



6th International Fall School
on Organic Electronics

Book of Abstracts



September 14-17, 2020
Moscow, Russia
<http://www.ifsoe.ru>

6th INTERNATIONAL FALL SCHOOL ON ORGANIC ELECTRONICS – 2020 (IFSOE-2020)

Organizers

Division of Chemistry and Material Science of Russian Academy of Sciences

The Ministry of Science and Education of Russia

Enikolopov Institute of Synthetic Polymeric Materials of Russian Academy of Sciences (ISPM RAS)

Lomonosov Moscow State University (MSU)

Printed Electronics Technologies Limited Liability Company (PrintElTech LLC)

Eklogit Limited Liability Company (Eklogit LLC)

Scientific program

- 1) **Fundamentals of organic electronics:** charge transport, modeling, photophysics, etc.
- 2) **Design and synthesis of materials for organic electronics:** organic conductors and semiconductors, dielectrics, substrates, etc.
- 3) **Organic field-effect transistors:** single crystal, polymer and monolayer OFETs, integrated circuits and related devices.
- 4) **Organic light-emitting devices:** OLEDs and OLETs, white light-emitting devices, TADF devices, organic lasers.
- 5) **Organic and hybrid solar cells:** small molecules and polymer photovoltaics, tandem cells, perovskites-based photovoltaics, etc.
- 6) **Organic sensors:** physical (pressure, temperature, photo, etc.) sensors, chemo- and biosensors.
- 7) **Characterization techniques:** various spectroscopy, microscopy, and x-ray scattering techniques, charge mobility measurements, thermal and surface analysis, HOMO and LUMO evaluation, biomedical applications, etc.
- 8) **Technologies of organic electronics:** printing of organic materials and devices, roll-to-roll techniques, ink formulations, encapsulation, etc.

School-conference Chairs

Prof. Sergey Ponomarenko (Enikolopov Institute of Synthetic Polymeric Materials of RAS, Russia)

Prof. Dmitry Paraschuk (Lomonosov Moscow State University, Russia)

International Advisory Board

Prof. Vladimir Agranovich (Institute for Spectroscopy RAS, Russia)

Prof. Mikhail Alfimov (Photochemistry Center of RAS, Russia)

Prof. Paul Berger (Ohio State University, USA)

Prof. Christoph Brabec (University Erlangen-Nürnberg, Germany)

Prof. Sergei Chvalun (National Research Center "Kurchatov Institute", Russia)

Prof. Vladimir Dyakonov (University of Würzburg, Germany)

Prof. Antonio Facchetti (Northwestern University, USA)

Prof. Sir Richard Friend (University of Cambridge, UK)

Prof. Marcus Halik (University Erlangen-Nürnberg, Germany)

Dr. Stephan Kirchmeyer (Heraeus Precious Metals GmbH, Germany)

Prof. Alexei Khokhlov (Lomonosov Moscow State University, Russia)

Prof. Guglielmo Lanzani (Politecnico di Milano, Italy)

Prof. Maxim Pshenichnikov (University of Groningen, the Netherlands)

Dr. Abderrahim Yassar (Ecole polytechnique, France)

Local Organizing Committee

Dr. Elena Agina – *Vice Chairman*

Victoria Chekusova – *workshop secretary*

Askold Trul

Daniil Anisimov

Polina Shaposhnik

School program

**The 6th International Fall School
on Organic Electronics – 2020 Time Schedule**
Moscow, Russia (GMT+3)

	Monday <i>September 14th</i>	Tuesday <i>September 15th</i>	Wednesday <i>September 16th</i>	Thursday <i>September 17th</i>			
	<i>School</i>						
9:45 - 10:00							
10:00 - 10:45					School opening Chihaya Adachi	Vladimir Dyakonov	
10:45 - 11:30					Christoph Brabec	George Malliaras	
11:30 - 12:00					Coffee-break		
12:00 - 12:30					Maxim Kazantsev	Maxim Scherbina	
12:30 - 13:00					Pavel Troshin	Artem Bakulin	
13:00 - 13:30					<u>Oral talks 1</u>	Dai Zhang	
13:30 - 14:30					Lunch		
14:30 - 16:00					<u>Poster session 1</u>	<u>Poster session 3</u>	
16:00 - 16:45					Coffee-break		Antoine Kahn
16:45 - 17:30	<u>Poster session 2</u>	<u>Poster session 4</u>	Daniel Frisbie	Natalie Stingelin			
17:30 - 18:00			Kostas Daoulas	Oana D. Jurchescu			
18:00 - 18:30				Johannes Gierschner			
18:30 - 19:00			<u>Oral talks 2</u>	<u>Oral talks 3</u>			
19:00 - 19:30				School closing			

Monday, September 14th

	Chair: <i>Dmitry Paraschuk</i>
9:45 – 10:00	School opening
10:00 – 10:45	T-1. <i>Chihaya Adachi</i> . Recent Progress in Advanced Blue TADF OLEDs
10:45 – 11:30	T-2. <i>Christoph Brabec</i> . Resolving Long Time Challenges in Emerging Photovoltaics with Autonomous Self-driven Labs
11:30 – 12:00	Coffee-break
	Chair: <i>Yuriy Luponosov</i>
12:00 – 12:30	I-1. <i>Maxim Kazantsev</i> . Highly-Luminescent Furan/Phenylene Co-Oligomers
12:30 – 13:00	I-2. <i>Pavel Troshin</i> . What is Killing Organic Photovoltaics: Light-induced Crosslinking as a General Degradation Pathway of Organic Conjugated Molecules
	<u>Oral talks 1.</u>
13:00 – 13:15	O-1. <i>Alexei Komolov</i> . Electronic Properties and Structuring of Vacuum Evaporated Molecular Films on Solid Surfaces
13:15 – 13:30	O-2. <i>Benedito A. L. Raul</i> . Excited State Dynamics in a Novel Solution Processable Triphenylamine-Based Small Molecule for Organic Optoelectronics
13:30 – 14:30	Lunch
14:30 – 16:00	<u>Poster session 1 (P-1 – P-17)</u>
16:00 – 16:30	Coffee-break
16:30 – 18:00	<u>Poster session 2 (P-18 – P-34)</u>

Tuesday, September 15th

	Chair: <i>Artem Bakulin</i>
10:00 – 10:45	T-3. <i>Vladimir Dyakonov</i> . Spectroscopy of Organic and Hybrid Materials and Thin-film Optoelectronic Devices - a Delicate Issue
10:45 – 11:30	T-4. <i>George Malliaras</i> . Electronics on the Brain
11:30 – 12:00	Coffee-break
	Chair: <i>Maxim Kazantsev</i>
12:00 – 12:30	I-3. <i>Maxim Shcherbina</i> . Modern Approaches to the Studies of Thin Films and Monolayers: X-Ray Reflectometry, Grazing Incidence Scattering and Standing Waves
12:30 – 13:00	I-4. <i>Artem Bakulin</i> . Ultrafast Spectroscopy of Electron-phonon Effects in Hybrid Perovskite Electronic Materials

