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8th INTERNATIONAL FALL SCHOOL ON ORGANIC ELECTRONICS

International Conference on Printed Electronics ICPE-2022

BOOK OF ABSTRACTS

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АКЦИОНЕРНОЕ ОБЩЕСТВО ГОЗНАК

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2022

Ultrafast singlet fission dynamics in pentacene and high quality rubrene single crystals

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Singlet fission (SF) is an inherently multielectron process in which one singlet exciton ***S*** coverts into a pair of triplet excitons ***T+T*** [1]. To elucidate and control SF mechanism, recently great attention has been given to identification of intermediate states in SF materials, which often appear elusive due to complexity and fast timescales of SF process[2]. Here we apply a set of transient absorption (TA) techniques to high-purity rubrene single crystals to disentangle the intrinsic fission dynamics from the effects of defects and grain boundaries and to identify fission intermediates. Using sub-10fs TA, we show that SF in rubrene is mediated by the formation of short-lived states with a hybrid singlet/triplet character which rapidly (~100fs) decay to either singlet or ***T+T*** triplet pair. We assign this intermediate the vibronically-assisted mixture ***[S:TT]*** of singlet state and triplet multiexciton. The relaxation of ***[S:TT]*** to ***S*** is followed by a relatively slow and temperature-activated (50 meV activation energy) incoherent fission process. The revealed SF competing pathways and intermediates unify the observations and models presented in the previous studies of rubrene and propose alternative strategies for the development of SF-enhanced photovoltaic materials.

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Spin-spin interactions in organic LEDs, or can spins make OLEDs better?

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Spin-spin interactions in organic light-emitting diodes (OLEDs) based on thermally activated delayed fluorescence (TADF) are of central importance, as radiative recombination is largely determined by triplet-to-singlet up-conversion, also called reverse intersystem crossing (RISC). This process is thermally activated and can be investigated by spin sensitive techniques such as electroluminescence detected magnetic resonance (ELDMR). The idea behind these experiments is that the static magnetic field applied to devices modifies only the energy levels of triplet states due to Zeeman splitting, thus changing the emission rates. We observed that resonant microwave radiation, applied to OLEDs by a stripline, led to an increase in electroluminescence. Crucially, the triplet exciplex states in OLEDs are highly spin-polarized and the characteristic spin-lattice relaxation T_1 time far exceeds the RISC time. We conclude that slow spin relaxation, rather than RISC, is an efficiency-limiting step for intermolecular donor-acceptor TADF systems[1].

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Intrinsic Visible Light Emission of Aggregated Non-Conjugated Organic Molecules - a Critical Analysis

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In the past few years, increasing attention has been paid to so-called 'non-conventional¡ emission phenomena, i.e. visible light emission arising from aggregated non-conjugated all-organic molecules.[1] This includes inter alia macromolecules like non-aromatic polymers and proteins as well as polypeptids and sugars, and even simple structures like imines and nitriles, imides, siloxanes, alcohols, boric acid or halogenated hydrocarbons. Furthermore, small π-conjugated molecules (like benzene, acroleine) are considered, which do not absorb and emit in the visible, but are suggested to do so upon cluster formation,[2] or hyper-conjugation when incorporated into non-conjugated polymers.[3]

Despite the multitude of reports, many of the research papers and reviews within this community stay rather phenomenological in their description. Scientific hypotheses on the specific electronic conditions of the constituting non-conjugated molecules remain often diffuse, and miss a systematic classification and rationalization based on the underlying electronic nature of the emitting electronic states. Similarly, the intermolecular interactions upon aggregation, which are supposed to drive further spectral shifts towards the visible region as well as the proposed luminescence enhancement stay rather descriptive. Terms like ‚through-space conjugation' and ‚clusterization' appear without proper contextualization with well-established concepts developed in the last century. Finally, alternative hypotheses, which may apply for some of the observations, like trapping by contaminations are hardly considered in this community.

To overcome the fragmentation of the field and to forge a link between the materials' community dedicated to non-conventional PL with the photophysics/-chemistry field with their well-established terminology and concepts, we undertake in the following a simple systematic classification of non-conjugated molecules with respect to the nature of the lowest excited state based on electronic structure considerations. This will be used to identify those fluorogenic functional groups, which are predestined to emit PL in the visible (or the near UV) already in the vapor phase or in solution under certain conditions, and which are in fact overseen in this community.

This will provide a distinctive criterion on the question what is specifically 'aggregation-induced' when we then turn to interacting fluorogenic functional groups in a systematic manner, identifying suitable candidates to show visible light emission, while excluding others. We will then finally discuss how exciton migration and disorder may assist or inhibit effective visible light emission in such aggregates.

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Physics of cell membrane opto-stimulation

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The overarching goal of our research is to manipulate the light-bio-matter interaction to obtain control over the functioning of living systems. Light can control cell activity, with high space and time resolution and a virtually infinite number of configurations, free from wiring constrains. We develop and study non-genetic cell opto-stimulation techniques based on artificial light actuators that establish functional abiotic-biotic interfaces able to transduce a light signal into a biological stimulus. This talk reports on the state of our research regarding organic bio interfaces for inducing light sensitivity in cells, both in vitro and in vivo. Light actuators comes in different shapes: planar patches, nanoparticle, intra-membrane probes. Their coupling mechanism is still far from being understood and attempts to shed light will be introduced. The research aims at a new technological platform for application in life enhancing technologies or new cyborg technologies. One of the most appealing application of this emerging technology is rescue vision in blind people.

Tailoring electronic structure of SWCNTs for optoelectronic applications

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Single-walled carbon nanotubes (SWCNTs) are among the strongest candidates for the replacement of commonly used transparent and conductive films (TCFs) based on doped metal oxides, such as indium tin oxide. SWCNTs possess unique multifunctional nature, which is based on their outstanding combination of mechanical strength and flexibility, chemical stability, exceptional electrical conductivity and optical properties. However, to fully utilize these properties in modern transparent electrode applications, SWCNT-based TCFs have to demonstrate the optoelectronic performance at the level of high-end ITO-based TCFs.

Using gold chloride as the most effective dopant for the SWCNTs, we improve their optoelectrical characteristics by optimizing the doping solvent and conditions. We examined various solvents to push the optoelectrical performance of the TFCs based on SWCNTs. As a result, we obtained the sheet resistance as low as 40 Ω/□ at the transmittance of 90% (at 550 nm) using 15 mM $HAuCl_4$ solution. This optoelectrical performance is better than that of ITO on PET substrates and satisfy most of the requirements for modern applications and relatively stable without additional protection over two years storing under ambient conditions. We propose a few interesting novel methods for SWCNT doping: aerosol doping and dip-coating methods will be discussed. Also, we propose a novel approach to enhance optoelectronic performance of SWCNTs using ionic liquid. The method provides fine and reversible tuning of optoelectrical properties of SWCNT films over a wide range of parameters. Using imidazolium-based ionic liquid with a wide electrochemical window ($BMIM\text{-}PF_6$), we achieved the film sheet resistance as low as 53 Ω/sq at the 90% transmittance, thereby shifting the SWCNT Fermi level up to 1.4 eV. We believe the results to promote collateral research of adjustable tuning of the electronic structure of carbon nanomaterials as promising components for future electronics, electrochromic devices, and ionotronics.

Although carbon nanotubes have been already demonstrated to be a promising material for bolometric photodetectors, the sensitivity enhancement while maintaining the speed of operation remains a great challenge. Treatment of carbon nanotube films with low frequency oxygen plasma allows fine tuning of electronic properties of the material. The temperature coefficient of resistance of our films is much greater than reported values for pristine carbon nanotubes, up to -2.8% K^{-1} at liquid nitrogen temperature. The bolometer prototypes made of the treated films demonstrate high sensitivity in a wide IR range, short response time, smooth spectral characteristics and low noise level.

And finally, we develop a novel transparent p-type flexible electrode based on SWCNTs combined with poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), molybdenum oxide and SWCNT fibers. We achieved a record equivalent sheet resistance of 17 Ω/sq with a transmittance of 90% at 550 nm and a high degree of flexibility. We demonstrate that our solar cells based on the proposed electrode and hydrogenated amorphous silicon (a-Si:H) yield an outstanding short-circuit current density of $J_{sc} = 15.03$ mA/cm^2 and a record power conversion efficiency of PCE = 8.8% for SWCNTs/a-Si:H hybrid solar cells.

This work was supported by the Russian Science Foundation (Project identifier: 22-13-00436) and RFBR (project number: 20-03-00804). A.G.N. thanks the Council on grants of the President of the Russian Federation grant number НШ-1330.2022.1.3.

Fluorescence nanoscopy as a tool for solid state physics and material science

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This tutorial lecture overviews history, main principles, advantages and perspectives of the scientific field of optical nanoscopy (superresolution fluorescence microscopy in terms of methods which use detection of multiple single label <quantum> emitters). We discuss experimental techniques for detection of single molecules in condensed matter, and quantum emitters in general (semiconductor quantum dots, color centers in diamonds, perovskite particles), incl. at cryogenic temperatures. The recent studies of our group (www.single-molecule.ru) will be shown, including single-molecule nanoscopy for study low-temperature dynamics of disordered solids (polymers, glasses, molecular crystals - Shpol'skii matrixes). The microscopic nature of the blinking photoluminescence effect of single QDs, the results of studies of local field effects, as well as the processes of spectral diffusion and electron-phonon coupling in impurity polymer media with quantum dots and organic molecules are considered. The results of a comparative analysis with data obtained by other methods (photon echo, Raman scattering, electron microscopy) are presented. The capabilities of the three-dimensional (3D-) fluorescence nanoscopy technique implemented according to the scheme of the double-helix point spread function (DHPSF) with the use of adaptive optics tools are demonstrated[1,2,3,4,5].

The lecture presents the results obtained by the team of authors of the Leading Scientific School of Russia headed by RAS Corr. Memb. A.V. Naumov (NSh-776.2022.1.2*)*.

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Conjugation in organic molecules

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The active development of organic electronics and photonics leads to the search for new highly efficient functional organic materials possessing semiconducting, light emitting or light harvesting properties. A large number of works are devoted to the synthesis and study of novel π-conjugated molecules and their application in organic field-effect transistors, organic light-emitting diodes and transistors, solar cells and other devices. A wide variety of molecular structures of organic molecules leads to different conjugation pathways within the molecule, which influence their HOMO and LUMO levels, bandgap, and hence their optical and semiconducting properties. Liner-, cross- and omniconjugation introduced by J.C. Hummelen in 2004 not only lead to understanding the difference in optical properties of many conjugated molecules of various structure, but also allows to designing novel organic molecules with linear π-conjugated pathways between all the substituents[1].

In this lecture, several classes of organic molecules with different conjugation patterns, peculiarities in their synthesis, properties and application in organic electronic and photonic devices will be considered (Fig. 1). Branched molecules based on 1,3,5-substituted benzene theoretically considered by Hummelen as non-conjugated can be also described as meta-conjugated molecules with some peculiarities in conjugation[2]. Branched oligoarylsilanes were found to be non-conjugated as a whole molecule, leading to molecular antenna properties with ultrafast intramolecular energy transfer between their branches[3]. Donor-acceptor molecules based on triphenylamine were found to be fully conjugated with internal energy transfer leading to low bandgaps[4]. Changing molecular structure of such molecules allows tuning their optical properties for various optoelectronics devices, even for such exotic as full-colour artificial retinas[5].

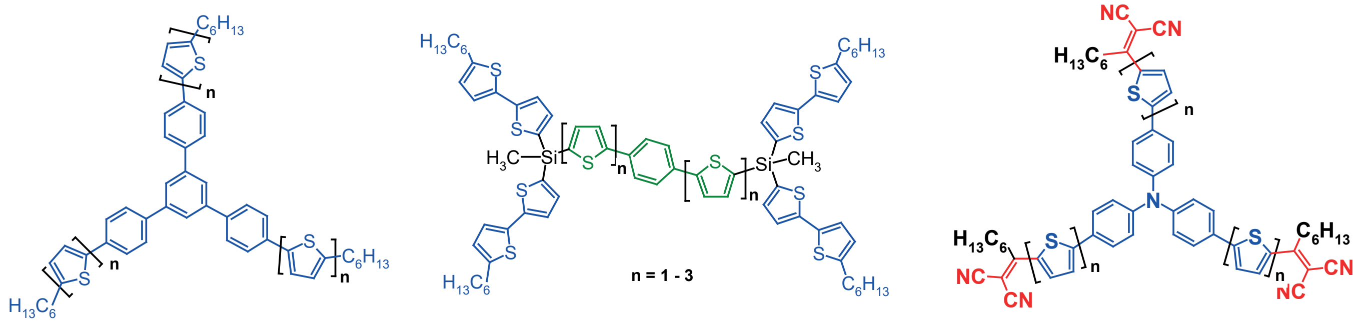

Fig. 1. Examples of π-conjugated molecules with different conjugation patterns

This work was supported by the Russian Science Foundation (grant 19-73-30028).

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Establishing structure/property interrelations of organic semiconductors using fast calorimetry

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Commercialization of differential scanning calorimetry (DSC) fifty years ago led to widespread use of calorimetric methods for thermal characterization. Modern DSC instruments can measure physical transitions, the kinetics of reactions, and other transformations quickly and easily. A material's glass transition temperature provides insights to its mechanical, chemical and thermodynamic properties. Measuring the glass transition temperature of many functional polymer systems is, however, often difficult due to varying molecular weights, dispersity, and low degree of crystallinity. Hence, traditional DSC methods are usually not sensitive enough to detect the heat response that reflect the material's glass transition. Fast scanning calorimetry (FSC) can measure at rates greater than 10,000 K/s, allowing for the measurement of isothermal crystallization and study of the formation of glasses. Some semi-crystalline polymers have reported glass transition temperatures that span 50 degrees Celsius or more. Knowledge of the 'true' glass transition, other important phase transitions and, e.g., their solidification kinetics can be obtained by measuring relaxation enthalpies with FSC. This method of quenching from the melt and isothermally aging the material provides a glass transition temperature that is not rate dependent and can provide information on the existence of mobile and rigid amorphous phases, all of which are important in material processing as well as in establishing relevant structure/property interrelations. We discuss how the FSC technique can be used for the identification of thermodynamic transitions of donor polymers (PCDTBT) and acceptor molecules (fullerene derivatives) commonly used in the organic solar cell area. Moreover, we provide examples how the change in glass transition temperature of PCDTBT can be tracked before and after UV-light curing. Other illustrations involve inorganic/organic hybrid materials of different crosslink densities and how this affects the glass transition of the final structures. Accordingly thermal analysis can be exploited to obtain important structural information of this new class of materials and, in turn, processing guidelines can be established towards materials of specific optical or electrical characteristics, and improved materials design for organic photovoltaic blends.

Towards understanding molecular structure – photostability relationships for design of new absorber materials for efficient and stable organic photovoltaics

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In the view of a rapid increase in efficiency of organic solar cells, reaching their long-term operational stability represents one of the main challenges to be addressed on the way toward commercialization of this photovoltaic technology. However, intrinsic degradation pathways occurring in organic solar cells under realistic operational conditions remain poorly understood.

In this report, we will discuss light-induced cross-linking of conjugated polymers and small molecules, including fullerene derivatives and non-fullerene acceptors (NFAs). A set of complementary techniques for studying light-induced aging of organic semiconductors under anoxic conditions will be presented. Intrinsic photostability of ~100 different organic materials will be compared and important correlations with the chemical composition and molecular structure will be drawn. Finally, we will introduce a prognostic model enabling a decent prediction of photostability of arbitrary chosen conjugated polymer structure considering the stability descriptors of the incorporated building blocks. The obtained results are expected to set the guidelines for rational design of new absorber materials for stable and efficient organic photovoltaics.

This work was supported by Russian Science Foundation (project 22-43-04427).

"Electronic nose": operation principle, manufacturing approaches and promising applications

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Smell is a vital function of human body, which is widely used in many industries. Unfortunately, organoleptic analysis by humans or specially trained animals is quite complex and expensive, so it is extremely important to replace the natural sense of smell with its artificial counterpart, the so-called «electronic nose». The electronic nose in most cases is an array of semi-selective gas sensors with different operating principles, supplemented by machine learning methods and artificial intelligence technologies.

The lecture will consider the main currently existing approaches to the creation of "electronic nose" devices, the types of sensors used in these devices and limitations preventing their wide implementation in the industry. A portable "electronic nose" based on an array of thin-film organic field-effect transistors with various receptor layers of metalloporphyrins will be presented. In combination with machine learning algorithms, the developed "electronic nose" allows not only detection of toxic gases in ultra-low concentrations, but also effective recognition them in a wide range of relative humidity up to 95%, including the possibility of quantitative determination[1]. In addition, using the developed device, we demonstrated the possibility of meat products spoilage detection at an early stage (Fig. 1), as well as the possibility of non-invasive express diagnostics of socially dangerous diseases transmitted by airborne droplets and associated with changes in metabolism, according to the analysis of the air exhaled by a person.

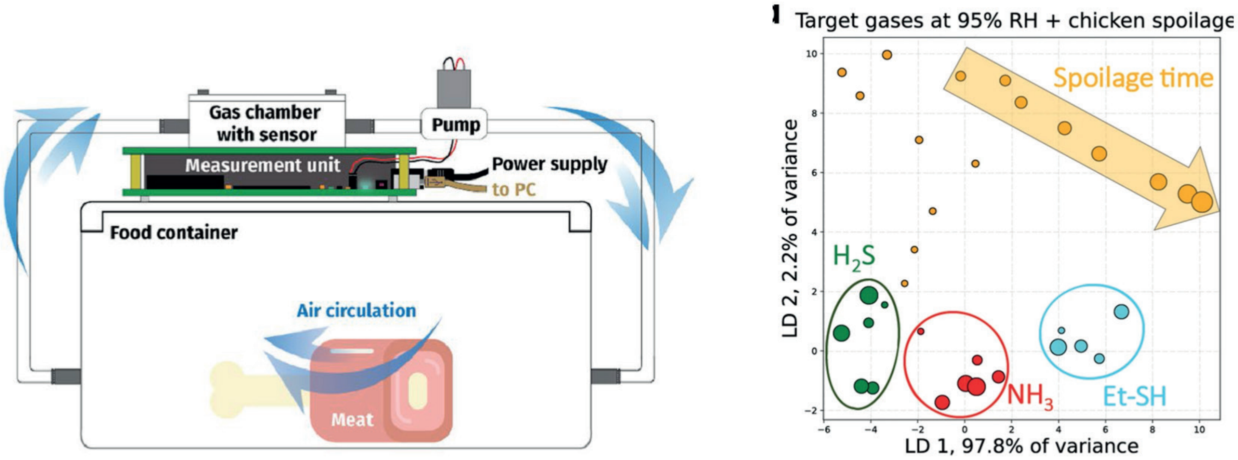

Figure 1 - Determination of food spoilage using an electronic nose

This work was supported by the Russian Science Foundation (project no. 19-73-30028).

