involves determining the temperature distribution and how this distribution changes over time.

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PGP-54

Investigation of multilayer samples of porous silicon with periodic structure by spectroscopic ellipsometry

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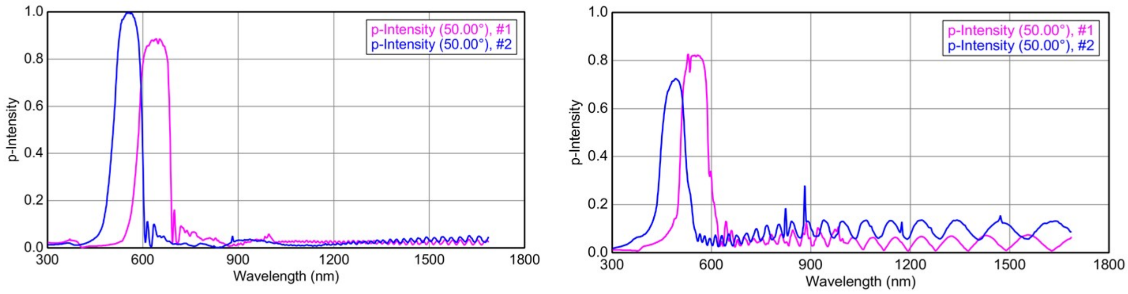
In this article, multilayer samples of porous silicon with a periodic structure, fabricated by electrochemical etching, are studied. The experimental dependences of the parameters ψ, Δ, as well as the intensities of the p- and s-components of the reflected light at different angles of incidence, on the wavelength before and after annealing, were obtained by spectroscopic ellipsometry. The samples differ in the thickness of the periodic layer and their porosity. Using the Complete EASE software [1], theoretical models were created that well describe the experimental dependencies obtained. The theoretical models were used to determine the total thickness, periodicity of the structure, and optical characteristics of the samples before and after annealing. It was found that after annealing, the structure of both samples of porous silicon changes and, accordingly, the refractive and absorptive indices n, k. The corresponding regularities have been investigated.

Fig. 1 shows typical experimental dependences of the p-component intensity on the wavelength at an incident angle of 50° for samples 1 and 2 before and after annealing (sample 1: layer thickness at manufacture - 30 μm, 166 layers; sample 2: layer thickness at manufacture - 5 μm, 34 layers).



a) b)

Fig. 1 Comparison between graphs of the p-component intensity distribution as a function of wavelength for samples (a) -No.1 and (b) - No.2, angle of incidence 50°. Distribution before annealing - pink line, after annealing - blue line.

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PGP-55

Universal force field minimization for predicting secondary structure changes in proteins due to post-translational modifications

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Human enzyme posttranslational modifications are important features of numerous diseases. Lipid peroxidation product 4-hydroxynonenal (4-HNE) is able to functionally modify specific proteins with implications for various diseases. Human monooxygenase CYP4F11 enzyme is involved mainly in lipid metabolism and xenobiotic degradation. CYP4F11 modification by 4-HNE was shown previously in malaria model, where phagocytosed malarial pigment hemozoin produced non-enzymatically 4-HNE in human monocytes. Enzyme activity was shown to be inhibited [1] but the structural changes were not studied yet.

The aim of the work is to investigate the modifications, elicited by 4-HNE in human CYP4F11 enzyme applying computational modelling.

The predicted structure of the CYP4F11 protein, generated by AlphaFold2 [2], was utilized. Specific residues (C45, C260, H261, H347, C354, K451) were manually modified by Michael addition with 9-carbon aldehyde 4-HNE, based on previously identified modification sites determined through mass spectrometry [1].

Subsequently, the modified structure was minimized using the Universal force field (UFF) [3] with the help of cheminformatics software RDKit v. 2023.09.1. The CYP4F11 unmodified AlphaFold2 structure was also minimized for a fair comparison. The secondary structure fractions were calculated using the dictionary of protein secondary structure (DSSP) v. 4.0.4. [4].