13:00 – 13:30	I-5. <i>Dai Zhang</i> . Revealing the Photo-physical Properties of Optoelectronic Materials at the Nanometer Scale Using Optical Microscopy
13:30 – 14:30	Lunch
14:30 – 16:00	Poster session 3 (P-35 – P-50)
16:00 – 16:30	Coffee-break
16:30 – 18:00	Poster session 4 (P-51 – P-66)

Wednesday, September 16th

	Chair: <i>Vladimir Dyakonov</i>
16:00 – 16:45	T-5. <i>Antoine Kahn</i> . Electronic Properties of Contacts to Organic Semiconductors
16:45 – 17:30	T-6. <i>Daniel Frisbie</i> . Imaging Defects and Electronic Disorder in Organic Semiconductors
17:30 – 18:00	I-6. <i>Kostas Daoulas</i> . Multiscale Modelling of Semiconducting Polymers
	Oral talks 2. Chair: <i>Oleg Borshchev</i>
18:00 – 18:15	O-3. <i>Alexandra Freidzon</i> . Thermally Activated Delayed Fluorescence in Organic Semiconductors: A Quantum Chemical Study
18:15 – 18:30	O-4. <i>Rishabh Saxena</i> . A Kinetic Monte Carlo Study of Triplet-triplet Annihilation in Conjugated Luminescent Materials
18:30 – 18:45	O-5. <i>Jeannine Grüne</i> . Interplay Between RISC and TTA in Exciplex-based TADF OLEDs
18:45 – 19:00	O-6. <i>Andrey Sosorev</i> . Organic Nanoelectronics Inside Us: Charge Transport and Localization Within tRNA Could Orchestrate Ribosome Operation
19:00 – 19:15	O-7. <i>Yuriy Luponosov</i> . Novel Star-shaped Donor-acceptor Molecules for Bulk Heterojunction and Single-material Organic Solar Cells

Thursday, September 17th

	Chair: <i>Dmitry Paraschuk</i>
16:45 – 17:30	T-7. <i>Natalie Stingelin</i> . The Principles of Manipulating the Phase Transformations, Solid-state Order and Properties of Organic Functional Matter
17:30 – 18:00	T-8. <i>Oana D. Jurchescu</i> . Charge Injection in Organic Field-Effect Transistors: from Fundamentals to Applications
18:00 – 18:30	I-7. <i>Johannes Gierschner</i> . Dual Emission: Classes, Mechanisms and Conditions
	Oral talks 3.
18:30 – 18:45	O-8. <i>Sergey Novikov</i> . Charge Carrier Recombination in Amorphous Organic Semiconductors

18:45 – 19:00	O-9. Nikitenko Vladimir . Extended Description of Hopping Transport by the Multiple Trapping Model
19:00 – 19:30	School closing

Poster session 1

Monday, September 14th, 14:30

Abramov, Anton A.	P1	Portable Device for Measuring of OFETs Array Parameters Allowing Detection and Determination of Various Gases
Agafonova, Ekaterina E.	P2	Revealing the Impact of Small Molecular Hole-Transport Materials on the Performance of Perovskite Solar Cells
Akbulatov, Azat F.	P3	Intrinsic Stability Challenges in Design of Absorber Materials for Lead Halide Perovskite Solar Cells
Avrorov, Pavel A.	P4	Electrochemical reduction of polyfluorinated quinoxalines
Avrorov, Pavel A.	P5	Electrochemical reduction of fluorinated/chlorinated 2,1,3-benzothia/selenadiazoles
Balakirev, Dmitry O.	P6	Novel donor small molecules based on benzotriindole and benzodithiophene cores: synthesis, properties and application in organic solar cells
Borzdu, Natalia I.	P7	Carboxyl-Containing Asphaltenes as Promising Acceptor Materials for Bulk Heterojunction Solar Cells
Chetyrkina, Margarita R.	P8	Biocompatibility assessment of organic semiconductors in the context of their application in wearable and on-skin electronics
Dolzhikova, Ekaterina A.	P9	Simple interfacial passivation for HTL-free perovskite solar cells with carbon top electrodes
Dyadishchev, Ivan V.	P10	Synthesis and properties of luminescent oligo(phenylene-thiophene)s with various types of solubilizing groups
Emelianov Nikita A.	P11	Neuro-like oscillators system based on PANI/PVDF-TrFE memristor
Fedina, Elena S. / Somova Anna I.	P12	Poly-(N-methylaniline) and dihydrophenazine-based copolymers as promising cathode materials for dual-ion batteries
Fedorenko, Roman S.	P13	High performance 2D field-effect transistors based on novel tetrathienothiophene derivatives
Gudeika Dalius	P14	Methoxycarbazolyl-substituted oxygafluorenes as bipolar hosts for PhOLED and TADF-based OLEDs
Kalinichenko, Nadezhda K.	P15	Synthesis and study of properties of linear oligothiophenes end-capped with methyldicyanovinyl and ethyl cyanoacetate groups
Kapaev, Roman R.	P16	New ladder-type conjugated polymer with hexaazatriphenylene fragments as a cathode material for Li-, Na- and K-based batteries
Komarov, Denis S.	P17	Novel Anolyte Material for High Voltage Non-Aqueous Organic Redox Flow Batteries

Poster session 2

Monday, September 14th, 16:30

Borshchev, Oleg V.	P18	New organic semiconductors for organic electronics
Borshchev, Oleg V.	P19	New organic luminophores for scintillation and wavelength shifting fibers
Komarov, Pavel V.	P20	Design of multiscale simulation models of photovoltaic polymeric nanocomposites

Krysko, Ilya D.	P21	Hole hopping in dimers of N,N'-di(1-naphthyl)-N,N'-diphenyl-4,4'-diamine (α -NPD): a theoretical study
Kushch, Nataliya D.	P22	Novel organic metal BEDO ₄ Dy(OH) ₆ ·4(H ₂ O) (H ₂ OW3-H-OW3H ₂), based on π -donor BEDO and [Dy(NO ₃) ₅] ²⁻ anion: synthesis, structural peculiarities and conductivity.
Kusnetsov, Ilja E.	P23	Synthesis of novel (X-DADAD) _n polymers with fluorene and phenylene X blocks and their application in organic solar cells
Mandal, Suman	P24	Organic field-effect transistors-based flexible temperature sensor for healthcare applications
Mikheeva, Aleksandra N.	P25	Incorporation of vanadium (V) oxide in hybrid hole transport layer enables long-term operational stability of perovskite solar cells
Mikheeva, Maria M.	P26	Exploring the substitution of Pb ²⁺ with Ca ²⁺ in the CsPbI ₃ perovskite system
Moshkina, Tatiana N.	P27	Benzodiazine derivatives: synthesis and fluorescence sensory ability
Mosina, Ekaterina V.	P28	Design of hybrid hole-transport layers for efficient and stable perovskite solar cells
Obrezkov, Filipp A.	P29	Polydiphenylamine-based cathodes for dual-ion batteries
Ozerova, Victoria V.	P30	Impact of surface passivation coatings on intrinsic photochemical and thermal stability of lead halide perovskites
Parfenov, Alexey A.	P31	Highly sensitive and selective ammonia gas sensor based on FAPbCl ₃ lead halide perovskite
Polinskaya, Marina S.	P32	Design and synthesis of functional derivatives of [1]benzothieno[3,2-B][1]-benzothiophene for use in organic electronic
Rohnacher, Valentina	P33	Design of a Novel Tetrapodal Self-Assembled Monolayer for Functional Engineering of Interfaces
Zaborin, Evgeniy A.	P34	Synthesis and properties of novel nanostructured organosilicon luminophores for scintillation and wavelength shifting fibers