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Simplified modeling of mesophases in semiconducting polymers: what can we learn?

K. Ch. Daoulas

Investigating structure-property relationships in semiconducting polymers on scales beyond several tens of nanometers with computer simulations requires simplified models. These descriptions achieve the necessary computational efficienciency by mapping large groups of actual atoms on single, effective, interaction centers. At the same time, although ultra coarse-grained models are standard for polymer physics, their implementation in semiconducting polymers might seem questionable. Indeed, drastic coarse-graining significantly simplifies the description of aromatic rings in the conjugated backbone and solubilizing side chains, i.e. reduces features that are crucial for the ordering of semiconducting polymers.

Yet ─ and this is one of the main ideas we aim to convey ─ the perspectives of simplified models are better than one might initially anticipate. One reason is that semiconducting polymers commonly exhibit pronounced structural disorder.[1] Even their crystalline phases have large Para crystallinity, whereas one often observes[1,2] only small-scale molecular aggregation and liquid-crystalline mesophases. This structural "noise", combined with the collective nature of ordering processes, might mitigate the reduction of microscopic details, rendering simplified models useful for addressing a certain spectrum of questions.

First, we will summarize some simplified models used in generic studies of polymer order, crystallization in particular. We will argue why these approaches are insufficient for polymeric semiconductors and highlight several simplified models that have been developed in the literature specifically for these materials. Next, we will focus on an approach[3,4] where near crystalline, sanidic, mesophases are described by combining a minimalistic representation of polymer architecture with generic anisotropic potentials. As an application, we will present our new results obtained in studies of texture of P3HT films,[5] where face-on and edge-on orientation of crystalline lamellae is favored at the bottom and top surface, respectively. Our results highlight the need for understanding the elastic properties of highly ordered, almost crystalline, mesophases of conjugated polymers.

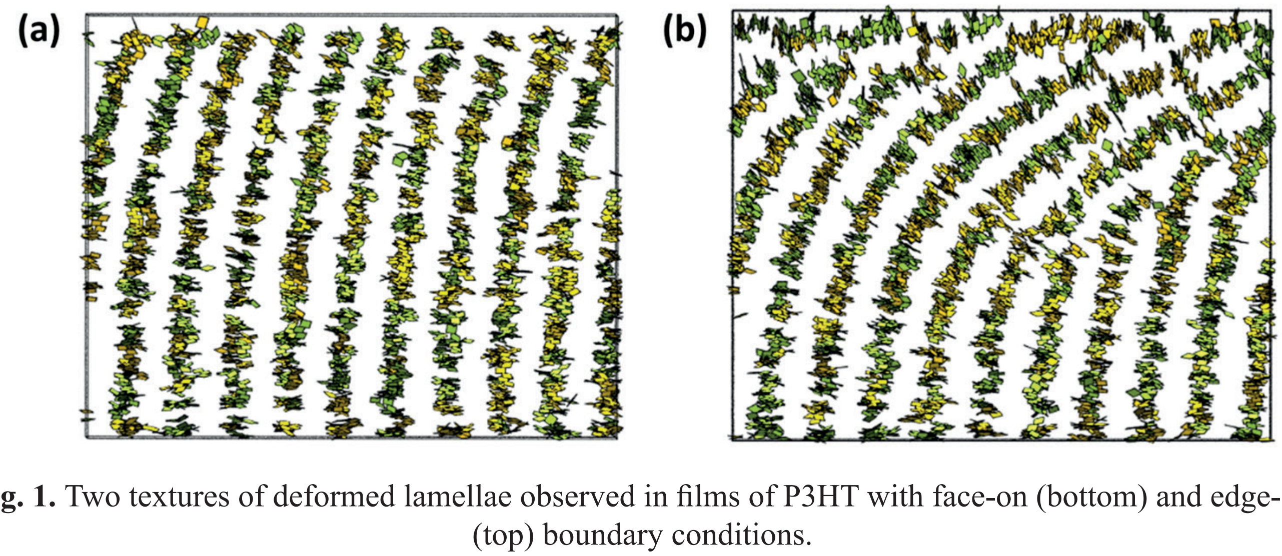

Fig. 1. Two textures of deformed lamellae observed in films of P3HT with face-on (bottom) and edge-on (top) boundary conditions.

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Doping of emissive organic semiconductor single crystals

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Organic light-emitting semiconductors are highly demanded in optoelectronics for application in light-emitting diodes, transistors and lasers.[1] The most prospective conjugated small molecules in organic optoelectronics attracting a reasonable attention include: oligothiophenes, distyrylbenzenes, thiophene-phenylene co-oligomers (TPCOs), oligofurans, furan-phenylene co-oligomers, and acene derivatives. To fine-tune their optoelectronic properties a number of approaches were exploited: variation of molecular backbone length and heterocycle composition, introduction of terminal substituents, polymorphism, specific crystallization and molecular doping. The latter is indispensable strategy for tuning of energy bandgap, charge transport, luminescence color and efficiency. However, the rational molecular design of doped semiconductor crystals is still not fully understood.

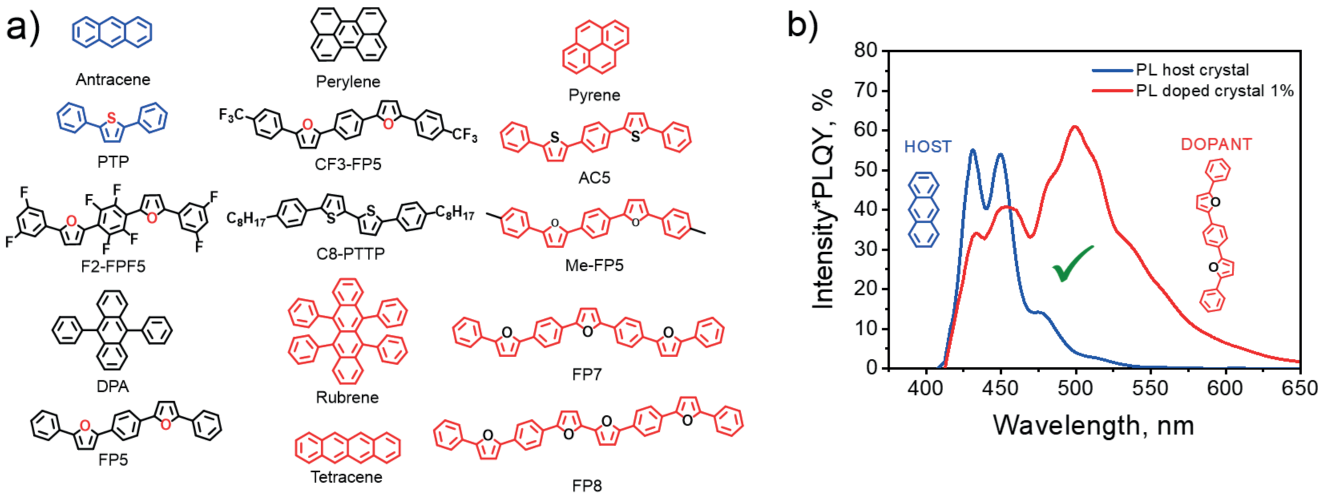

Fig. 1. a) Chemical structures of studied host-guest systems (the blue (red) color demonstrate materials used as host (guest) only) b) PL spectra of anthracene crystals doped by1,4-bis(5-phenylfuran-2-yl)benzene.

Here we discuss the molecular self-doping approach[2,3] allowing one to optimize the dopant concentration and control the optoelectronic properties without the needs of a dopant separate synthesis and specific purifications of host materials.[4] We also report the systematic study and literature analysis of the molecular host-guest doping of organic semiconductor single crystals of strategical importance in organic optoelectronics (Fig. 1) to rationalize the *molecular* host-dopant compatibility criteria in a series of luminescent linear symmetric conjugated molecules.[5]

This work was supported by RSF (project № 20-73-10090).

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Development of organic solar cells based on non-fullerene acceptors: materials to devices

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Organic solar cells (OSCs) have attracted considerable scientific and technological interest compared to conventional PV technologies based on traditional inorganic semiconductors, since printed, inexpensive, and mechanically flexible OSC modules can be fabricated on plastic substrates at low temperatures using less capital intensive, high throughput roll-to-roll solution-process methodologies such as slot-dye, bar coating, and gravure/flexo printing. Nowadays, non-fullerene OSCs are a major focus of the research in that field. Recent developments of novel non-fullerene acceptors (NFAs) led to a surge in PCE of OSCs with values approaching 20%[1,2]. NFAs have several advantages over their fullerene counterparts amon which the most impotrant is posibiity to tune morphology and electronic properties. In addition, the optical bandgap can be modified to broaden the absorption range. Due to the intensive development of NFAs, the search for new suitable donor materials for them has become an urgent task as well[3]. This lecture provides a short historical context for the development OSCs based on NFAs, and also addresses current thinking in these areas plus considers important manufacturability criteria as well as recent experimental results in this field.

The work was supported by the Russian Science Foundation (grant №19-73-10198).

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Using intermolecular interactions for suppression of dynamic disorder in organic semiconductors: insights from Raman spectroscopy and quantum-chemical simulations

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Efficient operation of organic electronic devices requires high charge-carrier mobilities in their active layers. It is now commonly assumed that charge transport in high-mobility organic semiconductor crystals (OSCs) is considerably hindered by the dynamic disorder induced by low-frequency vibrations, which results in fluctuations of charge transfer integrals. Hence, reducing this disorder is highly desirable. However, experimental technique for probing the dynamic disorder, as well as strategies for suppression of the latter were lacking for a long time.

In this talk, I present our results concerning the two abovementioned issues. I start with the description of our recently advanced means for assessment of the dynamic disorder using the low-frequency Raman spectroscopy. Using this approach, we show that the dynamic disorder can be significantly reduced via strengthening the intermolecular interactions between the adjacent molecules, e.g., by introducing the electronegative atoms.

The revealed feasibility of suppression the dynamic disorder via tuning the intermolecular interactions is then analyzed using the quantum-chemical calculations. Specifically, we show that the quantitative measure of the dynamic disorder in OSCs – relative variance of the charge transfer integrals between the molecules – is indeed inversely proportional to the energy of the intermolecular interactions, making strengthening of these interactions a promising way for reducing the dynamic disorder, in line with the Raman-based data. Thus, our results pave the way for both the experimental search and rational design of OSCs with weak dynamic disorder and high charge mobility.

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White OLED structures for display applications.

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In this time trends of OLED structures for information displays have active growth. Modern OLED displays have resolution up to 4K of full color screen and wide scale of diagonal. This device replace most traditional type of information displays like LCD and other.

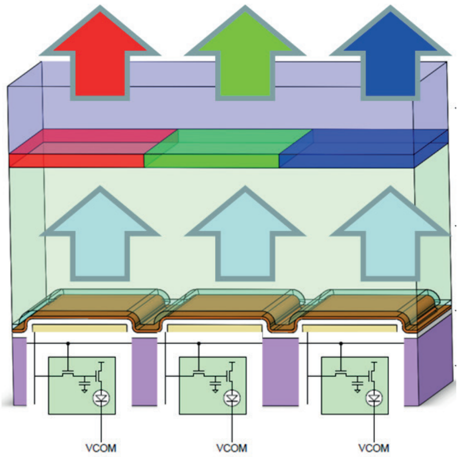

Fig. 1. Full color display pixel based on initial white OLED and RGB filter matrix.

This presentation introduced base construction of full color active-matrix OLED displays and method of forming color image by filter matrix. Most OLED displays productions usually apply wafer with active-matrix (AM) scheme. Each pixels of full color screen consist on three (RGB) subpixels controlling independently and luminance ratio of each other determine the color balance in all grayscale level. By the AM realized function of write and memory luminance level of all pixels (subpixels) during frame time.

Electrical, photometrical and spectral characteristics of initial white OLED structures was represented as well as modeling of RGB color separation and factors affecting color balance of full color image.

Copolyfluorenes with effective white electroluminescence

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Scientific and methodological approaches to the synthesis of copolyfluorenes that allow one to control their molecular weight, photoluminescent and electroluminescent properties for use in organic light emitting diodes (OLEDs) are developed. The purpose of this work was to develop and optimize methods for the synthesis of new copolyfluorenes with high electroluminescent properties and white emission color. To this aim, it was necessary to combine blue, green, and red luminophore groups in one polymer. In order to determine optimal compositions of these multi-luminophore copolymers, single-luminophore copolyfluorenes with only one type of luminophore groups were initially synthesized, and mixtures of these copolymers were prepared. Then, the weight fractions of these single-luminophore copolymers, providing white emission of polymer layers cast from their mixtures, were found and converted to molar ratios of all luminophore groups in the multi-luminophore copolymers.

It is shown that the way of introducing luminophore groups into copolyfluorenes strongly affects their electroluminescence characteristics. Thus, the copolyfluorene with 4-N-cyclohexylamine-1,8-naphthalimide green luminophore attached to the position 9 of the carbazole group in the polymer backbone via hexamethylene spacer (Fig. 1) has extremely high electroluminescence intensity but its color is not purely white although rather close to it,

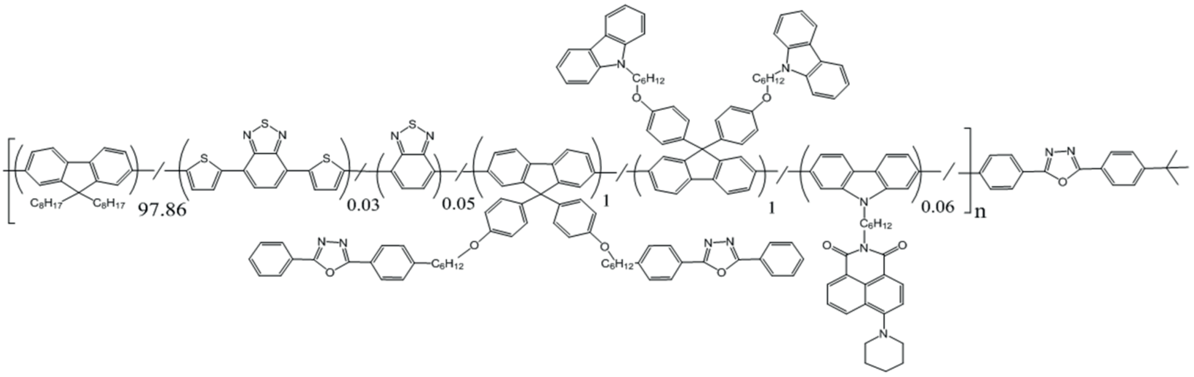

Fig. 1. The copolyfluorene structure providing the highest electroluminescence intensity (brightness 40600 cd/m^2, light efficiency 4.74 lm/W, CIE coordinates 0,343; 0,467)

while the copolyfluorene in which this luminophore is attached rigidly to the carbazole fragment (Fig. 2) has almost ideal white electroluminescence but its brightness is not so high.

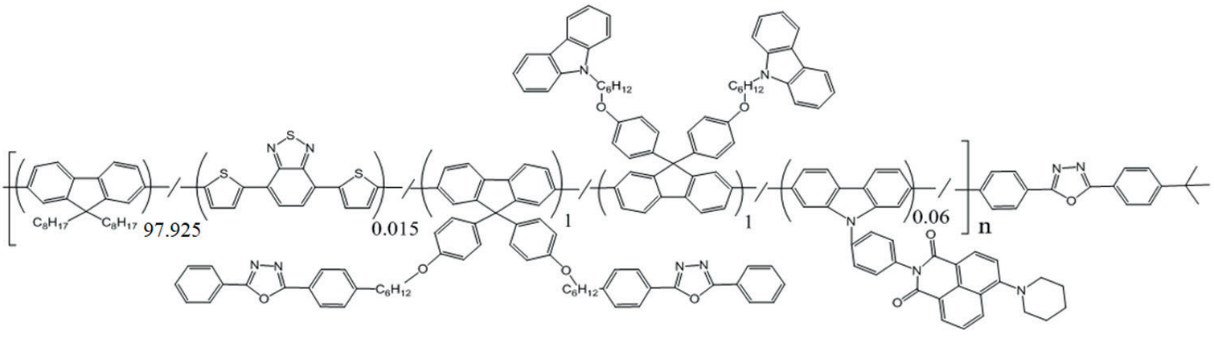

Fig. 2. The copolyfluorene structure with almost ideal white electroluminescence ((brightness 2650 cd/m^2, light efficiency 1.13 lm/W CIE coordinates 0,326; 0,345)

A concept of embedded dipole and its implications

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Self-assembled monolayers (SAMs) are frequently used for interface engineering in organic electronic and photovoltaic devices. The major goal of this approach is energy level alignment between the adjacent layers, e.g. the metal electrodes and organic semiconductor in field-effect transistors. For this purpose, SAMs are usually decorated with polar tail groups, which, however, not only optimize the energy level alignment but also affect the morphology of the adjacent layer. Alternatively, a polar tail group can be embedded into the molecular backbone, decoupling the electrostatic engineering and surface chemistry. In this context, we designed several novel monomolecular interlayers with embedded dipolar groups. As an example of potential usefulness of this novel class of films in organic electronics, their application in organic thin film transistors was demonstrated, resulting in decrease of the contact resistance by ca. three orders of magnitude accompanied by significant improvement in the performance and stability of the devices. The high potential of these transistors was highlighted by fabrication of functional electric circuits of their basis. In addition, beyond the usefulness for application, SAMs with embedded dipolar groups represent a versatile testbed for fundamental research, extending, in particular, our understanding of X-ray photoelectron spectroscopy beyond the standard concept of ´chemical shift´ and making it a versatile tool to study morphology and organization of polar monomolecular films[1,2,3,4,5,6].

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New organic luminophores based on 2,1,3-benzothiadiazole for organic electronics and photonics

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Various organic luminophores are widely used in science and technology. At the same time, one of the main directions of the development of chemical science is the creation of materials with specified properties. Understanding the basic patterns of structure-properties for various classes of compounds allows you to significantly reduce research work on the creation of new materials, and thereby reduce their cost. Therefore, the main scientific problem of this work is to identify patterns of structure-properties for new organic luminophores containing 2,1,3-benzothiadiazole fragment, and to assess the possibility of practical application of new molecules in organic electronics and photonics.