Independently, the FT-IR-spectrometry experiment indicates a decrease in the amount of alpha-phase by 0.23% and an increase in beta-phase by 2.12% in 4-HNE modified CYP4F11, in accordance with our computational analysis.

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PGP-56

Temperature evolution of Raman spectra and nature of phase transitions in $CuInP_2S_6$ and $Ag_{0.1}Cu_{0.9}InP_2S_6$ crystals

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2D van der Waals materials, due to their unique feature of strong interatomic bonding within the monolayer and weaker forces between the layers, can be divided into a single layer structure. Previously, the possibility of spontaneous polarization switching in $CuInP_2S_6$ ferrielectrics with a thickness of several structural layers was obtained [1]. This discovery has opened a new direction of fundamental and applied physical research in the field of nanoelectronics based on van der Waals multiferroics. A transformation of the ferrielectric first order phase transition, which is observed for $CuInP_2S_6$, into the subsequent paraelectric to ferrielectric second order phase transition and the isostructural first order transition with a sharp change in the polarization in the ferrielectric phase was revealed for $Ag_{0.1}Cu_{0.9}InP_2S_6$ mixed crystal [2]. The peculiarities of the phase diagrams of $CuInP_2S_6$ family ferrielectrics are related to the coupling between the sublattices of Cu^+ and In^{3+} cations located in the two-well and three-well local potentials, respectively, what could be traced by Raman spectroscopy. In the case of the $Ag_{0.1}Cu_{0.9}InP_2S_6$, an additional Raman band at 250 cm^{-1} appears which is similar to that observed in $AgInP_2S_6$ crystal [3] and corresponds to the lattice vibration resulting from the displacement of In^{3+} cations and the deformation of the anionic structural groups of $(P_2S_6)^{4-}$. Below 200 K a significant temperature transformation of the spectra is observed for both cases, which is associated with the anharmonic dynamics of indium cations. Upon heating from 200 K to 250 K, the Raman spectra of the $CuInP_2S_6$ crystal remain unaltered. In contrast, a significant transformation occurs for the case of the $Ag_{0.1}Cu_{0.9}InP_2S_6$ solid solution. This is related to the change in shape of the three-well local potential of In^{3+} cations due to change in internal chemical pressure at partial substitution of cooper by silver. For $CuInP_2S_6$ crystal in the range of 260 - 310 K the smearing of spectra is associated with thermal activation in the two-well potential of Cu^+ cations and the emergence of conditions for ionic conduction due to their penetration into the interlayer gaps. In the case of the $Ag_{0.1}Cu_{0.9}InP_2S_6$, the smearing of the spectra in the range of 270 - 290 K is related to a gradual decrease in the crystal structure spontaneous polarization during sequential phase transitions. In the paraelectric phase of $CuInP_2S_6$, above 315 K, there are no changes in the spectral distribution of Raman intensity, as Cu^+ cations have already filled the interlayer van der Waals gap. The Raman spectrum of the $Ag_{0.1}Cu_{0.9}InP_2S_6$ continues to exhibit significant temperature-dependent changes when heated in the paraelectric phase.

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PGP-57

IR and Raman spectra of Ukrainian beers: machine learning exploratory study

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Beer is one of the world’s favorite drinks. It is produced both at the large industrial level, and in smaller craft breweries. Both types of industries, as well as the distributors of this beverage, require cost-effective and reliable methods for its control and authentication. Traditional methods to assess specific properties of beer can be both time-consuming and costly [1]. However, IR and Raman spectra of beer, are both complex and likely sensitive to the differences in the fermentation, production, and storage of this beverage. Recently the robust machine learning classification and clustering methods drew attention of the industry and resulted in the search for the rapid, non-destructive, and automated beer quality assessment tools based on spectral data analysis, e.g [2].