Poster session 3

Tuesday, September 15th, 14:30

Anisimov, Daniil S.	P15	Predicting properties of OFET-based sensors by their electrical characteristics
Dominskiy, Dmitry I.	P36	Study of charge injection in thiophene-phenylene co-oligomers via their terminal substitution
Doroshkevich, Aleksandr S.	P37	Hydrophilic organo-inorganic composite systems based on ZrO ₂ nanopowders –the promising materials for adsorption electronics and power engineering
Khmelnitskaya, Alina G.	P38	Dielectric properties of polymer composites based on polydimethylsiloxane and carbon fillers
Proshin, Pavel I.	P39	Novel thiazolothiazole-based donor-acceptor conjugated polymers for large-area organic solar cells
Romadina, Elena I.	P40	New Low Bandgap Polymer for Self-Powered Organic Near-Infrared Photodetectors

Roy Dhrubojyoti	P41	Enhanced non-volatile attribute of FeFET based Memory Device via tuning of ferroelectric microstructure
Saunina, Anna Yu.	P42	An analysis of J-V characteristics of QD-based photovoltaic cells from a theoretical model
Saxena, Rishabh	P43	A kinetic Monte Carlo study of triplet-triplet annihilation in conjugated luminescent materials
Shcherbakov A. G.	P44	Polyimides based on NTCDAs and p- or m-phenylenediamines as cathode materials for potassium batteries
Shundrin, Leonid A.	P45	Ambipolar polyimides with pendant groups based on 9H-thioxanthene-9-one derivatives: synthesis, thermostability, electrochemical and electrochromic properties
Skorotetsky, Maxim S.	P46	Tetrathienoacene derivatives for monolayer field-effect transistors
Solodukhin, Alexander N.	P47	Effects of thiophene π -spacer length and fused triphenylamine core on properties of star-shaped molecules for organic solar cells and photodetectors
Sukhorukova, Polina K.	P48	Novel star-shaped benzotriindole-based donor-acceptor molecule for organic photovoltaics
Tepliakova, Marina M.	P49	Strength of Attraction: Pyrene-based Hole-transport Materials with Effective π - π Stacking for Dopant-free Perovskite Solar Cells
Trul, Askold A.	P50	Inkjet printed OFETs for gas sensing of toxic gases

Poster session 4

Tuesday, September 15th, 16:30

Bezsudnov, Igor V.	P51	Two-phase composite employing liquid-gas phase transition for large volume expansion
Chekusova, Victoria P.	P52	LS monolayer OFETs with outstanding electrical performance as highly sensitive gas sensors to ethyl mercaptan
Kuevda, Alexsey V.	P53	Photoluminescence anisotropy in organic 2D semiconductors
Mannanov, Artur L.	P54	Spectral technique for precise efficiency measurements of various types of advanced solar cells
Parashchuk, Olga D.	P55	Anisotropic low-frequency Raman scattering in organic semiconductors for probing non-local electron-phonon interaction
Shaposhnik, Polina A.	P56	Water-gated organic field-effect transistor based on the blend of 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene and polystyrene
Titova, Yaroslava O.	P57	Ink-jet printing of PEDOT:PSS for organic electronic devices
Trukhanov, Vasiliy A.	P58	Electroluminescent 2D organic semiconductor single crystals with high charge-carrier mobility
Ulyankin, Evgeny B.	P59	Photochemical synthesis of 4H-thieno[3,2-c]chromene derivatives
Ustinova, Marina I.	P60	Impact of lead substitution on stability and photovoltaic performance of lead halide perovskites

Vaneeva, Elizaveta E.	P61	Liquid metal melt electrodes for low-cost perovskite solar cells
Vavilina, Regina R.	P62	The influence of electron-transport layer materials on the electrochemical stability of perovskite solar cells
Yamilova, Olga R.	P63	Influence of the hole-transport layer on the electrochemical stability of perovskite solar cells
Zelenyak, Tatyana Yu.	P64	Studies of the influence of water molecules on the perovskite structure $\text{CH}_3\text{NH}_3\text{PbI}_3$
Zvyagina, Alexandra I.	P65	Self-assembly of Lanthanide Double-Decker Crown-substituted Phthalocyaninates into 1D-Supramolecular Semiconductors
Maslennikov, Dmitry R.	P66	Photocurrent vibrationally promoted electronic resonance spectroscopy for probing electron-phonon couplings in perovskite solar cells

Tutorial lectures

Recent Progress in Advanced Blue TADF OLEDs

J.U. Kim¹, T.B. Nguyen¹, C.-Y. Chan¹, M. Tanaka¹, H. Nakanotani¹, Ch. Adachi^{1*}

¹Center for Organic Photonics and Electronics Research (OPERA), Kyushu University

*e-mail: adachi@opera.kyushu-u.ac.jp

Organic light-emitting diodes (OLEDs) are one of the most promising devices for next-generation displays and lighting sources. By using thermally-activated delayed fluorescence (TADF) molecules as an emitter for OLEDs, internal electroluminescence (EL) quantum efficiency (IQE) of nearly 100% can be achieved.¹ However, an operational device lifetime of TADF-OLEDs, especially blue-OLEDs, still falls short to use for practical applications. Thus, the quest for a new generation, high-performance blue-OLED is still ongoing. In this talk, we mention our recent two promising strategies for enhancing the device performance of blue TADF-OLEDs.

In TADF system, triplet excitons are efficiently upconverted from a lowest triplet state (T_1) to the lowest excited singlet state (S_1) by a reverse intersystem crossing (RISC) process, governed by a small energy gap (ΔE_{ST}) between the S_1 and T_1 states, resulting in a maximum η_{int} of nearly 100%. Eventually, high external quantum efficiencies (η_{ext}) of over 20% have been achieved for TADF-OLEDs. Advanced blue TADF molecules with ideally short exciton lifetimes ($< 1 \mu s$) are thus essentially required for high stability OLEDs, since OLED stability is closely related to triplet population. According to the first-order perturbation theory, i.e., Fermi's golden rule, k_{RISC} between the two states is proportional to $\langle S_1 | \hat{H}_{SOC} | T_1 \rangle / \Delta E_{ST}$. Using this relationship, minimization of ΔE_{ST} is a widely adopted strategy to achieve efficient intramolecular charge-transfer (CT) of TADF molecules. However, the spin-flip processes, i.e., intersystem crossing ISC and RISC, between excited CT singlet (1CT) and triplet (3CT) states are very inefficient according to the El-Sayed rule because of the independent electric dipole moment with an electron spin, resulting from a weak SOC matrix element. In contrast, remarkably strong SOC can be expected when the spin-flip processes arise between the CT and energetically close-lying locally excited (LE) states with different spin multiplicities owing to the orbital angular momentum change between the two states. Several groups have reported that k_{RISC} is accelerated by the strong SOC matrix element between the 1CT (S_1) and 3LE (T_2) states, caused by non-adiabatic vibronic coupling (\hat{H}_{VC}) between the 3CT (T_1) and 3LE (T_2) states. In our first strategy, we demonstrate that a small modulation in excited states of an aromatic organic molecule, mediated by spin-orbit coupling between 1CT and 3LE states, greatly affects the rate constants of a TADF molecule. As a result, we attained an ideal nano-second-scale exciton lifetime of 750 ns in a deep-blue TADF molecule (TMCz-BO), which can drastically minimize efficiency rolloff in TADF-OLEDs.²