Benzothiadiazole is one of the most widely used acceptor moieties in low band gap materials for organic electronic applications. Motivation for incorporation of this heterocyclic unit into luminophores is its high absorption coefficient and luminescent quantum yield, large Stocks shift, low bandgap and excellent thermal stability. A large library of linear luminophores containing 2,1,3-benzothiadiazole fragment was synthesized.[1,2,3] The optical and thermal properties of the new compounds have been studied.

Recently we have developed a new class of highly efficient luminescent materials with unique properties - nanostructured organosilicon luminophores (NOLs).[4] These are branched molecules, where two types of organic chromophores are connected to each other via silicon atoms, which brake the conjugation between them and fix them specifically in the space at 1-2 nm distance necessary for efficient Förster energy transfer. NOLs possess several advantages: absorption in a wide optical spectral region; 5–10 times higher absorption cross-sections than those of the best low molar weight organic luminophores; very high photoluminescence quantum yield; luminescence spectra in the defined wavelength region; short luminescence lifetime. Thus, we synthesized a series of new NOLs containing benzothiadiazole unit, investigated their optical and thermal properties. The new NOLs obtained were used in various devices of organic photonics and electronics, such as plastic scintillators, spectral shifting fibers, organic light-emitting diodes (OLEDs), organic solar cells (OSCs) and others.

This work was supported by Russian Science Foundation (grants № 22-13-00255).

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Fibers Based on Carbon Nanotubes as a Perspective Instrument for Wearable Electronics

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Nowadays wearable electronics and smart devices, which are in direct contact with the human skin surface for the tracking of such vital signals as heart rate, arterial pressure, body temperature, *etc.,* are becoming essential tools for the preventive, personalized medicine and every-day human practices for well-being[1]. The more progressive technologies based on the recently developed flexible and stretchable devices target sensing more advanced parameters. As such, they help to identify some abnormal states, for example stress, diabetes, *etc.*, which are related to the levels of so crucial biological markers as cortisol, glucose, lactic acid, and others bio-molecules presented in sweat. Materials for wearable electronics applications should have a set of specific properties in order to provide users with stable and reliable physiological signals. Carbon nanotube fibers (CNTFs) satisfy all of the needed requirements: flexibility, reasonable stretchability, chemical inertness and stability. Besides, CNTFs geometry reminds those of regular yarns used in textile, so the design of devices based on CNTFs may be well-adapted in modern industrial protocols[2]. Despite the above-mentioned facts, electrical properties of the material are the point for improvement due to the still deficient interfacial contacts between individual elements, or carbon nanotubes.

Thus, in our work, we used the recently developed straightforward wet pulling approach for CNTFs manufacturing and evaluated how to improve the fibers' electrical properties through the various strategies directed to facilitate the electronic transfer[3]. The first approach is based on the densification of CNTFs occurring through a solvent evaporation and application of the mechanical forces, or twisting. By the twisting degree verification, we were able to monitor CNTFs structure-electrical properties and reach nearly the maximum electrical performance; 3990 S cm^{-1} for the twisted ones compared to the wet pulled fibers showing 278 – 748 S cm^{-1}. Besides, through the twisting procedure we have almost eliminated macro-structural defects such as holes and pores that resulted in formation of fibers with a higher quality and a tighter packing. Another strategy to improve fibers' electrical characteristics is based on the well-known doping effect and decoration procedure using $HAuCl_4$ dopant. By the combination of the several strategies, specifically densification, doping and gold in-twisting techniques, we were able to reach 8459 S cm^{-1} that is comparable with the previously reported for CNTFs made by other methods. As the main outcome of our work, to the best of our knowledge, this is the first presentation of the various strategies' combinations to improve the electrical performance of the wet pulled CNTFs which examines both fibers electrical behavior and morphology.

This research was supported by grant of the Russian Science Foundation № 21-73-10288, https://rscf.ru/en/project/21-73-10288/.

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Synthesis and properties of new polymeric hole-transporting materials based on triphenylamine

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Currently, the development of organic hole-transport materials that can be used in various optoelectronic devices, such as organic field-effect transistors, solar cells, and light-emitting diodes, is of great interest. Compared to their inorganic counterparts, organic hole-transport materials are soluble, film-forming, environmentally friendly, and have the ability to fine-tune their physicochemical properties through molecular design[1].

Such materials are π-conjugated polymers based on triphenylamine[2]. In addition to the presence of hole conductivity, such compounds are usually thermally stable, have high glass transition temperatures, and the amorphous structure of TFA polymers makes them soluble in various organic solvents and contributes to the appearance of good film-forming properties. The synthesis of polymers based on TFA with a donor-acceptor (D-A) structure makes it possible to control the energy of molecular orbitals, the values of the band gap, and the maxima of the absorption and emission spectra.

In this work, we present the synthesis of new polymers based on TPA D-A structures. The molecular weight characteristics of polymers have been studied, and the results of a comprehensive study of their optical, electrochemical, and thermal properties have been presented.

In this work, we present the synthesis of new polymers based on TPA D-A structures[3]. The polymers contain various acceptor groups in their structure and are distinguished by the presence of a thiophene π-spacer. The molecular weight characteristics of polymers have been studied, and the results of a comprehensive study of their optical, electrochemical, and thermal properties have been presented.

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Synthesis and properties of liquid π-conjugated luminescent oligomers with terminal solubilizing groups

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Liquid organic luminophores prepared by covalently attaching bulky, flexible, and low-melting side chains at the periphery of π-conjugated luminophores are a relatively new and class of materials, which have high processability owing to their fluidic nature and efficient fluorescence in pristine state[1]. However, the structure-property relationships of such compounds remain poorly understood. In addition, they exhibit luminescence in a limited short-wavelength region of the spectrum. The introduction of electron-withdrawing units and solubilizing groups of various nature into these molecules allows fine-tuning of the properties of the obtained materials. The absence of aggregation and the need to use solvents increases the manufacturability and environmental friendliness of the processes of manufacturing devices based on such functional materials and opens new areas of their application, such as emitting inks, OLEDs, electrets, scintillators and ect.

In the course of this work, oligomers based on 2,2’-biphenyl-4,4’-diylthiophene with linear and branched alkyl, trialkylsilyl and alkyloligodimethylsiloxane solubilizing groups were synthesized to study the influence of the type, length and branching degree of solubilizing groups on thermal stability, aggregate state, phase behaviour, rheology and optical properties[2]. When the most effective solubilizing group for liquefaction was identifying, the series of novel liquid benzothiadiazole-based luminophores containing phenylene or thiophene units with terminal trihexylsilyl groups on each side of the central core were synthesized. The high purity and specified structure of all the compounds obtained was proved by a complex of modern research methods. The influence of the nature, length and branching of the solubilizing groups and type of π-conjugated core on the optical properties, rheology, phase behavior and thermal stability of luminophores has been studied. Based on this study, the most suitable group was selected to reduce aggregation in a condensed state, using which new liquid luminophores of oligomeric structure were obtained, emitting light in various ranges of the visible spectrum. Some of the obtained oligomers were tested as scintillation detectors. Due to the high concentration of active phosphor fragments per unit volume in such materials, which cannot be achieved by preparing a simple solution based on them, and the relatively high fluorescence quantum yield in the block (45 - 75%), effective scintillators based on these oligomers were created.

This work was supported by the Russian Foundation for Basic Research (grant № 18-33-20224).

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A handy laboratory tool for spring-roll actuator assembly

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A multilayer configuration of DEA where the coated DE film is rolled around a spring core is called spring-roll actuator. To increase Maxwell's electrostatic forces that cause actuation, the DE film may be pre-stretched. As a result, voltage activation converts the planar expansion of the DE film into linear movement in the axial direction. Thus, spring-roll actuator, upon utilizing basic in-plane expansion, exploits the desirable features of elastomers such as the monolithic structure, flexibility, and multi-functionality. A fundamental challenge in developing robots is the creation of effective actuators to deform a soft body to achieve locomotion, manipulation, or other tasks. To date, only a few research groups[1, 2] tackled this challenge through spring-roll actuators because of the complexity of the fabrication process.

Herein we describe a simple tool for assembling DE wound spring-roll actuator including electrode deposition, coating and fabrication. To evaluate its performance as artificial muscle, we measured the free displacement of the loaded actuator at applied electric field. One end of the spring-roll actuator was held fixed and a 1 kg hanging weight was attached to the other end. At the applied voltage of 2 kV, equivalent to 90 V/µm electric field, the hanging weight was displaced by 2 mm. The latter corresponds to an axial strain of 6 %.

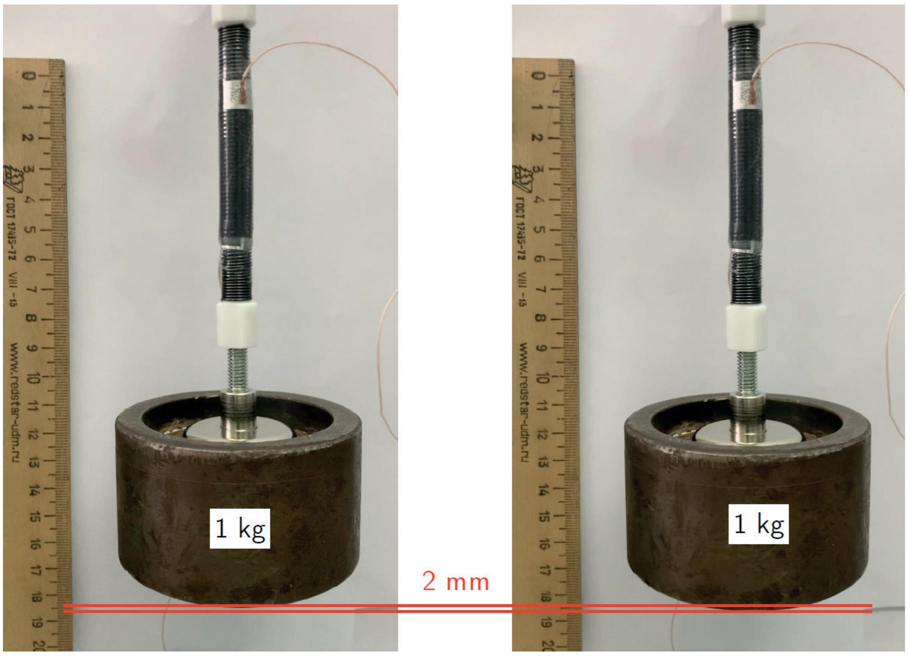

Fig. 1. Spring-roll actuator attached to a 1 kg weight without electrical power applied (*left*). The actuator is 52 mm long and weighs 5 g. The same actuator powered to 2 kV displacing the weight by 2 mm.

This work was supported by RSF (project № 19-73-30028).

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The impact of coulomb interactions on OFET-mobility

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We have used kinetic Monte-Carlo Simulations of OFETs to study the impact of coulomb interaction between charge carriers on the transfer characteristic of OFETs. At high charge carrier density, i.e. high gate voltage, we find the coulomb interaction to result in a curved transfer characteristics. In order to correctly capture the Coulomb interaction in this case, the Coulomb potential must be considered over a wide range with a cut-off radius of at least 40 nm. The effect of the Coulomb interaction on the transfer characteristics is mitigated by any additional energetic disorder in the semiconductor. Thereby, the filling of the density of states at large energetic disorder and low temperature can partially compensate the effect due to the Coulomb interaction.

Spectrally selective single-component organic photodetectors based on donor-acceptor conjugated molecules

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Photodetectors based on organic materials are attractive due to their tunable spectral response, flexibility, ease of manufacturing and biocompatibility, so they can become the basis for creating an artificial human eye[1]. Therefore, the development of narrowband spectrally selective organic photodetectors is of increased interest. One of the approaches to the creation of narrowband photodetectors is the use of a photoactive layer of a single donor-acceptor material with a narrow absorption spectrum, in which effective charge generation can occur. Single-component organic photodetectors also attract attention for their simplicity, especially in light of their possible biological applications. Donor-acceptor (D-A) conjugated molecules are among the most promising architectures for use as a photoactive material in organic solar cells and photodetectors. The wide possibilities of variation of the chemical structure of D-A conjugated molecules allow fine-tuning the properties of the materials obtained[2,3]. Materials with a suitable optical absorption spectrum and sufficiently high efficiency in single-component solar cells were selected from a huge library of previously synthesized molecules. Based on the most promising materials (Fig. 1), prototypes of single-component organic photodetectors were fabricated and characterized. These photodetectors demonstrated a sufficiently high responsivity and spectral selectivity comparable to those of cones and rods of the human eye. It has been shown that the response time of photodetectors based on the selected semiconductors is three orders of magnitude lower than the response time of photoreceptors in the human eye. The results obtained demonstrate the possibility of creating an artificial eye - a matrix of organic photodetectors with different spectral sensitivity, or photoactive “prostheses” for an eye devoid of sensitivity to light due to certain diseases.

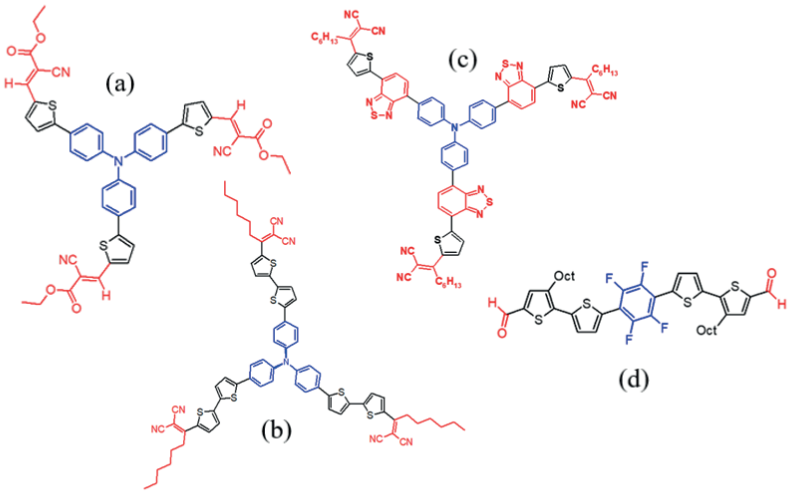

Fig. 1. Chemical structures of molecules that mimic human photoreceptors: a) rods, b) green-sensitive cones, c) red-sensitive cones and d) blue-sensitive cones.

This work was supported by Russian Science Foundation (grant number 19-73-30028).

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Petroporphyrins in small-molecule-based photovoltaics

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Complexes of etioporphyrin, EP with transition metals are present in noticeable quantities in heavy oils and bitumen deposits. Their laboratory synthesis yields molecules with a certain substitution type (see, Fig. 1), whereas not all possible I-IV isomers exist in nature[1]. Due to good heat resistance from one hand, and poor solubility from the other, the most suitable method for depositing thin films of EPs is vacuum thermal evaporation, VTE.

As shown recently[2], even such a minor alteration in molecular structure as peripheral regio-isomerism leads to remarkable difference in the morphology of VTE films, especially those grown on a hot substrate. The specific aggregation patterns could potentially be useful in organic electronics applications, *e.g.* photoconductivity in the hot-grown films increases by 2 orders of magnitude or more.

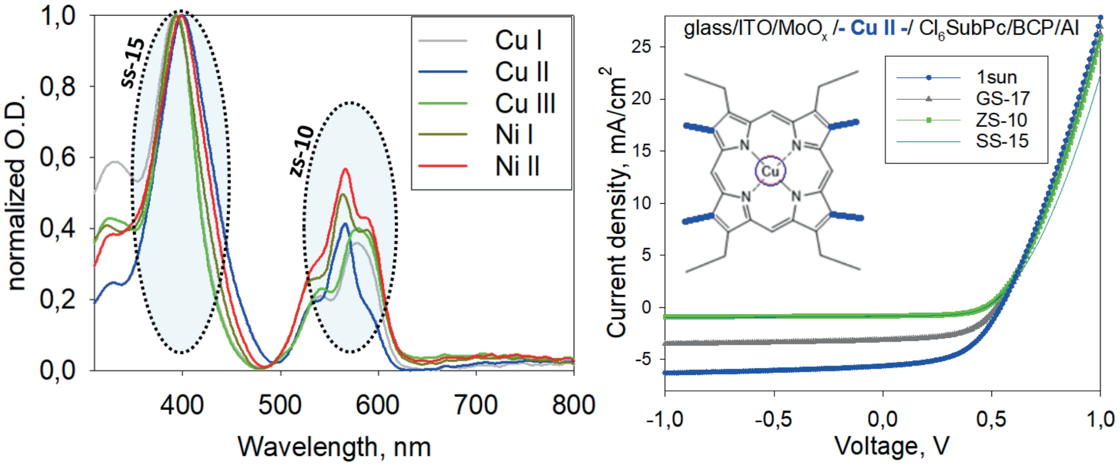

Fig. 1. Absorption profiles of the devices employing planar heterojunction with metal-EPs (left panel, w/o top electrode) and *J-V* characteristics under continuous 1sun or filtered illumination (right panel, II isomer of Cu-EP as donor)

A series of archetypal photovoltaic cells was tested, where EP-I,II,III isomers of Cu^{II} or Ni^{II} were paired with a small-molecule acceptor, hexachloro-subphthalocyanine Cl_6SubPc in a planar heterojunction. These cells were completely fabricated in the VTE process including both anode and cathode buffer layers. Depending on the complex type and measurement setup, the power conversion efficiencies ranging from 0.56 to 3.5% were obtained.

A distinct feature of such cells is a discontinuous absorption in the visible, as shown in Fig.1. This originates from the narrow-band excitation spectra of small-molecule photoabsorbers forming D/A junction, both of which have typically porphyrinoid *B*- and *Q*- bands in almost identical positions. The use of narrow-pass optical filters (Fig. 1) makes it possible to single out electronic transitions in the molecules or corresponding phases, thus highlighting integral contribution of excitons to the photocurrent. However, a portion of photons is lost when devices are illuminated by the sunlight, which limits their photovoltaic performance.

This work was supported by RSF (project № 20-13-00285).

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Synthesis and properties of new non-fullerene acceptors for organic photovoltaics

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Organic photovoltaics is an intensively developing area. Organic solar cells (OSCs) have received a lot of attention due to the potential for the production of lightweight and inexpensive flexible solar cells[1].