The present research explores the potential of IR and Raman spectroscopy, coupled with machine learning, to determine a number of quality properties of the beer produced by Ukrainian breweries. The FTIR and Raman (excitation wavelength 532 nm) spectra for the total of 30 samples of beer were collected. The results of the study indicate that machine learning methods can be useful for classifying fermented beverages, according to such properties as the scale of the production (industrial vs. craft), storage condition (can vs. bottle), and fermentation type (top vs. bottom). Models’ overfitting and ability to detect positive cases were evaluated. The obtained models demonstrate relatively high accuracy, though limited, in part, by a small number of samples tested.

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PGP-58

Features of stimulated Raman scattering of a laser dye mixture in media with multiple elastic scattering of light

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Stimulated Raman scattering (SRS) of laser dyes in multi scattering media (MSM) occurs together with random lasing (RL), whose continuous-spectrum emission together with incident monochromatic pump can form a set of driving forces to be resonant with molecular vibrations as in the CARS technique.

For this resonance, it is necessary that the continuous RL spectrum coincides (or at least overlaps) with the region of the Stokes lines of the Raman spectrum [1]. In this case all the lines, located within RL spectrum, manifest themselves in the SRS. This can be used to reconstruct the Raman spectrum of laser dyes, which is very difficult to do with other methods due to their very intense luminescence [2]. But only for a small number of dyes, the coincidence of their RL spectra and Stokes lines is satisfactory. More often they overlap only partially or do not intersect completely. Therefore possibility of extending this method to a wider class of dyes requires further research.

In presented work we report a successful attempt to solve this problem by using a mixture of investigated dye with another specially selected dye. The main requirement for an additional dye is the overlap of its RL spectrum with the region of Stokes lines of the dye under study. These requirements are satisfied by a pair well known dyes rhodamine 6G (R6G) and pyrromethene 597 (Pm597): the first corresponds to investigated one and second – to an additional one.

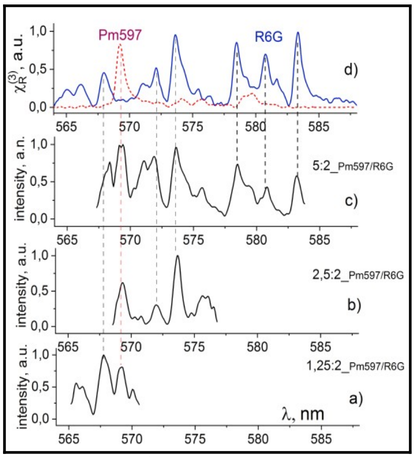

Fig.1 Dependence of SRS spectra of Pm597/R6G mixture dyes on their concentration.

The results are presented on the fig.1, where the SRS lines of Pm597/R6G mixture are displayed depending on their concentrations in units of mmol/l (a - c) in comparison with the Stokes lines of SRS spectra of individual dyes (d). The mixture was dissolved in a complex copolymer (vinyliden chloride + acrylonitrile + methylmethacrylate with 2,4,6-триазидопиримидин), from which a vesicular film was made to ensure multiple scattering. One can see that the increase in the concentration of the additional dye (Pm597) and conditioned by it broadening of its RL spectra causes manifestation of Stokes lines of SRS investigated dye (R6G). It proves that dye mixture extends the possibility of obtaining Raman spectra of laser dyes by the SRS method in MSM.

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PGP-59

Anionic polyacrylamide/gold nanoparticles/temoporfin hybrid nanosystem as a promising third-generation anticancer photodynamic therapy system

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Photodynamic therapy is a type of medical treatment that works by combining a special photosensitizing agent with light and molecular oxygen to generate cytotoxic reactive oxygen species (ROS). Right now it is used for a wide range of oncological and dermatological diseases. Such treatment has less side effects compared to traditional methods of chemotherapy and radiotherapy [1]. However, the are some limitations, namely poor water solubility and some dark cytotoxicity of most photosensitizers, as well as their nonselective accumulation in non-target tissues.