Next, we mention second strategy for enhancing blue TADF-OLEDs that use exciplexes. Exciplex is an excited-complex of a pair between electron-donating (exciplex donor) and electron-accepting (exciplex acceptor) molecules. Such pair can generate a highly spatial separation of a highest occupied molecular orbital (HOMO) from a lowest unoccupied molecular orbital (LUMO), effectively reducing energy splitting (ΔE_{ST}) between the lowest singlet and triplet excited states (S_1 and T_1). Thus, efficient reverse intersystem crossing (RISC) can be achieved. Therefore, it has been widely considered to develop TADF-exciplex systems aimed for high performance OLEDs. In this study, we propose an acceptor molecule designing strategy to enhance an operational device stability of exciplex-based OLEDs. We demonstrate that direct charge recombination onto an exciplex acceptor serves as a possible degradation mechanism. Under device operation, injected holes into an emissive layer (EML) can be accumulated and increase hole-density at the D/A interface. This high charge density, in turn, injects holes into the HOMO of acceptor molecules, leading to unwanted exciton generation, damaging the exciplex system. Second, we hypothesize that by adding an electron-donating group to an exciplex acceptor, the OLED stability can be greatly enhanced. Such an exciplex acceptor would possess both an electron donating (D) group and an electron accepting (A) group, hence named as a D-A type acceptor. The D group is responsible for HOMO, acting as a stabilizer for unwanted hole-injection. Further, careful selection of a D moiety would provide a TADF-type acceptor. When unwanted carrier recombination happens on the TADF-type acceptor, the electrically generated triplets can be converted to the S_1 state through RISC. After that, the S_1 energy of the acceptor molecule then again decays to the exciplex formation, i.e., "recycling" of excitons. We demonstrate that this strategy greatly contributes for enhancing device stability in blue TADF-OLEDs.³

This research was supported by JST-ERATO, Regional Innovation Eco-system Program (MEXT) and Kyulux Inc.

¹ H. Uoyama; K. Goushi; K. Shizu; H. Nomura; Ch. Adachi, *Nature*, 2012, **492**, 234.

² J.U. Kim; I.S. Park; Ch.-Y. Chan; M. Tanaka; Y. Tsuchiya; H. Nakanotani; Ch. Adachi, *Nature Communications*, 2020, **11**, 1765.

³ T.B. Nguyen; H. Nakanotani; T. Hatakeyama; Ch. Adachi, *Advanced Materials*, 2020, **32**, 9, 1906614.

Resolving Long Time Challenges in Emerging Photovoltaics with Autonomous Self-driven Labs

C.J. Brabec¹

¹Friedrich-Alexander Universitat Erlangen-Nurberg

The development of high performance, stable solar cell materials poses a multi-objective optimization problem in a considerable multidimensional parameter space. Solving it requires reproducible, user independent laboratory work and intelligent preselection of conducted experiments. However, research on emerging photovoltaics, including organic (OPV), perovskites (PSC) or quantum dot solar cells is a field where manual routines are still predominant, although other domains like pharmacy have long used robotics and automation.

To better utilize automation in materials science, we introduce AMANDA (Autonomous Materials and Device Application Platform), a generic software framework for distributed materials research and its research line LineOne (L1), a robotic facility for the production and characterization of solution processed solar cells. We integrated pipetting and transport robots with spin coating and evaporation units as well as characterization tools like spectrometers and electrical measurements into LineOne. With this setup, the AMANDA Platform automatically produces and measures solution processed solar cells without human interaction while it is capable of rapidly screening large materials and processing parameter spaces in a combinatorial approach at high precision. The current hardware configuration is fully scalable and allows the high throughput screening of up to 270 variations per day on LineOne. The output comprises the complete fabrication of solar cells, full characterization and comprehensive documentation of all applied process steps as well as compiled results for each individual solar cell. We demonstrate the capabilities of AMANDA by exploring the optimum in terms of efficiency and stability for OPV solar cells based on PM6:Y6 as well as by high throughput screening of stable perovskite compositions for efficient solar cells.

Spectroscopy of Organic and Hybrid Materials and Thin-film Optoelectronic Devices - a Delicate Issue

*V. Dyakonov*¹

¹Julius-Maximillian University of Würzburg

According to the title, the main purpose of the presentation is to draw attention to some issues related to the evaluation of carrier lifetime in organic or hybrid (perovskite) semiconductors and thin-film devices and the role of ions. Lifetime evaluation of solar cells is frequently conducted via both optical and electrical means with the purpose of obtaining a deeper understanding of the dominant performance limiting recombination mechanisms. However, these (relatively easily measurable) lifetimes are often strongly influenced by capacitive effects due to spatially separated charge carriers in devices, which leads to unrealistically long times and causes complicated interpretations of the sometimes observed differences between optically and electrically determined lifetimes. We will discuss the peculiarities and limitations of transient photovoltage and photocurrent techniques, as well as time-resolved photoluminescence applied to methylammonium lead iodide perovskite solar cells and films.^{1,2}

Another example is the role of mobile ions in perovskites and their influence on the optoelectronic devices. The difficulty in studying electronic properties of solar cells results from the screening effects as well as slow dynamics of mobile ions, particularly if they are located at the interfaces. A well-established experimental technique to study the space charge distributions in semiconductors is the Mott-Schottky (MS) analysis based on capacitance–voltage measurements. However, the characteristic MS behavior with a linear dependence of $C^{-2}(V)$, distinctive for a pn-junction, is not visible in pristine devices. We show how capacity and voltage measurements can nevertheless be used to identify the mobile ion concentration in perovskite solar cell devices.³

¹ K. Tvingstedt et al., *ACS Energy Lett.* 2017, **2**, 424.

² L. Kudriashova et al., *J. Phys. Chem. Lett.*, 2017, **8**, 4698.

³ M. Fischer et al., *ACS Appl. Energy Mater.*, 2018, **1**, 5129.