Already comparable to inorganic solar cell representatives, the high power conversion efficiency (PCE) reaches over 19% in non-fullerene bulk heterojunction (BHJ) photovoltaic devices[2,3]. This progress is largely due to the use of a new generation of acceptor materials - non-fullerene acceptors (NFA). The most effective NFA are conjugated compounds of donor-acceptor structure with a central condensed electron-donor fragment and terminal strong electron-withdrawing groups[1,4].

This work presents the synthesis of three novel non-fullerene acceptor molecules: BTPT-OD, BTPT-4F-OD, which are conjugated compounds of donor-acceptor structure with a central condensed electron-donor fragment and end strong electron-acceptor groups. The chemical structure of the compounds were proved by ^{1}H NMR, ^{13}C NMR techniques and by MALDI mass spectrometry analysis. The compounds are characterized by a high thermal and photo stability, efficient sunlight absorption in the red and near-infrared spectral ranges, good solubility combined with a high degree of crystallinity and possess appropriate energy levels of HOMO and LUMO levels to be used for OSCs. The photovoltaic data show, that contrary to predictions, the more complex fluorinated BTPT-4F-OD mixed with PM6 - donor material has a lower PCE (2.48%) than the fluorine-free BTPT-OD mixed with PM6 (4.30%). Besides in ternary OSCs, BTPT-OD, which has one of the simplest conjugated Y-series structures, in a mixture with PM6 and L8 achieves efficiencies up to 16.9%, which is comparable to the record values in this area.

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Electrolyte-gated organic field-effect transistors as biorecognition platform for biosensors

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For the healthcare system development, the progress in sensor technologies is increasingly important in applications such as biomolecules and viruses detection, medical diagnostics, environmental and food quality monitoring. Different types of biosensors based on various combinations of receptors (enzymes, antibodies, whole-cell, aptamers), transducers (electrochemical, electronic, optical, gravimetric, acoustic) and materials (nanoparticles, carbon nanotubes, quantum dots, dendrimers, polymers and oligomers) were reported, a lot of limitations, which hinder further development of the field and do not allow biosensors to invade the market, still remains. These limitations are associated with a number of requirements imposed to the biosensors: high selectivity and sensitivity, fast linear response, explicit accuracy of the results, reproducibility, stability, affordable manufacturing cost and user friendliness. Electrolyte gated organic field effect transistors (EGOFETs) are a promising platform for creating bioelectronic sensors.

A fast and simple technique based on Doctor Blade and Langmuir-Schaefer methods for functionalization of the semiconducting surface of C_8-BTBT-C_8 is reported, which allows fabricating large scale biorecognition layer based on novel functional derivative of BTBT containing biotin fragment in the structure with a huge area of sites for further biomodification. The proposed approach to a bioreceptor layer fabrication provides the possibility of creation of a universal streptavidin platform for further recognition bioevents by using of biotinylated aptamers or antibodies and viruses or some other biomaterials, which can bind to the biorecognition layer without significant altering the EGOFET properties. A specific response of created EGOFETs was demonstrated to a virus of influenza A. The elaborated approach to biorecognition layer formation allows fabricating several biosensors for various analytes on one substrate that paves the way to an "electronic tongue" creation.

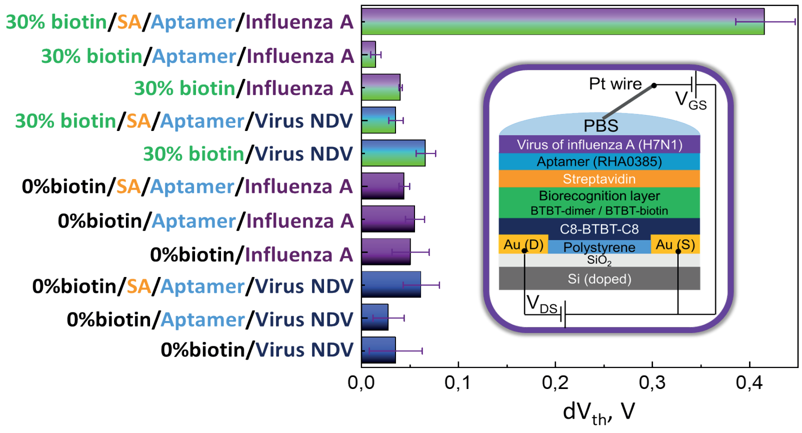

Fig. 1 Shift in threshold voltage of the fabricated EGOFET devices treated with different combinations of bioanalytes with the illustrated scheme of **BTBT-biotin**-based device with all deposited and sensing layers.

This work was supported by RSF (project № 19-73-30028).

Crystals of Diphenyl-Benzothiadiazole and its Derivatives: Growth, Structure, Phase behaviour and Spectral-Luminescent Properties

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N. I. Sorokina [1]***, O. V. Borshchev*** [2]***, M. S. Skorotetsky*** [2]***, E. A. Svidchenko*** [2]***, N. M. Surin*** [2]

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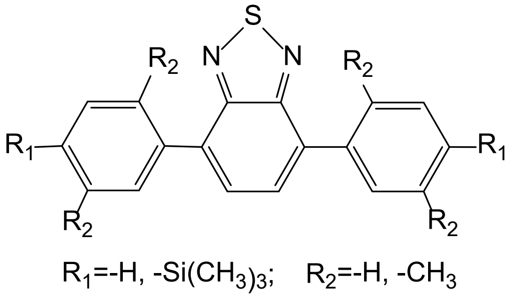
This paper presents a line of new 4,7-diphenyl-2,1,3-benzothiadiazole derivatives with terminal (-Si$(CH_3)_3$) and side (-CH_3) substituents (Fig. 1), which are effective luminophores. The solubility, growth from solutions, and the structure of crystals, as well as the parameters of phase transitions and the stability of materials upon heating, have been studied. For solutions in n-hexane, the absorption and luminescence spectra were studied, and the quantum yield and luminescence lifetimes were determined.



1a: R_1=-H, R_2=-H;
1b: R_1=-Si$(CH_3)_3$, R_2=-H;
2a: R_1=-H, R_2=-CH_3;
2b: R_1=-Si$(CH_3)_3$, R_2=-CH_3

Fig. 1. General chemical structural formula of the studied luminophores.

The synthesis and production of 4,7-diphenyl-benzothiadiazole derivatives were performed for the first time. The thermal properties of the crystals were studied in the temperature range from 293 to 523 K by the method of simultaneous thermal analysis on a STA Netzsch 449 F1 thermoanalytical complex in a dry argon flow. The melting parameters of the compounds have been established. Polymorphic transitions within the indicated temperature range were not revealed. The studies performed by DSC and TGA methods showed high stability of the compounds: the weight loss in the heating and cooling cycle does not exceed 3%, and melting peaks are reproduced during repeated thermal cycling. The solubility of compounds in *n*-hexane at 295 K was established by spectrophotometry. Crystals were grown from solutions in *n*-hexane by isothermal evaporation of the solvent at room temperature, as a result of which needle-like samples up to 10 mm long were obtained. The structure of single crystal samples was solved at temperatures of 293 and 85 K on an X-ray diffractometer XtaLABSynergy-DW, HyPix-Arc 150’ (RigakuOxfordDiffraction). The search for unit cells of the studied single crystals at 293 and 85 K ended with the choice of the following sp. gr.: **1a** - P-1 (Z=2), **1b** - P*naa* (Z=12), **2a** - $P2_1/n$ (Z=4), **2b** - $P2_1/c$ (Z=4). Polymorphic transitions with a decrease in temperature were not detected for the studied crystals. The optical spectra of solutions of the studied compounds have a similar structure. The presented luminophores are characterized by a large Stokes shift (103-106 nm), and the external quantum yield of luminescence in *n*-hexane solutions is about 80%. The luminescence lifetimes of the compounds in *n*-hexane solutions are in the range of 5÷7 ns. Thus, the presented compounds can be recommended as highly efficient optical emitters for photonic technologies.

This work was supported by RSF (project № 22-13-00255).

Flexible PVDF-based copolymers and terpolymers thin films- Dielectric and ferroelectric property study

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Ferroelectric high k-dielectric polymer thin film of Polyvinylidene difluoride (PVDF) copolymer (PVDF-TrFE) and terpolymer (PVDF-TrFE-CFE) were prepared using spin coating process on ITO coated PET substrates. The films were annealed in between glass transition and melting temperature. Annealed films cooled in two ways-i) Normally-cooling and ii) Fast-quenching, to study film crystallinity and ferroelectric property. Dielectric and leakage current property study of the prepared PVDF-TrFE and PVDF-TrFE-CFE thin film were done by making Metal/Insulator/Metal (MIM) device. MIM device was prepared by depositing aluminum electrodes of diameter 2 mm; 3 mm and 4 mm via thermal deposition on a 1 X 1 inch ITO coated PET substrates having ferroelectric polymer thin film as shown in Figure 1(a). The fast quenched PVDF-TrFE thin film shows higher dielectric constant and low leakage current compared to normal cooled PVDF-TrFE thin film. Similarly, dielectric properties was observed for normal-cooled and fast-quenched PVDF-TrFE-CFE thin films. For PVDF-TrFE, the fast quenched thin film shows higher remnant and saturation polarization at an applied electric field of 200 MV/m compared to normally cooled thin film as shown in Figure 1(b). Similarly, for PVDF-TrFE-CFE, the fast quenched thin film shows the better ferroelectric property as shown in Figure 1(c).[1, 2]

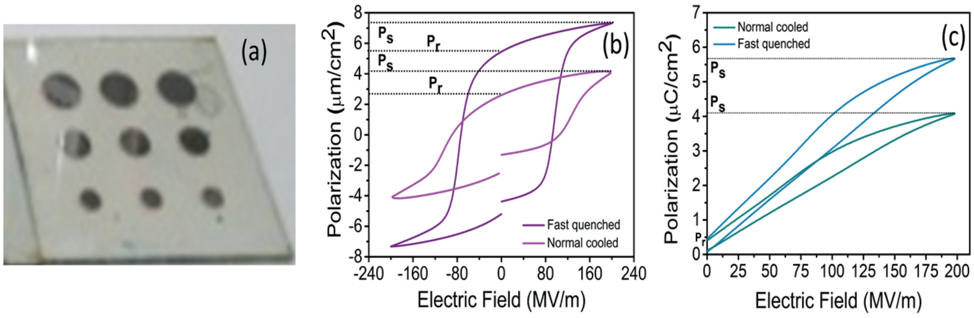

Fig. 1.(a) Shows the image of fabricated ferroelectric polymer based MIM capacitor, (b) Polarization Vs Electric Field (P-E) hysteresis loop of fast-quenched and normally-cooled P(VDF-TrFE) thin film and (c) Polarization Vs Electric Field (P-E) hysteresis loop of fast-quenched and normally-cooled P(VDF-TrFE-CFE) thin film.

This work was supported by SERB, India (project № PDF/2015/000111).

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Impact IGZO-thickness as electron-transport materials on J_{dark} of organic photodetectors with fullerene acceptors

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Organic π-conjugated molecules and polymeric macromolecules open up the new horizons for printed electronics offering wide functionality for optoelectronic devices. The integration of organic semiconductors into devices for detecting optical signals can change the classical concept of photodetectors applications[1]. Mixed indium-gallium-zinc oxide (InGaZnO, IGZO) has actively been researched for applications in the field of thin-film transistors. In this project, organic photodetectors were investigated using amorphous IGZO (a-IGZO) oxide as an electron transport layer. We used an inverted architecture (Fig. 1a) of organic photodiodes (OPDs) on a glass substrate with an ITO electrode: glass/ITO/ETL/PAL/HTL/Ag (ETL - electron transport layer, HTL - hole transport layer). Magnetron sputtered films of IGZO oxide (from a ceramic target of InGaZnO4 (In:Ga:Zn ¼ 1:1:1 at. %)) with thicknesses from 7 nm to 20 nm by were studied as ETL. The energy levels of a-IGZO (LUMO- 4.2 eV and HOMO - 7.5 eV), large band gap of 3.05–3.2 eV, high transmittance (>80%) in the visible wavelength range make it favorable for application as ETL. We used PCBM-based photoactive layer (Fig.1b) as a basic material for future finger-printing sensor arrays (Fig.1c and 1d).

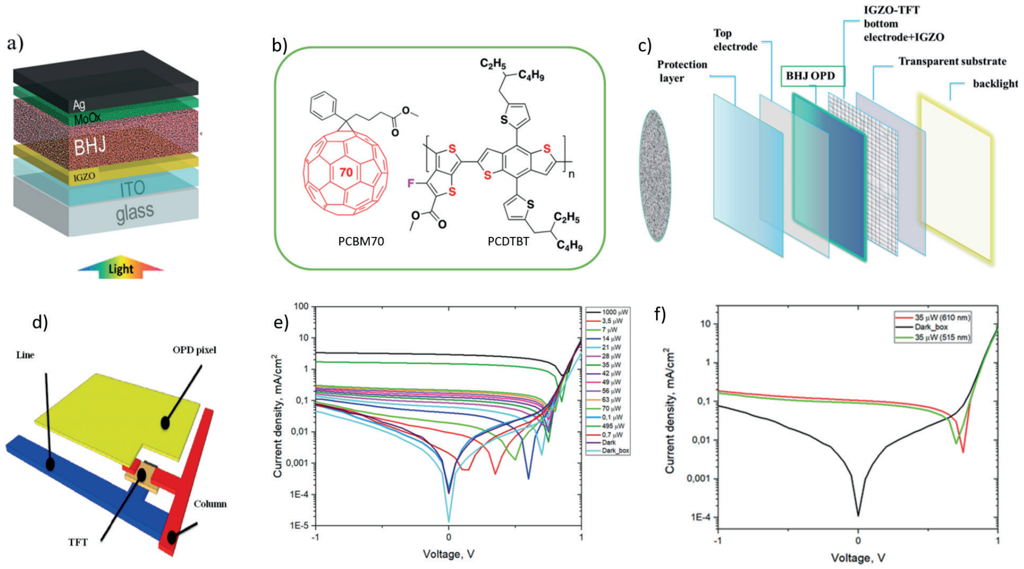

Fig. 1. Structure and I-V curves of the organic photodiodes with a-IGZO electron transport layer; c) and d) basic structure of printed photodetector array

An I-V curves (Fig.1e and 1f) of the photodiodes shows optimal IGZO thickness of 7 nm with balance between the extraction of photoinduced charges and the dark current. The dark current (I_{dark}) reached 7.8 nA. The current density under radiation (J_{photo}) is similar for all three types of devices with different ETL thicknesses, both under short circuit conditions and under reverse bias down to -3V. The maximum spectral sensitivity R for the sample reaches 0.45 A/W at 580 nm.

The work was carried out with the financial support by RSF (project № 19-73-30023)

Modeling of Charge Carrier Transport Depending on the Morphology of an Organic Layer

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The active semiconductor layer in organic electronic devices can be characterized by specific peculiarities in morphology. The film may contain amorphous, polycrystalline or crystalline aggregated phases. In this work Monte Carlo (MC) simulation of the charge carrier mobility in a polymer layer containing well-ordered nanosized regions (crystallites) with reduced disorder separated by regions with high energy disorder (amorphous phase) has been carried out. The modelled material is constructed from a point-like hopping sites that form a simple cubic lattice. Some fraction of the sites, V, belongs to the set of rectangular boxes, i. e. the crystallites, which are randomly centered and randomly distributed in their volumes. Each box is surrounded by the sites, which form an amorphous phase (the M_1 model). The hops involving crystallite sites occur faster due to presumed weaker localization of their wave functions. The energy distribution of the sites is a sum of the two Gaussians; the energies of crystallite sites are distributed according to the lower Gaussian (the variance is $\sigma_2 = \sigma_1/3$, σ_1=0.05 eV), which is shifted down by the energy E_t. For comparison, a purely amorphous medium is also modeled, formed by point-like centers with the same energy distribution (the M_0 model). The drift mobility, μ, has been calculated, see fig. 1, T=298 K.

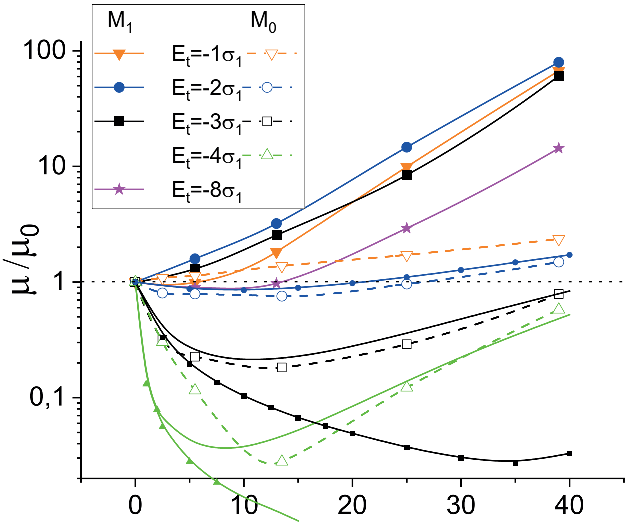

Fig. 1. The drift mobility, parametric in the mean energy depth of the lower Gaussian, E_t.

In the case of M_0 model, MC results agree better with the generalized multiple trapping and release (MTR) model[1] than with the simpler version of MTR model, based on the transport layer concept, see the solid lines without symbols and the solid lines with small filled symbols, respectively. In the case of M_1 model, the mobility may exceed the reference level $\mu_0 = \mu$ ($V = 0$) by several orders of magnitude. In both models, the mobility passes through the maximum at some value of E_t at a given fraction V. These results are important for optimization of OLEDs and photovoltaic devices.

This work was supported by Russian Science Foundation (project 22-22-00612).

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Doping of the EGOFETs based on C8-BTBT organic semiconductor in acidic solutions

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Electrolyte-gated field-effect transistors (EGOFETs) are proven to be a remarkable platform for ultra-sensitive and specific biosensors that could be utilized for point-of-care diagnostics[1]. Although EGOFETs are actively used for various sensing applications, still there is little information about mechanism of the EGOFET sensor response. It is considered that there are two main types of the interactions that can affect organic semiconductor (OSC) layer electronic properties in EGOFET: 1) analyte molecules create charge trap states or provide additional charges to OSC, which correspond to OSC chemical doping; 2) change in the electronic coupling that occurs during interactions at the gate or OSC interface, which could be attributed to the change of layer morphology or receptor conformation[2]. As the most popular application of EGOFETs is biosensing, the process of biorecognition and mechanisms of the sensor response to biological molecules attracts the most attention. However, it is also an interesting task to learn more about interactions of an EGOFET with the charged particles that always present in biological solutions – protons. Besides its oxidizing activity, protons could screen gate voltage, permeate the semiconductor and charge the substrate. Thus, in this work we aimed to take a closer look to the interaction of protons and small-molecule organic semiconductor to get a better understanding of the sensor response and operating limitation.