In our work, we prepared a three-component hybrid nanosystem that consists of star-like dextran-graft-polyacrylamide anionic polymer-nanocarrier, which encapsulates gold nanoparticles and temoporfin photosensitizer. Encapsulation of photosensitizers in nanocarriers is used to improve bioavailability, biocompatibility, selectivity, and phototherapeutic effects, as well as the stability and hydrophilicity of a drug [2]. Another novel approach of enhancing drug's anti-tumor efficiency is usage of metal nanoparticles. Namely, it was discovered that gold nanoparticles can be used to substitute and complement many chemotherapeutic drugs improving therapeutic responses [3]. Also, metal nanoparticles are well known and widely used to enhance various optical processes such as surface-enhanced Raman scattering (SERS), absorption (SEA), fluorescence (SEF), and photocatalysis by using the phenomenon of surface plasmon resonance.

We have performed optical characterization and analysis of the mentioned triple nanosystem, and observed significant enhancement of ROS generation compared to bare temoporfin. We have also determined optimal concentrations of the components which provides maximum photodynamic efficiency of developed hybrid nanosystem.

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PGP-60

Raman Non-Coincidence Effects of C=O Stretching Modes of Ethyl, Buthyl, and Amyl Acetates Probed by Polarized Raman Spectroscopy

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Vibrational spectroscopy methods have numerous applications in biological, chemical, and environmental sciences. In particular, it is widely used to determine dynamic structural changes during the life activity of living organisms [1].

In this work, we examined the polarized Raman characteristics of C=O stretching modes of ethyl (EA), butyl (BA), and amyl acetates (AA), which are widely used as solvents in industry. The isotropic and anisotropic spectral bands of these liquids in their neat condition were recorded in the experiment. The isotropic and anisotropic wavenumbers of these spectral bands were determined to be 1738 and 1743 cm^{-1}, respectively. As a result, the non-coincidence effect (NCE) of the C=O stretching mode in all three liquids is $\Delta\nu$=+5 cm^{-1} (According to the literature [2], the value of NCE for ethyl acetate is +5,3 cm^{-1}.). From this result, it can be predicted that EA, BA, and AA have almost similar molecular orientation, and as a result, they form the same transition dipole-transition dipole resonance couples. The concentration dependence of the Raman NCE of the C=O stretching bands of acetates is investigated in acetates/CCl4 mixtures. The results in these binary mixtures were compared with the theoretical model of the Onsager-Fröhlich dielectric continuum model. In this work, we have provided the data necessary to understand the non-covalent interactions in EA, BA, and AA dimer clusters. Initially, the ABCluster code, which performs global optimization, was used to generate the global minima structures of acetates dimer clusters. The located geometries have been optimized at the Density functional theory (DFT) method with B3LYP/6–311++G(d,p) function using Gaussian 09 suite of programs. We found isotropic and anisotropic spectral bands with wavenumber peaks in the calculated Raman spectra. According to these values, the value of the Raman NCE was found to be the same ($\Delta\nu$ =+10 cm^{-1}) for all three liquids. The effect of various solvents ($\varepsilon_{CCl_4} < \varepsilon < \varepsilon_{C_2H_6O}$) on the NCE phenomenon was investigated by DFT/PCM calculations. We also determined and compared the MEP, HOMO-LUMO gap energies, and transition dipole moments for each of these liquids. In addition, intermolecular interactions in dimer clusters of these liquids were studied using various topological (NCI, RDG, ELF, and LOL) analyses.

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PGP-61

Spectral and Photoelectric Properties of Ionic Liquid Crystals Tuned by Nanoparticles

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Glass materials with nanoparticles (NPs) represent a new class of electro-optical structures with unique properties. The photoelectric and physical characteristics of these structures can be precisely adjusted using nanoparticles of definite size and composition. These nanocomposite materials attract increasing attention of researchers because of promising possible applications in optoelectronics, photonics, sensing, electrochemistry, catalysis, biomedicine, etc.