Electronics on the Brain

G. Malliaras¹

¹Department of Engineering, University of Cambridge

One of the most important scientific and technological frontiers of our time is the interfacing of electronics with the human brain. This endeavour promises to help understand how the brain works and deliver new tools for diagnosis and treatment of pathologies including epilepsy and Parkinson's disease. Current solutions, however, are limited by the materials that are brought in contact with the tissue and transduce signals across the biotic/abiotic interface. Recent advances in organic electronics have made available materials with a unique combination of attractive properties, including mechanical flexibility, mixed ionic/electronic conduction, enhanced biocompatibility, and capability for drug delivery. I will discuss the mechanism of operation of these devices and explain how organic electronic materials can be utilised to study the brain and treat its pathologies.

Fundamental Electronic Properties of Contacts to Organic Semiconductors

*A. Kahn*¹

¹Dept. of Electrical Engineering, Princeton University

Electrode-organic contacts play a key role in the operation of organic electronic devices. Efficient charge carrier injection and collection across interfaces requires control of interface chemical and electronic properties. Yet a simple prediction of interface electronic structure based on the electronic properties of the separated constituents is generally not possible. The first part of the talk reviews very fundamental issues of metal-semiconductor interfaces, including various mechanisms of interface Fermi level pinning. We then look at examples of interactive vs. non-interactive organic interfaces and consequences for energy barriers and carrier injection. Finally, we look at the process of modifying electrode-organic interfaces via self-assembled monolayers of dipolar molecules, or via chemical doping to render the electrode material and work function irrelevant.

Imaging Defects and Electronic Disorder in Organic Semiconductors

C.D. Frisbie^{1*}

¹ *Department of Chemical Engineering and Materials Science, University of Minnesota*

*e-mail: frisbie@umn.edu

The central thesis of this talk is that many structural defects in crystalline organic semiconductors have surface potential signatures that can be recorded and imaged by scanning Kelvin probe microscopy (SKPM) with sub-100 nm resolution.^{1,2,3,4,5} This allows straightforward visualization of defects that are difficult to detect by other methods. Additionally, we argue that surface potential fluctuations are a direct measure of static electronic disorder, namely band edge variations, that will impact electron and hole transport. Thus, surface potential imaging not only reveals defects in crystalline organic semiconductors but importantly provides a direct link to electronic disorder (e.g., traps, scattering centers) that degrade transport performance. This talk will focus on three illustrative examples based on thin films and single crystals of benchmark organic semiconductors,^{2,4,5,6} including one case where we can make a thorough connection between structure, surface potential, and field effect transport.⁵ We propose that in many cases the surface potential contrast associated with a given defect arises due to inhomogeneous strain around the defect. To support this, we further describe the first direct measurements of the strain-surface potential relationship for macroscopic single crystals of rubrene³ and tetracene.⁶ Overall, we suggest that surface potential measurements are a powerful approach to understanding correlated structural and electronic disorder in soft organic semiconductors.

We acknowledge funding by the US National Science Foundation.

¹ K. Puntambekar, J. Dong, G. Haugstad, C.D. Frisbie, *Adv. Funct. Mater.* 2006, **16**, 879.

² V. Kalihari, D.J. Ellison, G. Haugstad, C.D. Frisbie, *Adv. Mater.* 2009, **21**, 3092.

³ Y. Wu, A.R. Chew, G. Rojas, G. Sini, G. Haugstad, A. Belianinov, S.V. Kalinin, H. Li, C. Risko, J.L. Bredas, A. Salleo, C.D. Frisbie, *Nature Commun.* 2016, **7**, 10270.

⁴ Y. Wu, X. Ren, K.A. McGarry, M.J. Bruzek, C.J. Douglas, C.D. Frisbie, *Adv. Electron. Mater.* 2017, **3**, 1700117.

⁵ T. He, Y. Wu, G. D'Avino, E. Schmidt, M. Stolte, J. Cornil, D. Beljonne, P.P. Ruden, F. Wuerthner, C.D. Frisbie, *Nature Commun.* 2018, **9**, 2141.

⁶ Z. Zhang, G. Yu, J.G. Barriocanal, Z. Xie, C.D. Frisbie, *ACS Appl. Mater. Interfac.* 2020, **12**, 40607.

The Principles of Manipulating the Phase Transformations, Solid-state Order and Properties of Organic Functional Matter

N. Stingelin^{1*}

¹Department of Materials and Centre for Plastic Electronics, Imperial College London

*e-mail: n.stingelin-stutzmann@imperial.ac.uk

In the past decade, significant progress has been made in the field of organic functional materials with many new opportunities arising in the field of bioelectronics, energy harvesting and storage, organic electronics and photonics, etc. This progress has predominantly been due to important improvements of existing materials and the creation of a wealth of novel compounds. Many challenges, however, still exist. Intimate knowledge of relevant structure/processing/performance interrelations are required to further advance this interesting class of materials and to open new application platforms. Here, examples are given of how materials scientists 'tools' may be utilized to gain further understanding of organic functional matter and how the physical organization, from the molecular to the macroscale of functional organic matter such as polymer semiconductors can be controlled. To this end, we present a survey on the principles of structure development from the liquid phase of this materials family with focus on how to manipulate their phase transformations and solid-state order to tailor and tune the final 'morphology' towards technological and practical applications.

Charge Injection in Organic Field-Effect Transistors: from Fundamentals to Applications

*O.D. Jurchescu*¹

¹Department of Physics and Center for Functional Materials, Wake Forest University

Organic semiconductors are intensely studied for incorporation in low-cost, lightweight, flexible devices, but their commercialization is delayed by inadequate performance. Inefficient charge injection at the electrode/semiconductor interface represents a significant hurdle in the pursuit of the promised potential of organic semiconductors. Moreover, with increasing the effective mobility of organic semiconductor layer and reducing the channel dimensions, this problem becomes even more prevalent. In this talk, I will describe the origin of contact effects in organic devices, with emphasis on organic field-effect transistors (OFET). I will introduce several different methods used for evaluation of contact resistance. Several types of manifestations of contact effects will be presented, as well as their impact on the device characterization.¹ I will discuss methods for reducing contact resistance and will describe a simple strategy consisting of developing high work function surface domains at the surface of the injecting electrodes to promote channels of enhanced injection.² This led to contact resistances of 200 Ωcm and device charge carrier mobilities of 20 cm^2/Vs independent of the applied gate voltage. The proposed approach is efficient for both small molecule and polymeric thin-film transistor devices and can be generally applied in all common processes and device architectures. In addition to allowing the demonstration of high-mobility transistors with near ideal current-voltage characteristics, the use of this method will also lead to accurate measurement of the charge carrier mobility, a critical step in a rational material design.

¹ M. Waldrip, O. D. Jurchescu, D. J. Gundlach, and E. G. Bittle, *Adv. Funct. Mater.*, 2020, **30**, 1904576.

² Zachary A. Lamport, Katrina J. Barth, Hyunsu Lee, Eliot Gann, Sebastian Engmann, Hu Chen, Martin Guthold, Iain McCulloch, John E. Anthony, Lee J. Richter, Dean M. DeLongchamp, and Oana D. Jurchescu, *Nature Commun.*, 2018, **9**, 5130.