In this work we have manufactured EGOFET devices from the blend of 2,7-dioctyl[1]benzothieno[3,2-b]benzothiophene (C8-BTBT) and polystyrene[3]. To get the response to pH variation we prepared two series of the experiments using hydrochloric acid in one case and *p*-toluenesulfonic acid in the other. We obtained the same results for both acids, which was a notable positive shift of the threshold voltage for pH lower than 5. In the range of pH 5-2.8 this dependence was linear, however, there was no pH dependence for the higher pH (5-5.8) values. Similarity of the results for different acids proves that this effect is due to protons rather than anions. We have also obtained the same results for two types of the substrates (Si/SiO_2 and polyethylene naphthalate), which indicates that the substrate is not the reason of the effects observed. As was mentioned earlier[4], the positive shift of the threshold voltage can be associated with chemical doping of the semiconductor.

Thus, we have demonstrated the ability of protons to dope C8-BTBT semiconductor in acidic solutions (pH < 5). This effect is significant enough for using C8-BTBT/polystyrene EOFET as a sensor in acidic solutions, but does not hinder biosensing application in near-neutral solutions.

This work was financially supported by a grant from the Russian Science Foundation (No. 19-73-30028).

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Application Oriented Molecular Engineering of Small Molecules for Photonic Devices

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Small organic molecules with suitable photophysical and electronic properties have attracted great attention towards Hi-tech applications based on photonic devices, such as dye sensitized solar cells, organic solar cells, emissive displays such as organic light emitting devices; electronic materials, such as organic semiconductors and security printing. Organic solar cells or organic photovolatics are emerging as one of the promising technologies for renewable energy sources because of their potential low-cost fabrication, color-tunable feature, and mechanical flexibility. Many research activities have endeavoured to develop new organic materials and device configurations for improving the efficiency and practical durability of the devices. Our research groups are actively demonstrating development of new and stable organic molecules for various applications. In this event, I will be presenting our recent development on hole-transport materials for perovskite solar cells. The talk will start with a brief introduction of solar cells followed by industrial application and commercialization of dye molecules. The details of perovskite device architectures are depicted in Figure 1.[1]

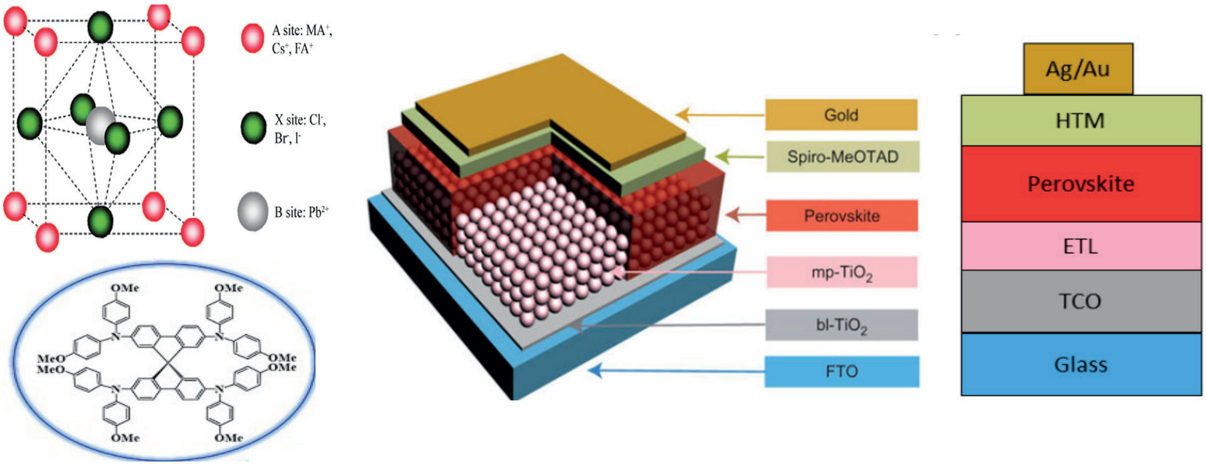

Fig. 1. Perovskite device architectures

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Influence of Terminal Alkyl Substituents Chain Length to the Electrical and Sensory Properties of BTBT-based Siloxane Dimers

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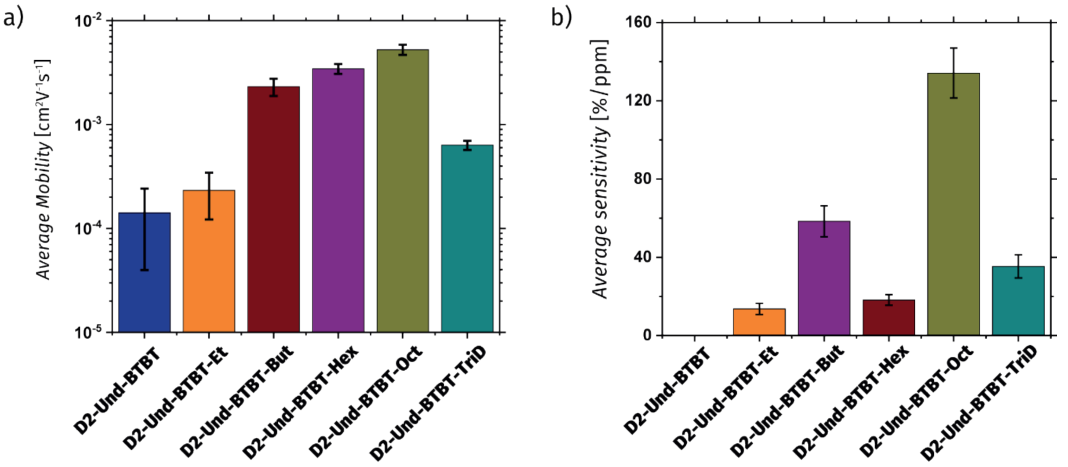
One of the promising ways for the inexpensive portable gas analyzer creation is based on the use of (ultra) thin-film organic field-effect transistors (OFETs) as sensor devices for detecting various gases in the air atmosphere. Such devices are quite promising due to the strong dependence of the OFETs electrical properties on the environment, which is achieved due to the direct interaction between the OFET thin-film conductive layer and the analyte. [1] Previously published works show that siloxane dimeric molecules based on BTBT are successfully used in such devices as organic field-effect transistors,[2] chemosensors.[3] However, there is no systematic study regarding electrical and sensory properties dependence on chemical structure of the dimer. Thus, we started such studies, which can shed some light on the working mechanism of such type of sensory devices.



Picture 1. Dependence of the average mobility (a) and device sensitivity (b) on terminal alkyl group length of the dimers investigated.

In this work, the influence of terminal alkyl group length on electrical and sensory properties was thoughtfully investigated. The devices investigated demonstrate typical p-type behavior with extracted charge carrier mobilities, threshold voltages, and on–off ratios in the range of 10^{-5}–10^{-2} cm2 V^{-1} s^{-1}, −24 to +14 V, and 10^{2}–10^{7}, respectively. Corresponding dependences on terminal alkyl group length are showed at Picture 1.Clear difference in the trends in the growth of electrical and gas-sensitive properties with a terminal group length increasing leads to the conclusion that the sensory properties of the OFETs are weakly related to its electrical characteristics. Further morphology investigation demonstrated that sensory properties of the device mostly dependent on semiconducting layer morphology and the best properties were obtained at the devices based on dimer with octyl terminal group with the smoothest and uniform active layer.

The work was carried out within the framework of grants of the President of the Russian Federation (project no. MK-2915.2022.1.3).

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New polysiloxanes modified with [1]Benzothieno[3,2-b][1] benzothiophene (BTBT) derivatives

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A. Bakirov, S.Chvalun, S. Ponomarenko

Institute of Synthetic Polymer Materials RAS

[1]Benzothieno[3,2-b][1]benzothiophene (BTBT) attracts lots of researchers in organic electronics due to its highly efficient performance, air-s and thermal stability. BTBT is a π-conjugated molecule caused by it heteroaromatic backbone. Most of π-conjugated polymers are used to produce organic field-effect transistors (OFET), electrochromic devices[1], chemo- and biosensors[2,3], semiconductor lasers[4], photovoltaic cells and photodiodes[5], supercapacitors[6], etc. Polymers in organic electronics make it easier to produce large area flexible electronic devices because of low cost and manufacturability.

Recently, we developed various BTBT-based devices that show good charge mobility in different applications[7,8,9].

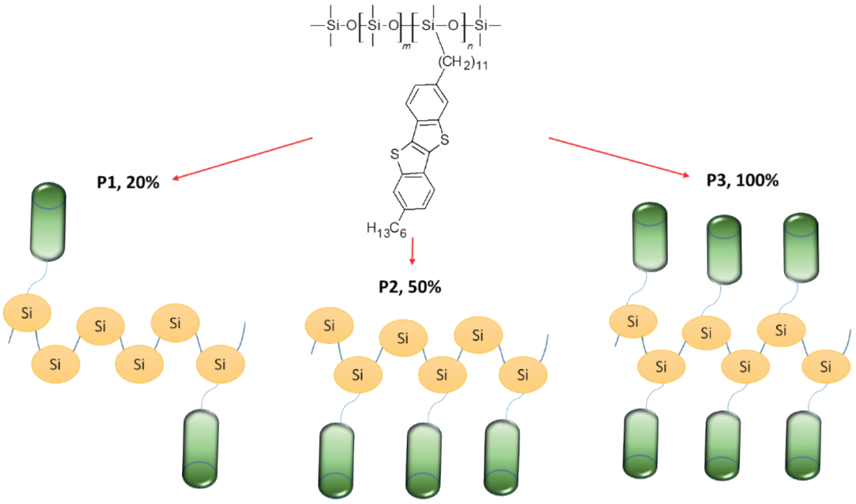

Fig.1 Scheme of polymers functionalized with BTBT-derivatives.

In this work the idea of producing BTBT polymer takes place. We report on a synthesis of a range of polymers functionalized with BTBT-derivatives (Fig.1) and show their properties.

This work is supported by the Ministry of Science and Higher Education of the Russian Federation (contract No. 0071-2021-0005)

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Mechanism of NO_2 detection using organic field-effect transistor based on C8-BTBT

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Sensing is one of the most promising applications of organic field-effect transistors since they combine high sensitivity with low production cost[1]. It can be applied for environmental monitoring, exhaled breath analysis, food quality monitoring and many more[2]. Nitric dioxide detection is of high importance in environmental monitoring tasks. And OFETs feature high sensitivity to NO_2, while the detection mechanism remains unclear. OFET is a device with three electrodes and a non-linear current-voltage characteristic, therefore, there are plenty of methods to measure OFETs sensor signal varied by input voltage amplitude, pulse form and duration. We propose that accurate comparison if sensing properties in different measurement techniques is essential for both mechanism unraveling and properties optimization.

Most researchers are using transient measurements in saturation regime without any rationalization[3]. This is probably due to a higher current density and sensor response signal-to-noise ratio, while effect of the operation regime on the sensor sensitivity were not discussed. Others use transfer curve method due to a more data provided by multiparametric approximation[4]. We compare pulsed and transfer measurement approaches in saturation and linear regimes to determine optimal configuration for OFETs sensing application and suggest that this comparison shed light on the interaction of the adsorbed nitric dioxide and organic semiconductor.

In this work we compare C8-BTBT OFET sensitivity to NO_2 using transfer and transient methods in linear and saturation regimes. Transient measurements in linear regime with low duty cycle are found to provide the highest sensitivity of 232 %/ppm due to low current density and many vacant deep traps. Deep traps are considered as an effective receptor site and thus, NO_2 sensing process is competing with for traps with injected charges. We suggest that for obtaining higher sensitivity to electron-withdrawing gases like NO_2 OFETs are better to kept in linear regime at lower current density.

This work was supported by the Russian Foundation for Basic Research project #20-03-00810.

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Fully printed reusable gas sensor for ammonia and toluene detection

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In this work we present an approach to the creation of a fully printed polymer device applicable as a reusable capacitive gas sensor. Technique and optimal conditions for consistent polymer layers (conductive contacts, dielectric, gate) fabrication by screen printing were developed and the printed polymer device (capacitor) were obtained [[1]]. Efficient adhesion of printed functional layers to each other and to the substrate surface was provided using substrates/dielectric surfaces modification by oligo-3-aminopropyltriethoxysilane (oAPTS) followed by thermal annealing [[2]]. It was shown that fabricated sensors reversibly respond to ammonia presence at wide range of concentration from 0 to 24 ppm with the limit of detection of 1,5 ppm and also don't lose their performance in humid air up to 40% relative humidity, although the limit of detection increases in humid air up to 4 ppm. In addition, printed devices can be used as disposable sensors for the toluene presence in the atmosphere at concentrations of 0.1 -15 vol.%, that allows to use them for toluene leaks detection (Fig. 1).

Using of the printed capacitive sensors (PCS) in combination with gas sensors based on organic field-effect transistors makes possible to significantly expand the range of measured ammonia concentrations: from concentrations comparable to the TLV of residential areas to concentrations requiring immediate evacuation.

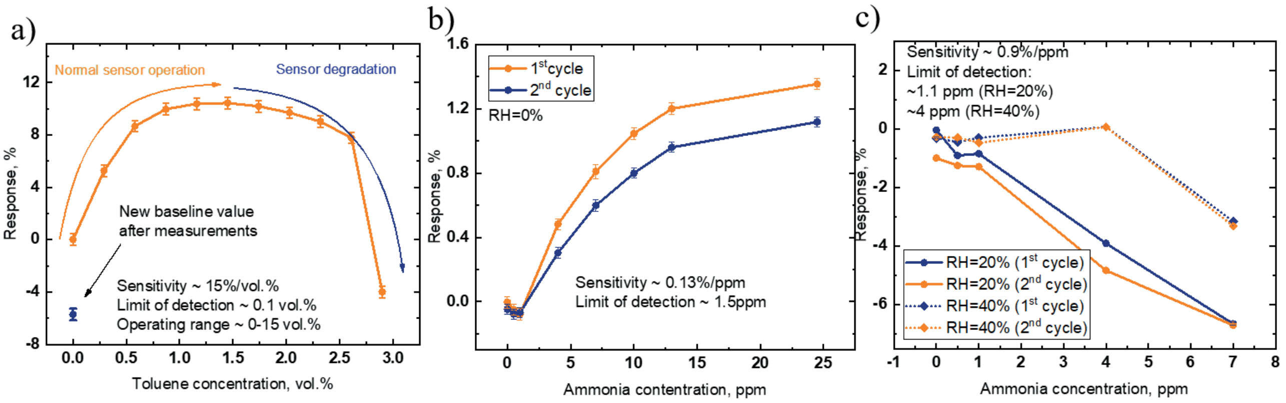

Fig. 1. Response curves for sensing of toluene (a) and ammonia in dry (b) and in humid (c) air with relative humidity of 20% and 40%, respectively.

This work was supported by RSF (grant 19-73-30028).

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Impact of terminal substituents on molecular packing, charge injection, and chargecarrier mobility in thiophene-phenylene co-oligomer single crystals

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Single crystals of thiophene-phenylene co-oligomers (TPCO) are promising optoelectronic materials for light-emitting devices, as they combine efficient chargecarrier transport and high luminescence[1,2]. These properties can be controlled via chemical modification of the TPCO molecule that changes the electrostatic potential distribution and molecular packing in the crystal.

Here, we study the impact of modification of the phenylene-thiophene-thiophene-phenylene (PTTP) conjugated core with different terminal groups (R = H, F, CH_3, CF_3, $Si(CH_3)_3$, $C–(CH_3)_3$, $O–CH_3$) on the structural and electronic properties of single crystals and thin films using X-ray diffraction, electronic structure calculations, and field-effect transistor (FET) measurements.

Our experimental data show that the variation of the molecular terminal group maintains the herringbone packing of the molecules but changes their inclination vs. their basal plane.

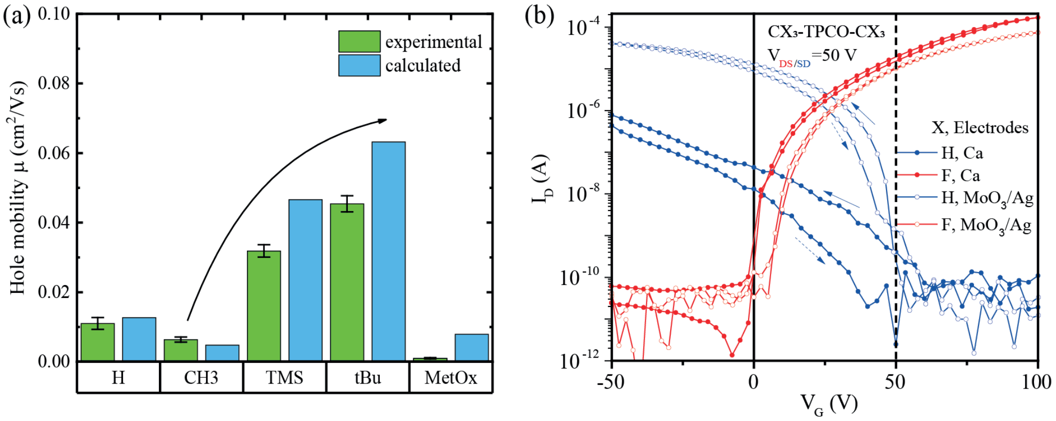

Fig. 1. (a) Comparison of experimental and calculated isotropic hole mobilities in a series of RPTTPR single crystals, (b) transfer characteristics of thin-film RPTTPR FETs (R = CH_3, CF_3).

The calculated frontier-orbital energies for isolated TPCO molecules show their small variation with the terminal group; however, the change in the molecular inclination angle significantly impacts the overlap of neighbouring molecular orbitals, affecting the charge-carrier mobility (Fig. 1a). Moreover, some terminal groups can alter the type of injected charges in the organic FET device (Fig.1b), which we demonstrate to arise due to a change of the electrostatic potential in the array of packed TPCO molecules[3]. We discuss the FET performance in relation with structural features of the TPCO single crystals.

This work was supported by the Russian Science Foundation (project No. 18-12-00499).