In this work, we studied the cadmium octanoate $Cd^{+2}(C_7H_{15}COO^-)_2$ (abbreviation CdC_8) ionic liquid crystals with several types of NPs. A distinctive property of the CdC_8 matrix acting as a nanoreactor is the possibility to control the size and uniformity of NPs during the synthesis. Nanocomposite materials including semiconductor, metallic and hybrid NPs in the CdC_8 matrix are investigated. The shape and size of NPs are measured using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). These methods allowed us to obtain high-resolution images and precisely study the distribution and characteristic sizes of the NPs in the CdC_8 matrix. The SEM and TEM results show that the CdC_8 matrix represents a suitable environment for positioning NPs since it assists in the formation of nanocomposite materials with uniformly distributed NPs in the material with minimal size dispersion and without aggregation. Obtained data are used to analyze the correlation between the structural characteristics of NPs and their optical properties. The photoelectric properties of these materials are studied using ultraviolet and visible range light sources of different intensities. The results demonstrate that synthesized nanomaterials have great potential for the design of photoelectric elements and optical sensors.

Acknowledgment

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PGP-62

Influence of athermal microwave action on PL spectra SiC/por-SiC/Dy_2O_3 structures

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To reduce of the concentration of defect states at the oxide-semiconductor interface the additional external treatments, such as temperature annealing, γ-irradiation, and microwave processing are often used. Thus, previously the authors observed the effect of a decrease in the absorption coefficient for SiC/SiO_2 and SiC/TiO_2(Gd_2O_3, Er_2O_3) structures after microwave exposure.

In this work, we investigated the effect of short-term athermal microwave exposure on the occurrence of radiative recombination processes in 4H-SiC/por-SiC/Dy_2O_3 structures.

In Fig. 1 shows the characteristic normalized PL spectra upon excitation of PL radiation with $h\nu_{ex}$=2.33 эВ< E_g(4H-SiC)=3.23 eV for SiC/por-SiC/Dy_2O_3 structures before and after microwave exposure.

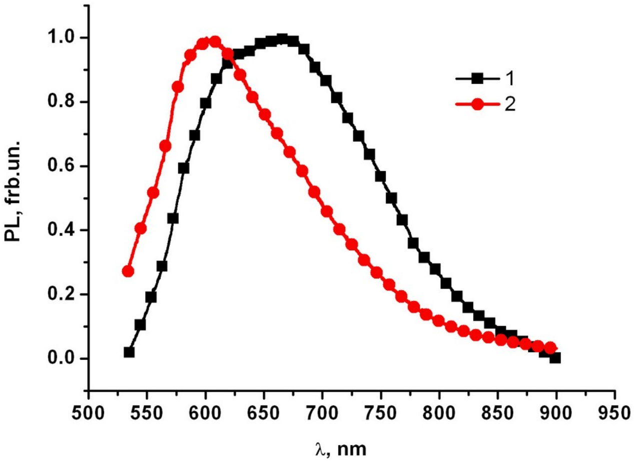

Fig. 1 Normalized PL spectra for the SiC/por-SiC/Dy_2O_3 structure before (1) and after (2) microwave exposure

As can be seen from Fig. 1, after microwave treatment, the PL spectra of the SiC/por-SiC/Dy_2O_3 structure exhibit a short-wave shift in the maximum of the integral band and a decrease in the half-width of the integral PL spectrum. The observed shift of the integral maximum of the PL band of the SiC/por-SiC/Dy_2O_3 structure to shorter wavelengths under the influence of microwave treatment is most likely associated with an increase in the intensity of the 577 nm band, which is caused by change in the symmetry of the coordination environment of the Dy^{3+}

The change in the symmetry of the coordination environment of the Dy^{3+} ion under the influence of microwave treatment confirms the assumption that microwave exposure leads to changes in the defect sublattice due to the movement of dislocations.

AUTHORS INDEX