Invited lectures

Highly-Luminescent Furan/Phenylene Co-Oligomers

M.S. Kazantsev^{1*}

¹N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry SB RAS,

*e-mail: maximkazantsev1988@gmail.com

Materials combining high luminescence efficiency and efficient charge transport are in strong demand for organic optoelectronics due to potential applications in various light-emitting devices, e.g. light-emitting diodes, transistors and lasers.^{1,2} Attainment of both functionalities possesses a great challenge because high mobility requires close molecular packing that usually leads to very weak emission.³ However a lucky combination of these properties were reported for materials based on heteroaryl-containing co-oligomers which are considered to be the most promising emissive organic semiconductors. Furan incorporation was also proved to be a powerful tool for an increase of luminescence efficiency, molecular rigidity and solubility, highly favorable for industrial applications.⁴

This talk overviews our recent progress on the synthesis and systematic study of a linear furan/phenylene co-oligomers, their optoelectronic properties^{4,5} to suggest tools^{6,7} for tuning of their crystal packing, physico-chemical properties and performance. The effects of conjugation length, introduction of substituents, full or partial introduction of fluorine atoms in phenyl(ene) rings, full or partial annulation and doping are discussed.

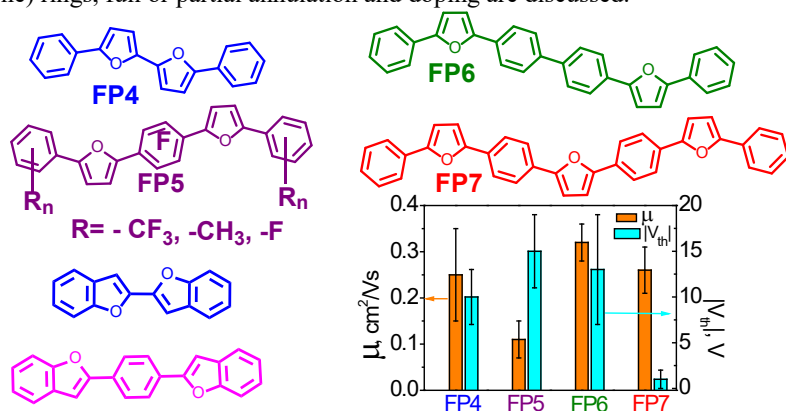


Figure 1. Chemical structures of furan/phenylenes and their modifications by annulation, partial fluorination and substitution; effect of the conjugation length on the charge transport.

This work was supported by RSF (project 20-73-10090).

¹ S. Hotta et al., *J. Mater. Chem. C*, 2014, **2**, 965.

² J. Gierschner et al, *Adv. Optical. Mater.*, 2016, **2**, 348.

³ S. Varghese et al., *J. Phys. Chem. Lett.*, 2011, **8**, 863.

⁴ M. Kazantsev et al, *RSC Adv.*, 2016, **6**, 92325.

⁵ M. Kazantsev et al., *Org. Electron.*, 2019, **56**, 208.

⁶ M. Kazantsev et al., *CrystEngComm*, 2017, **19**, 1809.

⁷ A. Sonina et al., *Acta Crystallogr. B*, 2018, **74**, 450.

What is Killing Organic Photovoltaics: Light-induced Crosslinking as a General Degradation Pathway of Organic Conjugated Molecules

O.R. Yamilova^{1,3}, I.V. Martynov³, A.V. Akkuratov³, L.N. Inasaridze³, A.V. Mumyatov³, N. Stingelin², P.A. Troshin^{1,3}

¹Skolkovo Institute of Science and Technology

²Georgia Institute of Technology

³Institute for Problems of Chemical Physics of Russian Academy of Sciences (IPCP RAS)

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. The light-induced dimerization of fullerene-based acceptor materials discovered recently is considered to be one of the main causes for burn-in degradation of organic solar cells. In this work, we reveal the mechanism of the light-induced dimerization of the fullerene derivatives and establish important correlations with their molecular structure and electronic properties.

We also show that conjugated polymers and small molecules undergo similar light-induced crosslinking regardless of their chemical composition and structure. In case of conjugated polymers, crosslinking leads to a rapid increase in their molecular weight and consequent loss of solubility, which can be revealed in a straightforward way by gel permeation chromatography analysis via a reduction/loss of signal and/or smaller retention times.

Our results, thus, shift the paradigm of research in the field toward designing a new generation of organic absorbers with enhanced intrinsic photochemical stability in order to reach practically useful operation lifetimes required for successful commercialization of organic photovoltaics.

Modern Approaches to the Studies of Thin Films and Monolayers: X-Ray Reflectometry, Grazing Incidence Scattering and Standing Waves

*M. Shcherbina*¹

¹Enikolopov Institute of Synthetic Polymeric Materials RAS

The review concerns modern experimental methods of structure determination of thin films of different nature. The methods are based on total reflection of X-rays from the surface and include X-ray reflectivity, grazing-incidence X-ray scattering and X-ray standing waves. Their potential is exemplified by the investigations of various organic macromolecular systems that exhibit the properties of semiconductors and are thought to be promising as thin-film transistors, light-emitting diodes and photovoltaic cells. It is shown that combination of the title methods enable high-precision investigations of the structure of thin-film materials and structure formation in them, i.e., it is possible to obtain information necessary for improvement of the operating efficiency of elements of organic electronic devices.

Considered X-ray methods are nondestructive and do not require special sample preparation. They are used to obtain valuable and versatile information on specific features of the morphology and quality of the surface of thin films and on structure formation in them. This, in turn, serves as methodological basis for new approaches aimed at optimizing the structure and improving the efficiency of thin-film electronics devices. Further progress in X-ray materials science is associated with utilization of modern sources of synchrotron radiation and high-performance computational facilities to elucidate the 3D structure of materials including synchrotron X-ray.

This work is supported by the Russian Scientific Foundation (Project No. 19-73-20236).

Ultrafast Spectroscopy of Electron-phonon Effects in Hybrid Perovskite Electronic Materials

A.A. Bakulin^{1*}

¹Department of Chemistry, Imperial College London, London SW7 2AZ, UK
*e-mail: a.bakulin@imperial.ac.uk

Over the past several years, organohalide perovskites have proven to be one of the most interesting and promising materials for next-generation solar cells. However, they possess unusual properties of soft structure and high dynamic disorder, which arise from the interplay between the organic and inorganic sublattices that make up the material. Overall, we still lack a comprehensive understanding of the dynamical behaviour of within organohalide perovskites and how electron-phonon coupling effects electronic properties of the material on fast and slow timescales.

In this contribution, I will present several case studies that help to shed light on the electron phonon interactions and dynamics of the organic cations that make up the organic sublattice in these materials. The 2DIR approach reveals the orientational cation dynamics in the material and how these dynamics are effected by the material composition,¹ doping and by the interfaces with carrier extraction layers,² typically used in perovskite optoelectronic devices. Finally, using new photocurrent-based electron-vibrational spectroscopy I will show how electronic states are affected by their interplay with the organic sublattice and how this interplay may give rise to coupling between the organic and inorganic parts of the perovskite.