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Donor-acceptor molecules for 2D organic light-emitting transistors

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2D organic semiconductor films that consist of mono or a few molecular layers are promising materials for ultrathin, flexible, and transparent light-emitting devices. 2D organic materials have demonstrated high charge-carrier mobility[1], but high performance organic light-emitting transistors (OLETs) is still a challenge.[2]

In this work, we synthesize a novel donor-acceptor thiophene-phenylene co-oligomer (Figure 1). 2D films were grown from ortho-dichlorobenzene solution spin-cast at concentrations of 0.2-0.5 g/l on Si substrates with thermally-grown SiO_2. 2D films with lateral dimensions in the range of 200–500 µm were grown (Figure 2a). Atomic-force microscopy data showed that the thickness of thin films was 1.6 nm, which is much less than the calculated length of the molecule. This suggests that the molecules are tilted. OLETs were fabricated on SiO_2/Si substrates with bottom gold electrodes. OLETs demonstrated ambipolar transport and electroluminescence (Figure 2b,c). We conclude that the donor-acceptor molecules studied are promising materials for 2D OLETs.

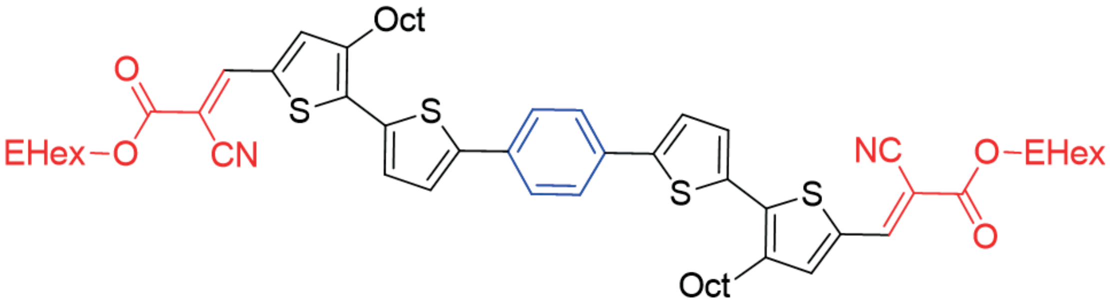

Figure 1. Molecular structure of a donor-acceptor molecule studied.

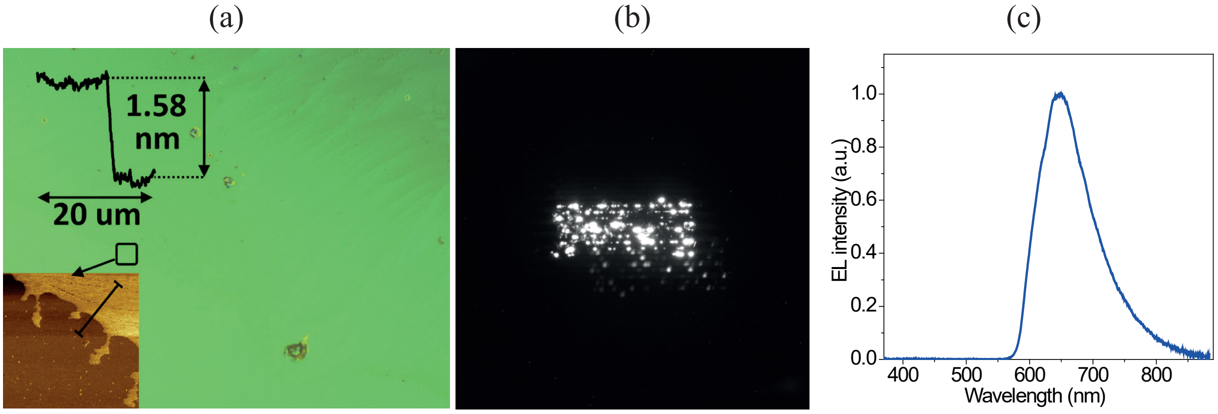

Figure 2. Optical image of 2D films (a); electroluminescent image of the OLET during its operation (b); electroluminescence spectrum (c).

This work is supported by Russian Science Foundation (project 18-12-00499).

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Electrolyte-gated organic field effect transistors on the basis of 2,6-dioctyltetrathienoacene

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Electrolyte-gated organic field effect transistors (EGOFETs) provide a versatile platform for ultra-sensitive, fast, and reliable detection of biological molecules in liquid media using low-cost bioelectronic sensors. The key functional layers of the EGOFETs are the semiconductor and bioreceptor layers based on conjugated organic molecules, which are subject to high requirements for the stability of operation in various electrolytes when detecting analytes.

Thus, we have developed a technique for manufacturing OETs compatible with printing technologies based on a new semiconductor material - 2,6-dioctylthieno[3,2-b]thieno[2',3'':4,5]thieno[2,3-d] thiophene with a bioreceptor layer based on a biotin-containing [1]benzothieno[3,2-b]benzothiophene derivative applied by the Langmuir-Schaeffer method. The possibility of stable operation of the fabricated EGOFETs in electrolytes with different pH and their fast sensory response to the pH of the electrolyte, which makes it possible to use the developed devices in real conditions, is demonstrated. The optimal transistor parameter for measuring the sensory response (threshold voltage) and the optimal mode for long-term measurements are determined. It has been shown that the biosensing properties of OET can be ensured by creating a bioreceptor layer on the semiconductor surface containing functional biotin groups, which are reactive centers for biotin-streptavidin interaction.

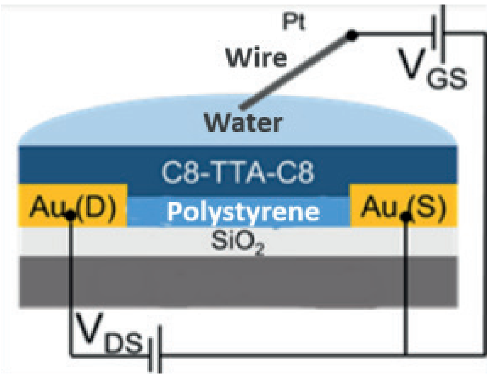

Fig. 1. OET architecture (Au - contact material (gold), D - drain, S - source).

This work was supported by RSF (project № 19-73-30028)

Elastomer composites based on siloxanes and carbon nanoparticles as a compliant electrodes

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Dielectric elastomer actuators (DEA) are mechanically flexible actuators made of functional polymer materials and composites acting as artificial muscles.[1] DEA is a multi–component high-tech device that includes a dielectric elastomer (DE) membrane, compliant electrodes, voltage source and control electronics. When voltage is applied to the electrodes, the thickness of the DEA membrane decreases, and the membrane area increases due to the conversion of electrical energy into mechanical work.[2] An important part of creating actuators is to obtain compliant electrodes. The main requirement for DEA electrodes is that they must deform without loss of conductivity to the same extent as the DEA membrane is deformed, i.e. have sufficient adhesion to the DEA material, function reliably for a long time, maintaining continuity, acceptable conductivity, etc.

The purpose of this work was to create conductive electrodes based on polydimethylsiloxanes and various carbon fillers (MWCNT, SWCNT, aminated graphene).

The main results of the study of the effect of different types of carbon fillers on the conductive and mechanical properties of composites will present in the work.

This work was supported by Grant of the Russian Science Foundation (project No 19-73-30028).

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Polyvinylidene fluoride copolymers with grafted chains of polyethyl methacrylate and polyacrylonitrile: synthesis, thermal and dielectric properties

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Ferroelectric polymers such as polyvinylidene fluoride (PVDF) and copolymers based on it exhibit piezoelectric and pyroelectric effects. Such properties allow them to be used as functional materials for creation of flexible thin-film sensors of pressure and temperature, as well as memory devices based on organic transistors and self-powered electronics[1].

Double and ternary copolymers based on polyvinylidene fluoride with grafted polyethyl methacrylate (PEMA)[2] and polyacrylonitrile (PAN)[3] chains were synthesized by photoinduced reversible deactivation radical polymerization (RDRP) using a minimal amount of a catalytic system (Fig. 1). Four series of grafted polymers were obtained, and the dependence of the content of grafted chains on the synthesis time was investigated.

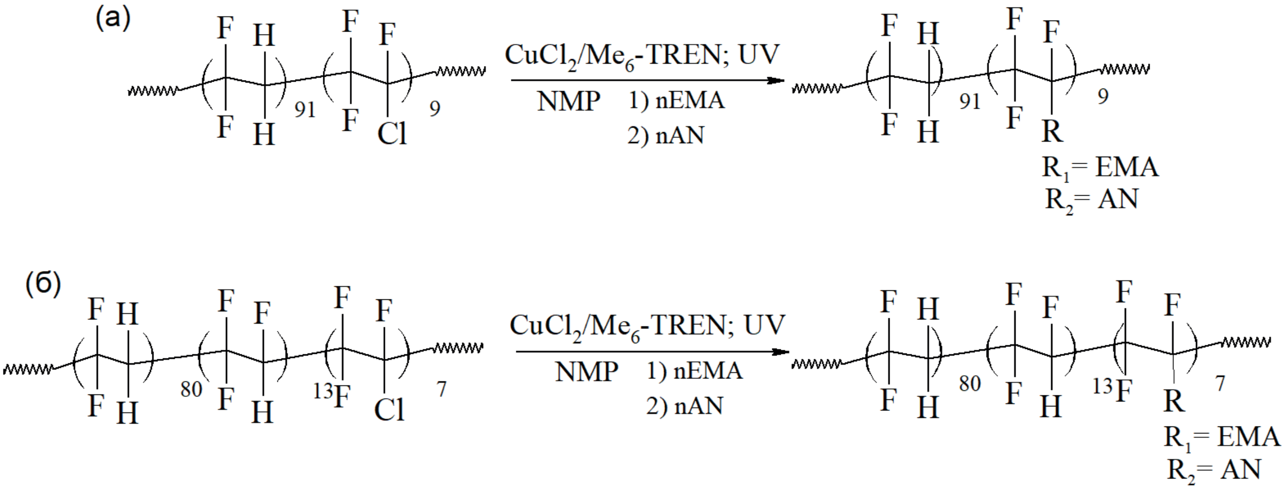

Fig. 1. Scheme of the synthesis of grafted double p(VDF-co-CTFE) copolymers (a) and ternary p(VDF-co-TFE-co-CTFE) copolymers (b) based on PVDF with grafted chains of ethyl methacrylate (R_1=EMA) and acrylonitrile (R_2=AN).

It was shown that an increase in the degree of grafting leads to a nonlinear change in the dielectric properties and also affects the thermal and thermal-oxidative stability compared to the initial polymers. In a series of copolymers with grafted PEMA chains, the values of the dielectric constant decrease, but at the same time, dielectric losses also decrease. Moreover, an increase in the degree of grafting significantly improves the film-forming properties of all the polymers obtained by reducing the degree of crystallinity and lowering the melting point.

This work was supported by the Russian Science Foundation (project № 19-73-30028).

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Impact of terminal groups and molecular doping on photoluminescence of single crystals of thiophene-phenylene oligomers

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Molecular doping allows control of photoluminescence (PL) in crystals of organic semiconductor oligomers[1],[2]. PL in molecularly doped organic single crystal requires understanding factors of host–dopant exciton transfer efficiency, but they have been poorly studied.

In this work, we present PL data in variously doped single crystals of thiophene-phenylene oligomers R-PTTP-R (Figure 1) with identical thiophene-phenylene conjugate core (PTTP) and different terminal substituents (R): -H, -F, -CF_3, -CH_3, -MetOx, tBu, -TMS.

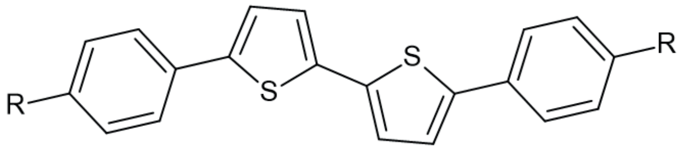

Figure 1. Chemical structure of R-PTTP-R molecule

We show that the efficiency of host–dopant exciton transfer which can be extracted via PL red shift depends on terminal groups and the doping level (Figure 2).

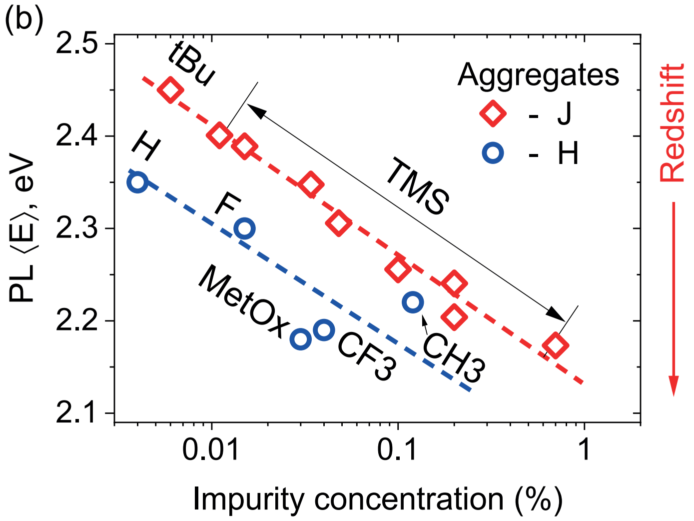

Figure 2. A red shift of PL as a function of the doping level (impurity concentration) in R-PTTP-R single crystals; the points signatures stand for terminal substituents R

For explaining the efficiency of host–dopant exciton transfer in variously doped R-PTTP-R crystals, we propose an exciton diffusion model. We show that the model explains the PL features in doped R-PTTP-R crystals.

This work was supported by RSF (project № 18-12-00499).

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Impact of the chemical purity on the semiconductor properties of 2D single crystals

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2D organic semiconductor single crystals are promising materials for organic field-effect devices[1]. In this contribution, we study the impact of chemical impurities on charge transport in 2D organic semiconductor single crystals in organic field-effect transistors (OFETs). In 3D materials, it is known that they can act as charge traps and affect the optical properties. We focus here on impurities that are detected by photoluminescence (PL) spectroscopy and reveal themselves as an intra bandgap PL band. We assume that the impurity is a self-dopant — a longer conjugated molecule appeared as a by-product of chemical synthesis[2]. We used oligothiophenphenylene 1,4-bis (5'-hexyl-2,2'-bithiophene-5-yl) benzene (DH-TTPTT) with a self-doping level of 0.01% and 0.2% evaluated from PL measurements in solutions. A drop of solution was applied by spin coating at a concentration of 0.1–0.6 g/l on a Si substrate with SiO$_2$ layer working as a gate dielectric.[1]The top electrodes of the organic field-effect transistors (OFETs) were plotted from PEDOT:PSS suspension.[2]

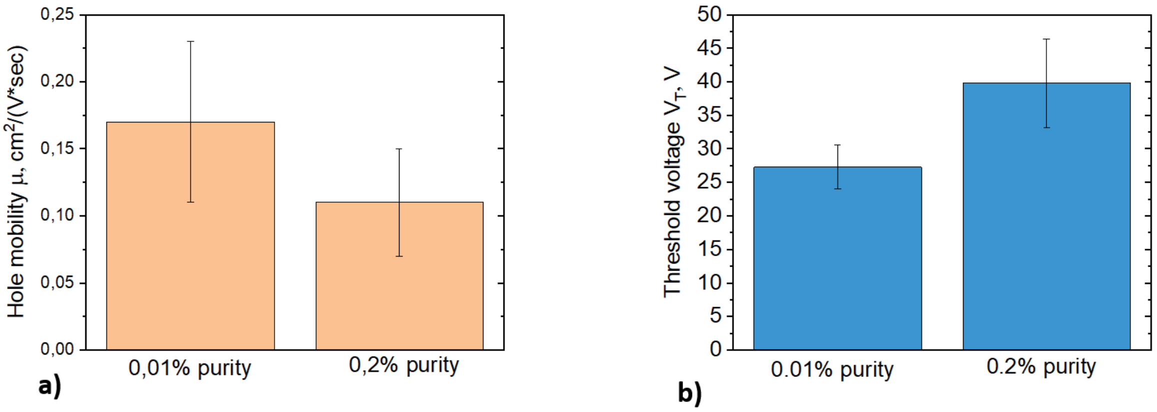

Fig 1. OFET data for two sets (6 & 8 transistors for 0.01% & 0.2%, respectively) with different self-doping level of the active layer: the average hole mobilities (a) and the average threshold voltages (b).

The PL data in the 2D crystals showed that the self-dopant is incorporated in the crystals. The measured OFET data show that that the hole mobility values for the self-doping levels coincided within the measurement accuracy limits, but the threshold voltage is sensitive to the doping (Fig. 1). Accordingly, we conclude that the self-dopant species seemingly act as deep traps for charge carriers. From DFT calculations of various possible self-dopants and experimental PL spectra of the self-doped samples we suggest that the most plausible self-dopant is the starting molecule with oxidized thiophenes (sulfones).

This work is supported by Russian Science Foundation (project 18-12-00499).

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Synthesis of a new semiconductor material based on 1,10-diaza-18-crown-6 for OFET-based sensors applications

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1,10-diaza-18-crown-6 (Kryptofix® 22) as a specific class of azocrown ethers is known for its high affinity and selectivity for binding transition metals[1]. The unique structure and properties of these compounds have made them a popular choice for a wide range of applications over the past few years. One of the possible applications of the high affinity for transition metals of this ether may be its use as a sensor layer in organic field-effect transistor (OFET) -based sensors. It is expected that the binding of crown ether by transition metal atoms will lead to a change in the electronic structure of the compound, which will ultimately affect the semiconductor and the sensory properties of the material[2]. It is advisable to use [1]benzothiene[3,2-b][1]-benzothiophene (BTBT) as a semiconductor fragment for this material, due to the high mobility of charge carriers in this fragment, as well as its high stability[3].

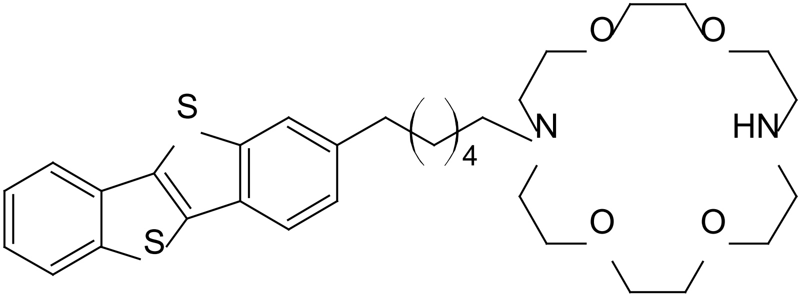

Fig. 1. Chemical structure of synthesized compound.