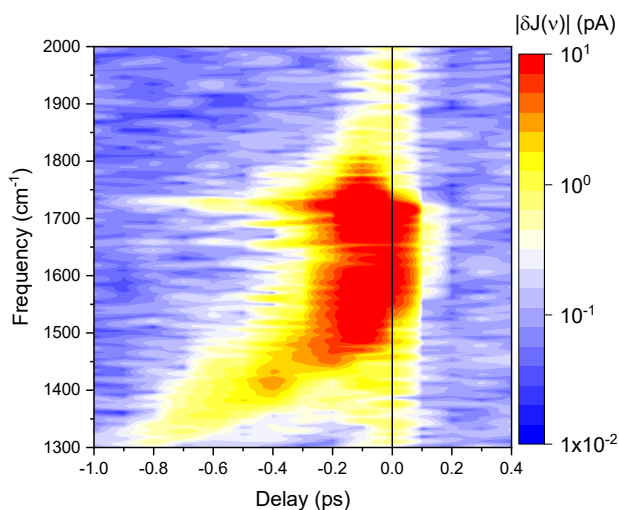


Figure 1. Photocurrent VIPER signal in FAPbBr₃ perovskite, showing coupling between cation vibrations and electronic states of the material.

¹ Gallop N.P., et al , Rotational Cation Dynamics in Metal Halide Perovskites: Effect on Phonons and Material Properties, *J. Phys. Chem. Lett.* 2018, **9**, 5987

² Sung, W; et al. Preferred orientations of organic cations at lead-halide perovskite interfaces revealed using vibrational sum-frequency spectroscopy, *Mater. Horiz.*, 2020, **7**, 1348-1357

Revealing the Photo-physical Properties of Optoelectronic Materials at the Nanometer Scale Using Optical Microscopy

*D. Zhang*¹

¹Eberhard Karls University of Tübingen

Multiscale Modeling of Semiconducting Polymers

P. Gemünden¹, C. Poelking¹, K. Kremer¹, D. Andrienko¹, K. Ch. Daoulas^{1*}

¹Max Planck Institute for Polymer Research

*e-mail: daoulas@mpip-mainz.mpg.de

Electronic properties of polymeric semiconductors are frequently affected by morphological features across multiple scales¹. Charge-transport is an important example that is sensitive to both: the local atomistic structure and mesoscopic polymer organization (molecular alignment, grain boundaries, domains with different phases). Therefore, theoretical, molecular-based, interpretations of electronic properties require large *and* atomistically resolved morphologies. Generating such samples with single-scale simulation methods, e.g. all-atom Molecular Dynamics, is computationally not feasible, motivating the implementation of the multiscale method of hierarchical backmapping.

We develop a hierarchical backmapping strategy² for partially-ordered mesophases of polymeric semiconductors. The cornerstone of our method is a mesoscopic model with anisotropic potentials capable of describing different types of partial order: from simple nematic³ to lamellar-sanidic mesophases⁴. Here, we use this model to prepare large morphologies with biaxial liquid-crystalline order³, considering poly(3-hexyl)thiophene (P3HT) as a test system. These mesoscopic morphologies are refined by reinserting the degrees of freedom of an intermediate model, derived from systematic coarse-graining. This fine-graining facilitates the final reinsertion of all-atom details. We focus on technicalities and challenges of our back-mapping procedure. However, we briefly highlight the use of back-mapped all-atom morphologies in studies of electronic properties, e.g. by considering the dependence of spatial correlations in the energy landscape on mesophase order. We conclude with an outlook, emphasizing the need to backmap mesophases with lamellar order⁴.

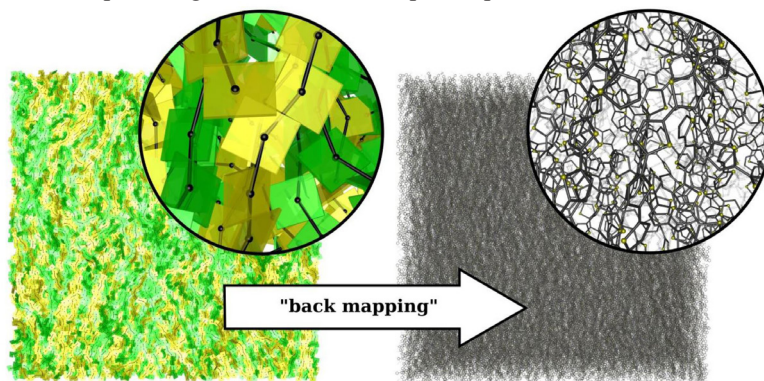


Fig. 1. Example of a large P3HT morphology (system size about 25 nm) before (left) and after (right) the final reinsertion of all-atom details. Adapted from ref [2].

¹ Noriega R., Rivnay J., Vandewal K., Koch F. P. V., Stingelin N., Smith P., Toney M. F., Salleo A., *Nat. Mater.* 2013, **12**, 1038-1044.

² Gemünden P., Poelking C., Kremer K., Daoulas K.Ch., Andrienko D. *Macromol. Rapid Commun.* 2015, **36**, 1047-1053.

³ Gemünden P., Poelking C., Kremer K., Andrienko D., Daoulas K.Ch. *Macromolecules* 2013, **46**, 5762-5774.

⁴ Greco C., Melnyk A., Kremer K., Andrienko D., Daoulas K.Ch. *Macromolecules* 2019, **52**, 968-981.

Dual Emission: Classes, Mechanisms and Conditions

S.K. Behera¹ S.Y. Park,² J. Gierschner^{1}*

¹ Madrid Institute for Advanced Studies, IMDEA Nanoscience.

² Department of Materials Science and Engineering, Seoul National University

*e-mail: johannes.gierschner@imdea.org

Dual emission (DE) materials have found much interest in the past years for materials and life science applications. In fact, DE materials have been successfully used in sensing (ratiometric fluorescence sensors, free volume in polymers, fluorescent pH or ion indicators), multicolor cell imaging, super-resolution fluorescence microscopy, ultrahigh-density data recording and storage, lasing, and in organic (O)LEDs for triplet harvesting, to generate materials with large apparent Stokes shifts, or single component white light generation. Although for some DE phenomena (extensive) reviews are available, others are less acknowledged. Moreover, ambiguities, misunderstandings and misinterpretations are frequent, which may impede a deeper perception of the subject. Even worse, older insightful works are often insufficiently recognized or completely ignored. Last but not least, there are increasing number of very recent works, which artfully combine different DE strategies, to create new functional DE materials. For all these reasons, we give here a short systematic overview on DE phenomena in the condensed phase of pure organic compounds. This includes a classification of DE, which can occur either from one emitter with two emitting states (DE1), two independent emitters (DE2), or two correlated emitters (DE3). We then categorize DE phenomena relevant for materials science application, briefly discuss the underlying mechanisms and the conditions that trigger DE.