The synthesis of the target compounds was carried out using a combination of successive Friedel-Crafts acylation reactions, keto group reduction, and direct amine alkylation. The first two reactions are well studied and give relatively high yields, while the addition of an alkylated derivative is carried out by us for the first time and requires the selection of reaction conditions. Molecule structure-property relationship as well as possible application will be discussed.

This work was supported by Program of President of Russian Federation for supporting of young scientists (MK-2471.2022.1.3)

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Development of organic luminophores with branched structural fragments

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One of important issues of molecular design of π-conjugated compounds is finding a way of combining different functional fragments in one molecule, which avoids the loss of useful characteristics of each of them. It is possible to achieve by using of a spacer that interrupts the conjugation. It could be an aliphatic chain or a silicon atom. The last was successfully applied for efficient absorption, emission and energy transfer in organosilicon nanostructured luminophores. A special advantage of applying the concept of no coupling in molecular design is the predictability of the properties of novel structures. However, the disadvantage of using a spacer that breaks the conjugation is increased molecular weight and sometimes the impossibility of reaching the desired HOMO and LUMO energy levels.

This work deals with the way of conjugation of absorbing and emitting fragments that don't interrupt their spectral properties and allows efficient intramolecular energy transfer between them. Utilizing of 1,3-disubstituted benzene ring with phenyl or diphenyl substituents promotes an efficient absorption in medium UV region. The placement of (2,1,3)benzothiadiazole unit in the meta-position relative to these substituents leads to the formation of 4,7-diphenyl(2,1,3)benzothiadiazole (PBP) fragment that is an excellent emitting chromophore with relatively low absorption cross-section. The resulting molecules (fig. 1) possess the spectral properties of the isolated model moieties. It was shown by successful approximation of the absorption spectra of novel luminophores with linear combination of the spectra of model compounds that present themselves isolated absorbing and emitting fragments.

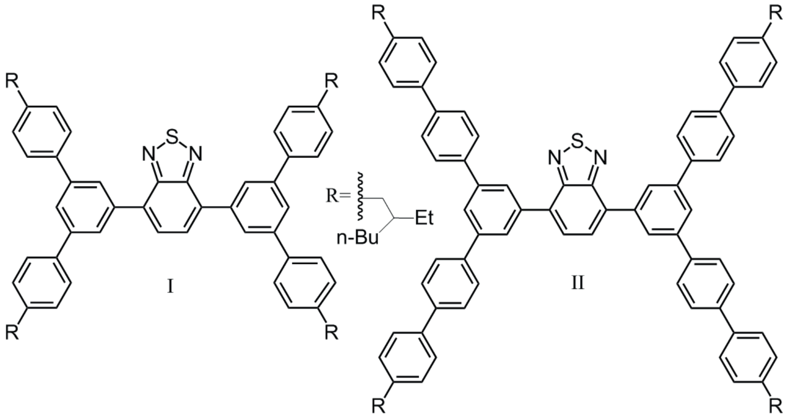

Fig. 1. Chemical structures of novel organic luminophores with branched fragments

The emission spectra of novel compounds are identical to the spectrum of PBP alone. However, there is a fundamental difference in the quantum yields (QY) of fluorophores. Diphenyl substituents possess QY of 75% and higher, but substitution with phenyls drastically decreases QY to 33-44%. Efficient absorption in medium UV and high quantum yield of fluorescence in the bluish-green range of the conjugated PBP with meta-disubstituted diphenylbenzene make it possible to consider this branched luminophore as a promising material for optoelectronics and plastic scintillators.

This work was supported by a grant of the President of Russian Federation for financial support of Leading scientific schools No. NSh-3843.2022.1.3.

Dynamic disorder in structurally close organic semiconductors

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Dynamic disorder manifested in fluctuations of charge transfer integrals considerably hinders charge transport in high-mobility organic semiconductors (OSs). However, management and control of dynamic disorder in OSs is far from being well studied. We suggest a novel promising strategy for suppression of dynamic disorder — tuning the molecular electrostatic potential. We show that the intensities of the low-frequency (LF) Raman spectra for crystalline organic semiconductors differ significantly, indicating significant differences in the dynamic disorder.

We present a combined experimental and theoretical study of the four π-isoelectronic compounds — chrysene, benzothieno[3,2-b][1]benzothiophene (BTBT), naphtho[1,2-b:5,6-b′]dithiophene (NDT) and tetrathienoacene (TTA). Their annulated structure enables high hole mobilities in their derivatives, e.g., C_8-BTBT is a popular high-mobility OS.[1,2] We observe an unexpectedly strong relative LF Raman intensity (as compared with the HF one) for crystalline BTBT and attribute it to the strong dynamic disorder; this is confirmed by solid-state DFT calculations. On the contrary, the relative LF Raman intensity is moderate for chrysene, NDT and TTA. For the former two compounds, the lower relative LF Raman intensity is attributed to suppression of the dynamic disorder, for TTA, it is assigned to a strong HF Raman signal originating from a larger reorganization energy and a narrower bandgap. In turn, the difference in the dynamic disorder stems from the stronger intermolecular interactions in chrysene and NDT as compared to those in BTBT and TTA. These strong interactions are enabled by favorable distribution of the electrostatic potential highlighting the efficiency of tuning the latter for suppression of the dynamic disorder. By comparison the LF Raman spectra of C8-TTA and C8-BTBT, we show that alkyl substituents can reduce dynamic disorder. The more rigid crystal structure of C8-BTBT and C8-TTA results in weaker dynamic disorder in the lasts with compared to TTA and BTBT.

Our studies, first, suggest guidelines for strengthening the intermolecular interactions in OSs and suppression of the dynamic disorder for efficient charge transport and, second, highlight the efficiency of Raman spectroscopy in monitoring the disorder/rigidity of OSs, at least within the series of materials with similar molecular structures.

This work was supported by Russian Science Foundation, project #22-72-10056.

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Synthesis of push-pull small molecules based on donor indolo[3,2-b]indole unit

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Synthetic organic semiconductor materials are of great interest; they are being actively developed and investigated, giving prospects for development in many modern fields of science and technology: organic photovoltaics, electronics, sensors, etc. Organic molecules consisting of condensed heteroaromatic units occupy a separate platform in the growing base of organic conducting compounds. The rigid condensed structure of these compounds provides a π-conjugation with good conductivity, high oxidation stability and dense molecular packing in the block [1]. Among all heteroacenes, benzothieno[3,2-b]benzothiophene derivatives (BTBT) have already managed to stand out and prove themselves as excellent p-type semiconductors, they are actively developed in many studies and give good results [2]. But materials based on the BTBT block usually have insufficient solubility to be processed, and usually can act only as p-type conductors. Of great interest is a block of indole[3,2-b]idol (IDID) similar in structure to that of BTBT, but having benzopyrrole fragments instead of benzothiophene, which makes it possible to modify alkyl or aromatic substituents in two NH-positions, thereby controlling the solubility and conductive properties of materials [3]. It is expected that molecular D-A structures based on this block may show not only a better solubility and hole mobility, but also have ambipolar charge transport, which will allow them to be used not only in organic field-effect transistors, but also in sensors and lasers, as well as single-component organic solar cells.

This work deals with the synthesis and investigation of the new group of IDID-based oligomers, which have various aliphatic and aromatic substituents and show promising properties for organic electronics and photovoltaics.

Thy synthesis and investigation of oligomers for organic solar cells were supported by the Russian Science Foundation (project № 19-73-10198).

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Influence of terminal alkyl substituents chain length to the structure, electrical and sensory properties of siloxane dimers based on benzothieno[3,2-b][1]benzothiophene

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D.S. Anisimov,[1] *E.V. Agina,*[1] *S.A. Ponomarenko*[1]

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Organic semiconductors are very promising materials for microelectronics due to their great diversity and tunability of their optoelectronic properties[1]. Previously published works show that siloxane dimeric molecules based on BTBT are successfully used in such devices as organic field-effect transistors[2], chemosensors[3] and memristive devices[4]. The data obtained earlier allow us to conclude that the BTBT derivatives, which have an anchor siloxane group and an optimal length of an aliphatic spacer, have sufficiently high semiconductor characteristics when applying films by Langmuir methods. At the same time, the study of the influence of terminal groups of different molecular structure on the packing, terminal, electrical and other properties of BTBT-containing compounds is an urgent task now. Here the synthesis and investigation of organosilicon derivatives of benzothieno[3,2-b][1]benzothiophene (BTBT) with different length of terminal alkyl groups (from C2 to C13) or without it capable to self-assembly on the water-air interface is described. All the compounds were obtained with high yields and purity, which was proved by ^{1}H, ^{13}C and ^{29}Si-NMR spectroscopy, gel permission chromatography and elemental analysis. The study of their phase behavior by differential scanning calorimetry and polarizing optical spectroscopy showed that all the compounds are crystalline at room temperature. However, those with terminal alkyl substituents form enantiotropic smectic A mesophases, while the compound without terminal alkyl groups form a monotropic nematic mesophase. An increase of the alkyl chain length from C2 to C8 leads to higher temperatures of both phase transitions. The investigation of electrical and sensory properties to NO_2 of the monolayer OFETs based these compounds revealed the dependence of charge carrier mobilities values and sensitivity parameters mainly on the surface morphology of the organic semiconductors. The OFETs based on the siloxane dimer with octyl terminal substituents showed the best characteristics. A comparison of the sensory and the semiconductor properties for different organic semiconductors investigated revealed independency of these parameters.

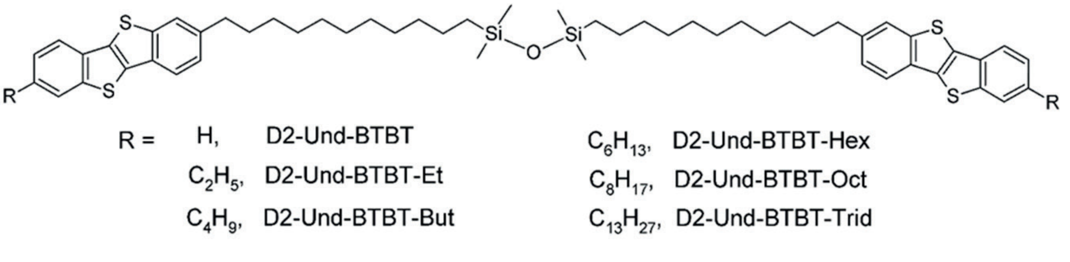

Fig. 1. Structural formulas of the compounds synthesized.

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Synthesis nanostructured luminophores with carbon branching center and comparison of their optical properties with organosilicon analogues

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Svidchenko E.A.[1]***, Ponomarenko S.A.***[1]

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The development of scientific knowledge has opened a new class of nanostructured organosilicon luminophore, which typically demonstrate efficient Förster resonance energy transfer (FRET)[1]. These materials have found application as the functional basis for plastic scintillators, organic light-emitting diode (OLED) and fluorescent labels in medicine and molecular biology. This work compares similar nanostructured luminophores with silicon and carbon branching centers[2]. They consist of 4 identical donor and 1 acceptor moieties. As the donors alkyl derivatives of p-terphenyl (EH-3P) and 2,5-diphenyloxazole (PPO) were used. All synthesized compounds have the same acceptor – POPOP.

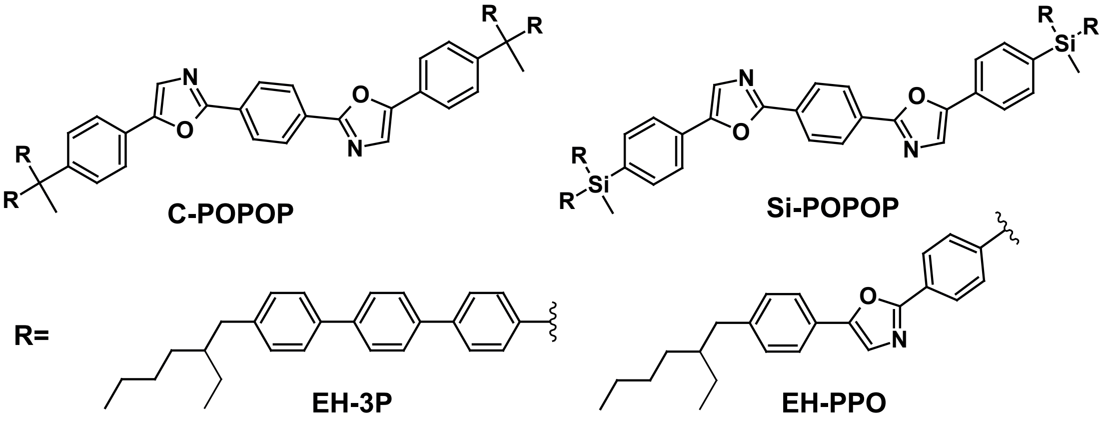

Fig. 1. Structure of obtained chromophores.

The work discusses a method for the preparation of previously unstudied carbon branching center, which is a key precursor in the chosen synthesis route. It is shown that of the two possible ways only one led to desirable result. The subsequent steps are based on the direct cross-coupling reaction and the preparation of precursors for coupling using the Van Leusen reaction. The structure of the compounds was confirmed using by ^{1}H NMR spectroscopic data, the purity of the new luminophores was determined using gel permeation chromatography. Optical properties in dilute THF solution for all compounds are also discussed.

This work was supported by a grant of the President for a leading scientific school NSh-3843.2022.1.3.

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Synthesis and optical studies of benzothiadiazole-based luminophores with high torsion angle

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Recently donor-acceptor systems have attracted considerable interest for organic electronic applications. Researchers are making efforts to improve molecule properties by varying single moieties. 2,1,3-Benzothiadiazole (BTD) is widely used as an acceptor block due to its remarkable opto-electronic properties and usually form efficient luminophores with donor blocks.[1],[2]

Addition of 1,4-dimethylbenzene to BTD molecule can lead to an increase in the torsion angle between these units. That will be affect the planarity of the molecule and impose to a conjugation disruption and a change in the optical properties.

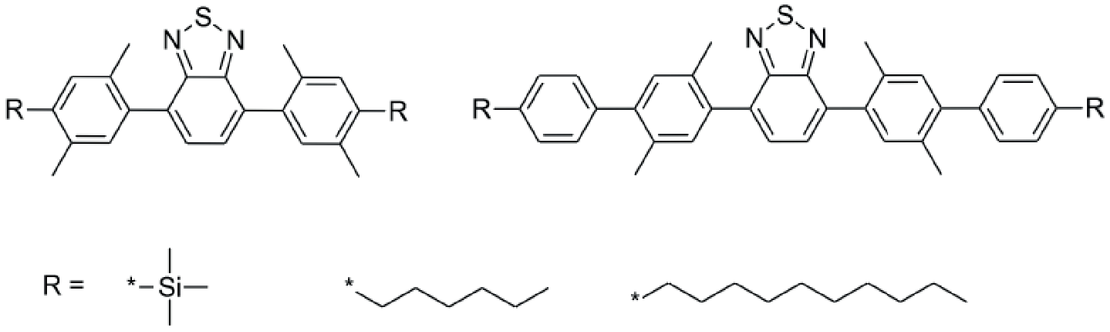

Fig. 1. Chemical structure of the obtained luminophores

In this work a synthesis procedure for new symmetrical luminescent molecules consisting of BTD electron-withdrawing core, 1,4-dimethilbenzene and benzene fragments was elaborated via Pd-catalysed cross-coupling Suzuki reaction. The main aim of this work is to investigate structure-property relationship of such twisted systems. To study crystal packaging, molecules with different terminal substitutions like trimethylsilyl derivatives, and derivatives with hexyl and octyl chains were also synthesized.

This work was supported by a grant of the President for a leading scientific school NSh-3843.2022.1.3.

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Vapor Growth of Centimeter Scale Pentacene Single Crystals

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Pentacene (**Pc**) is one of the best known efficient organic semiconductors. Pc crystals are of great interest for the development of organic optoelectronic devices. Due to the extremely low solubility, at present, the main method for obtaining single crystal samples is the physical vapor transport method (PVT). Despite the works on the growth of Pc crystals available in the literature, there is practically no information about obtaining single crystal samples of centimeter scale. This work is devoted to the development of methods for growing pentacene crystals from vapor phase for fundamental and applied problems of optoelectronics.

Commercial pentacene (triple-sublimed grade ≥ 99.995%, Sigma-Aldrich) was used for research. The conditions for growing Pc crystals of centimeter scale under the conditions of the PVT method are determined. Studies on crystal growth in a two-zone temperature field have shown a significant improvement in growth characteristics in comparison with growth according to the classical method based on a gradient thermal field (Fig. 1). At a fixed temperature T_1 of the hot zone (the zone of sublimation) and a variable temperature T_2 of the cold zone with the same growth periods (72 hours), a change in the morphology and average sizes of crystals is observed (Fig. 1).

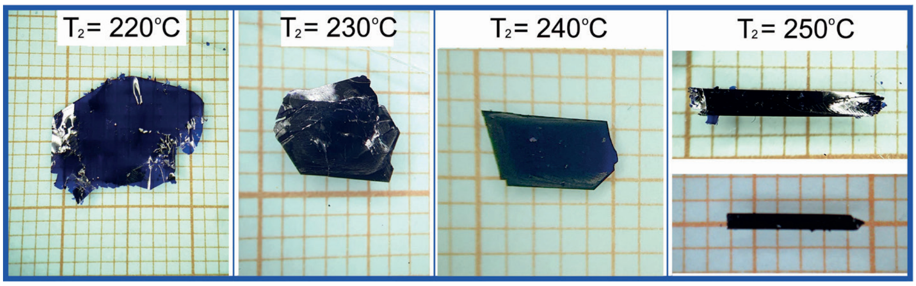

Fig. 1. Pentacene crystals on millimetre paper grown at various temperatures of the cold zone (T_2) for 72 hours (T_1=290ºC).

Pc crystals were studied by single crystal X-ray diffraction (SCXRD) on a XtaLABSynergy-DW, HyPix-Arc 150’ (RigakuOxfordDiffraction) diffractometer at 295 and 85 K. During the study of the features of the growth of Pc crystals under conditions of PVT method, needle crystals of centimetre scale pentacene derivative - 5,14-dimethylene-5,14-dihydropentacene, which is part of a commercial reagent as an impurity, were isolated and studied for the first time by the SCXRD method at 295 and 85 K. Optical absorption and luminescence spectra of pentacene and its dimethylene derivative in toluene solutions were analyzed.

The effect of isothermal annealing in an inert atmosphere on the electrical properties of organic field-effect transistors based on the initial and purified pentacene sputtered on silicon substrates by vacuum thermal deposition is investigated[1].

This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the State assignment for the FSRC “Crystallography and Photonics” of the RAS.

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Photothermal deflection spectroscopy of organic thin films

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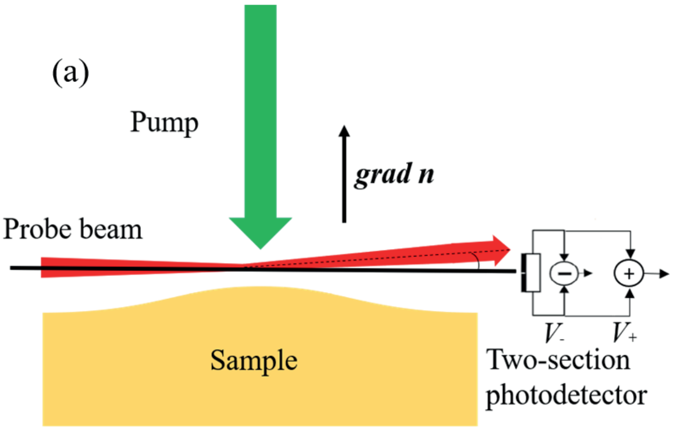
Photothermal deflection spectroscopy (PDS) is a group of highly sensitive methods for determining optical absorption of weakly absorbing samples. PDS is based on the measurement of photoinduced changes in the thermal state of the sample. PDS allows measuring the optical density of solid samples, which can be significantly less than one percent, which is not available to conventional spectrophotometers[1]. Such ultrasensitive absorption measurements are required to determine the absorption of 2D crystals, as well as to determine small concentrations of impurities in organic semiconductor thin films. One of the popular PDS methods is the transversal one or the "mirage effect" method. The peculiarity of this method is the weak dependence of the photothermal signal on the diameter of the excitation beam on the sample. In addition, the "mirage effect" is undemanding to the optical quality (transparency, uniformity, smoothness of the surface) of the sample, because the test beam propagates over it[2]. The scheme of the method is shown in Fig. 1a.



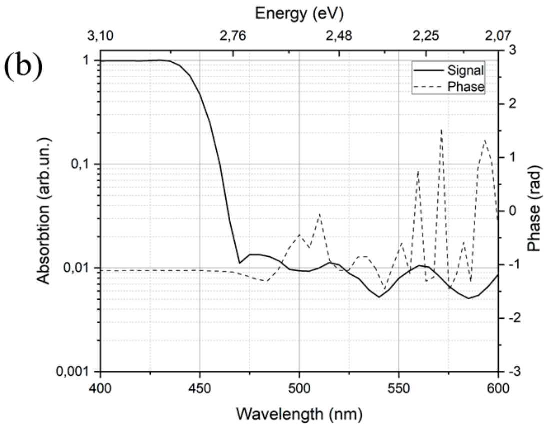


Fig. 1a. Scheme of PDS method "mirage effect".

Fig. 1b. Photothermal absorption spectra of an organic crystal of TMS-PTTP-TMS.

In this work we have developed the PDS methodology and measured ultra-low absorption spectra of organic thin films. We have identified the reasons for limiting the dynamic range of measurements so that the noise level was lower than $\Delta V_-/V_+ = 5 \cdot 10^{-6}\ 1/\sqrt{Hz}$ in the difference channel, where ΔV_- is the - noise voltage in the difference channel, V_+ is the voltage of the - summary signal (Fig. 1a), which provided the dynamic range more than 1000. A PDS spectrum of an organic crystal of 5,5‘-bis[4-(trimethylsilyl) phenyl]-2,2‘-bithiophene (TMS-PTTP-TMS) is shown in Fig. 1b as an example. We discuss approaches to further increasing the sensitivity of our PDS technique and its extension for measuring the absorptivity of 2D samples in terms of optical density.

This work was supported by RSF (project № 22-79-10122).

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Synthesis and properties of heteroacenes for organic electronics

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Organic electronics has been actively developed in recent years due to their advantages such as ease of processing, low manufacturing cost, and mechanical flexibility. Among a large variety of organic semiconductors, heteroacenes (Fig.1) have been widely investigated as promising organic semiconductors in high-performance OFETs. Fused-thiophene structure lead to unique properties, such as extensive conjugation, strong intermolecular S–S interactions, and rigid coplanar conjugated core, which contributes to attractive charge-transfer properties[1].

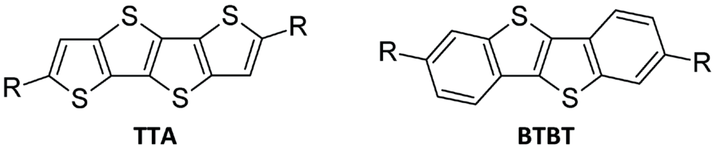

Fig. 1. Structural formulas of tetrathienoacene (TTA) and benzothienobenzothiophene (BTBT) derivatives.

This work describes the synthesis, properties and application of new aliphatic and aromatic derivatives of heteroacenes in various optoelectronic devices[2,3]. The characteristics of organic field-effect transistors based on them, obtained by both solution and vacuum methods, have been investigated. Fast and simple technique based on Doctor Blade and Langmuir-Schaefer methods for functionalization of the semiconducting surface of C_8-BTBT-C_8 allowing to fabricate large scale biorecognition layer based on the novel functional derivative of BTBT containing biotin fragment as a foundation for further biomodification[4]. As a proof-of-concept, we demonstrate the specific response of the BTBT-based biorecognition layer in EGOFETs to a virus of influenza A (H7N1 strain). The influence of dynamic disorder on charge transfer inside annelated organic semiconductors is also discussed[5].

This work was supported by Russian Science Foundation (project № 22-73-00258).

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Synthesis and properties of novel star-shaped donor-acceptor molecules for organic electronics

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Molecules based on triphenylamine (TPA) units are widely used as active layer materials for organic electronics devices. However, triphenylamine molecular geometry hinders planar layer packing, due to sp^3–hybridized nitrogen. Triazatruxene (TAT) is a π-conjugated planar molecule being a truxene analogue but with three nitrogen atoms instead of carbon atoms at 5, 10 and 15 positions. This structural feature allows the TAT core to exhibit planarity and high charge transfer ability. Another structural feature is the easily modifiable NH moieties, which allows the addition of various alkyl substituents to increase the target materials solubility. Simple wide-bandgap TAT derivatives have shown interesting and valuable properties, which are good charge transporting properties, efficient luminescent, large two-photon absorption ability, etc[1,2]. An alternating donor – acceptor approach enables fine-tuning of the physicochemical properties of organic conjugated polymers and small molecules by varying electron-rich and electron-deficient units and the length of the π-conjugated thiophene spacer between them[3].

Here we report on the series and investigation of oligomers based on either TPA or TAT cores and conjugated through bi- or terthiophene π-spacers with 2-ethylhexylcyanoacetate or hexyldicyanovinyl terminal electron-withdrawing groups. All precursors and the target compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy and size exclusion chromatography in an individual state. Optical, thermal and electrochemical properties of molecules were studied and compared. The molecules were tested as donor materials with ITIC as the acceptor in organic solar cells and as hole-transporting materials in perovskite solar cells.

This work was supported by the Grant of the President of the Russian Federation for state support of the leading scientific schools of the Russian Federation (grant № NSh-3843.2022.1.3)

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Organic electrochemical transistors with inkjet printed PEDOT:PSS active layer

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Organic electrochemical transistor (OECT) is a three-contact device with a liquid electrolyte, which is often used in the field of chemical and biosensing and has high detection sensitivity.[1] Conductive polymer material PEDOT:PSS, which is a complex of poly(3,4-ethylenedioxy-thiophene) with polystyrene sulfonic acid, is often used as a functional layer in OECT.[2] Such a layer can be obtained by the method of inkjet printing, which has such advantages as high speed and contactless printing of functional layers of arbitrary shape and size. For stable multiuse operation of the device in electrolyte a good adhesion of the active layer to the substrate is required.[3]

In this work, an effect of the functional organosilicon modification layer on the stability of OECT operation was investigated. For this purpose, a series of OECT devices was афикшсфеув on silicon substrates by vacuum deposition of gold source and drain electrodes and inkjet-printing of the PEDOT:PSS active layer. To improve adhesion of the active layer for preventing its delamination under measuring in liquid electrolytes, the substrate surface was preliminary modified with (3-aminopropyl)triethoxysilane (APTS) (Fig. 1, a). The active layer was deposited by inkjet printing of the inks prepared from commercially available PEDOT:PSS PH 1000 solution by the addition of deionized water and Triton X-100 surfactant to optimize viscosity and surface tension, respectively. As a result, reusable OECTs were obtained with a stable operation in physiological solutions having a complex ionic composition – Ringer or Ringer-Locke solutions used as the electrolytes (Fig.1, b).

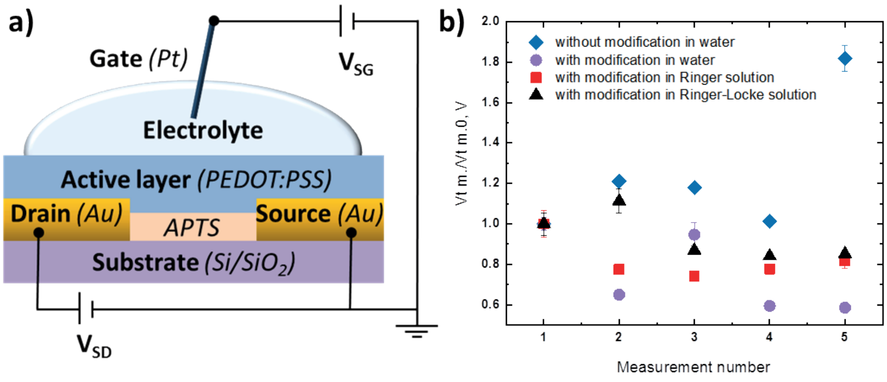

Fig. 1. OECT device architecture (a) and dependence of the normalized threshold voltage on the measurement cycle of modified and non-modified OECT in different electrolytes: water, Ringer solution and Ringer-Locke solution (b)

This work was supported by the Russian Science Foundation (grant 19-73-30028).

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Electrical and Sensory Properties of BTBT-based Siloxane Dimers with Different Terminal Groups

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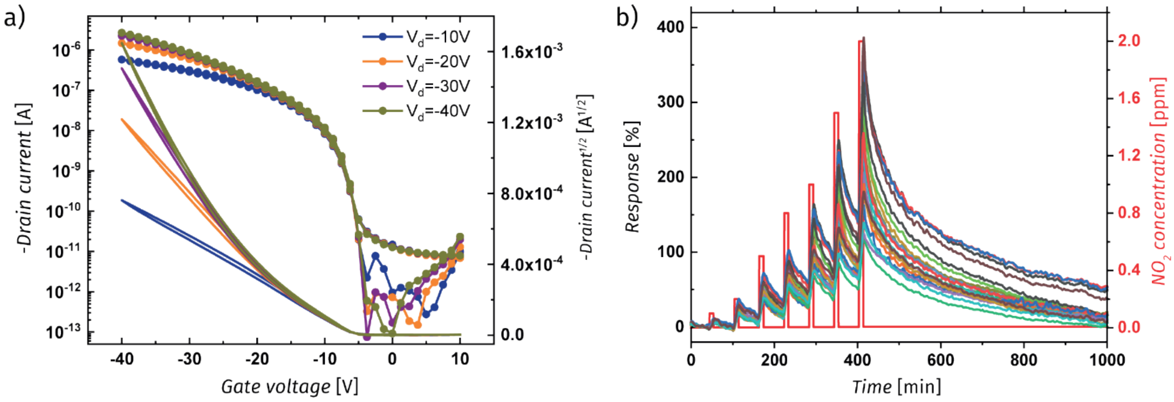
The usage of (ultra)thin-film organic field-effect transistors (OFET) as sensor devices for detecting various gases in the air atmosphere is one of the most promising directions in the creation of inexpensive portable gas analyzers. This creation is possible due to the fact that OFETs have a strong dependence of electrical properties on the environment, which is achieved by the direct interaction of active layer of the OFET with the analyte.[1] Siloxane dimer molecules based on BTBT can be successfully used in devices such as OFETs[2] or chemosensors, as shown in previously published works.[3] However, it is worth noting that there is no systematic study of the dependence of electrical and sensory properties on the chemical structure of the dimer. On the other hand such studies are quite important for understanding the working principle of such sensing devices.



Picture 1. Typical transfers curves (a) and response to NO_2 concentrations (b) of the OFETs investigated.

In this work, the properties of OFETs based on BTBT dimer with different terminal alkyl group length were thoughtfully investigated. The devices investigated demonstrate typical p-type behavior with extracted charge carrier mobilities, threshold voltages, and on–off ratios in the range of 10^{-5}–10^{-2} cm2 V^{-1} s^{-1}, −24 to +14 V, and 10^2–10^7, respectively (typical transfer curves are shown in Fig.1a). Such devices demonstrated good sensitivity to NO2 – up to 134%/ppm (typical response curves are shown a Fig.1b). At the same time, morphology investigation showed that devices with smooth and uniform morphology demonstrated better sensory properties. Probably, this is the reason why dependence of the device sensitivity on terminal alkyl group length is not monotonical. It also worth to mentioned that more investigations will be done in future to check if such morphology influence is common for other analytes.

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Order in crystalline and amorphous structures of π-conjugated organic molecules experimentally probed by low-frequency Raman spectroscopy

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High charge-carrier mobility in organic π-conjugated structures is a key for high performance organic electronic devices. In ordered structures the charge transport is expected to be more efficient, which is caused by strong intermolecular interaction limiting high magnitude intermolecular vibrations[1]. This effect could give an opportunity to use low-frequency (LF) Raman spectroscopy to control and estimate order in organic π-conjugated structures[2].

In this work crystalline and amorphous π-conjugated structures are used to demonstrate the lower relative intensity in the LF region of Raman scattering in more ordered structures in comparison with less ordered. As crystal structures we used the organic semiconductors with a relatively high theoretically calculated electron mobility. Those are four derivatives of naphthalene diimides with cyclo-hexyl (NDI-CHex)[ii], hexyl (NDI-Hex)[ii], butyl (NDI-But) and cyclo-pentyl (NDI-Cpen) substituents. As amorphous organic samples we investigate DNA and ribosome (rRNA) biomolecules[3] in different compactization states.

For samples with a crystalline structure, the relative intensity of LF Raman spectra correlates with the theoretical estimate of the ratio of the fluctuations of the transfer integral to the its value (that is a measure of order in crystalline structures) and with theoretical estimates of the charge mobilities. Thus, it is shown that in samples with a strong intermolecular interaction and, consequently, with a higher order, the intensity of vibrations in the LF region is weaker.

The amorphous structures of DNA and ribosome in more compacted states, which are considered as more ordered structures, demonstrate the lower relative intensity of LF Raman spectrum. We also track the changes in the DNA and ribosome spectra with time and observe that for the former, clear decrease of the LF intensity associated with solvent evaporation and denser packing is observed, while for the latter, the spectrum changes slightly because of the inherited compaction of the ribosome. Thus, in more ordered amorphous structures, the intensity of vibrations in the LF region appears to be weaker.

We show that the intensity of LF Raman scattering can be used to estimate and control the order in crystalline and amorphous organic π-conjugated structures.

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Time-resolved and spatially localized photoelectric effect in organic field effect transistors: modeling and experiment

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Organic field-effect transistors (Fig. 1a) can exhibit a photoelectric effect, i.e. act as phototransistors. Photoelectric effect should be more efficient in ambipolar transistors because both photogenerated electrons and holes can contribute to the photocurrent. In ambipolar transistors, the position of the electron-hole recombination zone in the channel can be controlled by the gate voltage, V_G. The typical width of this zone is in the range of 15-200 nm.[1] The ability to control the spatial position of the recombination zone can be used for studying the fundamental processes in organic semiconductors[2] and also is promising for development of new devices, such as optical image scanners with high spatial resolution.[3] In such ambipolar organic field-effect transistor, the recombination zone acts as a photosensitive region where the maximum electric field is achieved so that the photogenerated electron-hole pairs are efficiently separated. Using numerical modeling, it was shown that the normalized photocurrent J_{ph}/J_{dark} dependences on V_G can reproduce the spatial profiles of incident light intensity across the phototransistor channel, after transformation of the V_G-scale to x-scale in accordance with the position dependence of the electric field peak, x_{peak}, on V_G (Fig. 1b).[3]

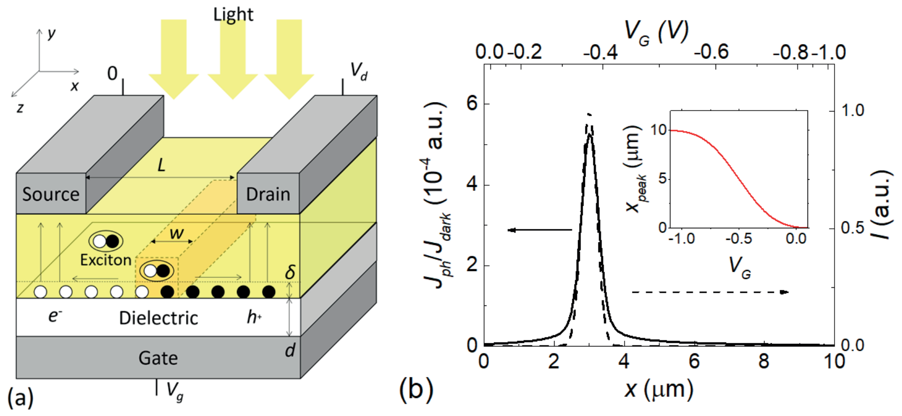

Fig. 1. Organic phototransistor scheme (a), response of the phototransistor (normalized photocurrent J_{ph}/J_{dark} vs V_G) to incident radiation with Gaussian distribution along x-axis (dashed line) (b).

Also modelling showed that the response times of such phototransistor can be about several nanoseconds.[4] Further it was shown by numerical modeling that the phototransistor performance with spatially localized photoelectric effect largely depends on the form of the e/h-pair dissociation rate dependence on the electric field; different forms of such dependences were studied. The results of modeling were supported by experimental data: spatially-localized photoelectric effect was observed in ambipolar organic field-effect transistor based on thin film of six-ring thiophene-phenylene co-oligomer with trimethylsilyl end groups.

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