Oral talks

Electronic Properties and Structuring of Vacuum Evaporated Molecular Films on Solid Surfaces

A.S. Komolov^{1*}, E.F. Lazneva¹, S.A. Pshenichnyuk², V.S. Sobolev¹, O.V. Borshchev³,
S.A. Ponomarenko³, D.Yu.Paraschuk⁴

¹St. Petersburg State University

²Institute of Molecule and Crystal Physics, Subdivision of the Ufa Federal Research Centre of the RAS

³Enikolopov Institute of Synthetic Polymeric Materials of the Russian Academy of Sciences

⁴Physics Department, Moscow State University

*e-mail: a.komolov@spbu.ru

In this presentation some background information on electron spectroscopic studies of thin films of conjugated organic molecules on solid surfaces will be discussed. Electronic properties of the surface organic layers can be tuned by means of the influence of the substrate material and by introducing polar substituents into the molecules. At the same time, film crystallinity, uniformity of the organic layer or tendency of island formation have a major affect on the electronic properties and on possible ways of device application. Thiophene/phenylene co-oligomers (TPCO) and diphenylphthalide based molecules (DPP) (Figure 1) were used for thermal deposition of thin and ultrathin layers of the molecular materials investigated. Native silicon oxide, polycrystalline Au and binary semiconductor ZnO prepared by the atomic layer deposition (ALD) method were used as substrate materials for the film deposition. Investigations of the energy positioning of the maxima of unoccupied electronic states and of the process of the formation of the potential boundary barrier were carried out by the method of total current spectroscopy (TCS).¹ The structure of the films was studied by X-ray diffraction (XRD). Atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) were used to determine the film surface roughness and atomic composition.

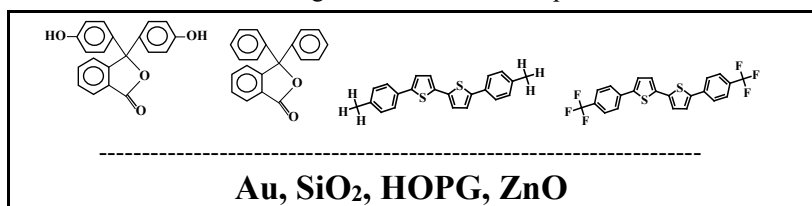


Figure 1. The schematics of the interfaces formed by phthalide films and by TPCO films on metal and semiconductor surfaces.

The work was supported by RFBR grants 18-03-00020 and 20-03-00026. The TCS investigation of the phthalide films was supported by the Russian Science Foundation (project № 19-13-00021). The experiments were performed using the equipment of the Research park of St. Petersburg State University.

¹ A.S. Komolov, E.F. Lazneva, S.N. Akhremtchik, N.S. Chepilko, A.A. Gavrikov. *J. Phys. Chem. C*, 2013, **117**, 12633.

² A.S. Komolov, E.F. Lazneva, N.B. Gerasimova, Yu. A. Panina, V.S. Sobolev, A.V. Koroleva, S.A. Pshenichnyuk, N.L. Asfandiarov, A. Modelli, B. Handke, O.V. Borshchev, S.A. Ponomarenko. *J. Electron Spectr. Rel. Phenom.*, 2019, **235**, 40.

Excited State Dynamics in a Novel Solution Processable Triphenylamine-Based Small Molecule for Organic Optoelectronics

B.A.L. Raul^{1*}, *Y.N. Luponosov*^{2,3}, *T.L.C. Jansen*¹, *S.A. Ponomarenko*^{2,3}, *M.S. Pshenichnikov*¹

¹Zernike Institute for Advanced Materials, University of Groningen

²Enikolopov Institute of Synthetic Polymeric Materials of the Russian Academy of Sciences

³Moscow State University, Chemistry Department

*e-mail: b.a.l.raul@rug.nl

Triphenylamine (TPA) containing small organic molecules with the push-pull character originally introduced by Roncali and coworkers,¹ have recently gained a lot of attention for applications as donors in organic solar cells (OSCs)² and hole transporting materials in perovskite solar cells.³ Among them, unsymmetrical TPA-based push-pull molecules can be considered as one of the simplest classes of donor small molecules for OSCs.⁴ In this work, we investigate the excited state relaxation pathways and exciton diffusion dynamics in a novel solution processable TPA-based small molecule (TPA-T-DCV-Ph-F). By employing time-resolved photoluminescence spectroscopy, we demonstrate that the excited state lifetime in solutions (~ 0.04 ns in toluene and ~ 0.4 ns in chloroform) are surprisingly shorter compared to neat film (4 ns). Time-dependent density functional theory indicates that this unusual behavior originates from excited state non-radiative deactivation induced by a conical intersection between the ground and singlet excited state potential energy surfaces. We further investigate the thin films by combining photoluminescence quenching measurements with Monte-Carlo simulations, and extracted exciton diffusion length of ~ 16 nm. Our findings unravel the excited state dynamics in TPA-T-DCV-Ph-F and pave the way for simple, stable, and solution processable TPA-based materials with long exciton diffusion length for organic optoelectronics.

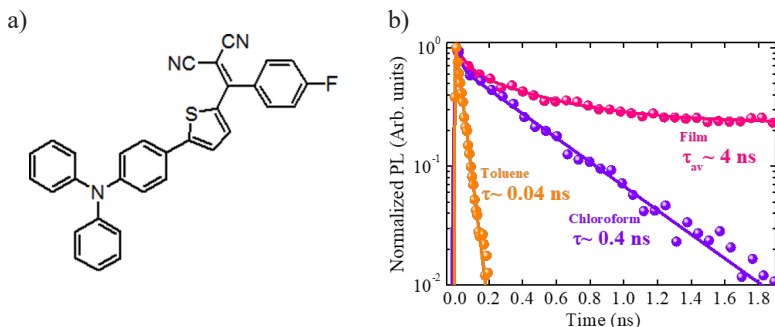


Figure 1. (a) Chemical structure of TPA-T-DCV-Ph-F. (b) PL transients of molecules in neat film (pink), diluted chloroform (violet) and toluene (orange) solutions. The circles represent the experimental data points, while the solid lines are the respective fitting. The excitation wavelength was set to 520 nm, near the absorption maximum.

¹ S. Roquet *et al.*, *J. Am. Chem. Soc.* 2006, **128** (10), 3459–3466.

² P. Blanchard *et al.*, *Polym. Int.* 2019, **68** (4), 589–606.

³ S. Paek *et al.*, *Adv. Mater.* 2017, **29** (35), 1606555.

⁴ E. Ripaud *et al.*, *Adv. Energy Mater.* 2011, **1** (4), 540–54.

Thermally Activated Delayed Fluorescence in Organic Semiconductors: A Quantum Chemical Study

A.Ya. Freidzon^{1,2*}

¹Federal Research Center "Crystallography and Photonics" Photochemistry Center, Russian Academy of Science

²National Research Nuclear University MEPhI (Moscow Engineering Physics Institute)

*e-mail: freidzon.sanya@gmail.com

Molecules capable of thermally activated delayed fluorescence (TADF) are promising as emitters in organic light-emitting devices. Processes leading to and competing with TADF in 4,5-di(9H-carbazol-9-yl)-phthalonitrile (2CzPN) are analyzed in detail with the extensive use of multireference quantum chemistry. It is demonstrated that the key features of an efficient TADF emitter include the presence of two triplet states of different nature with potential energy surfaces crossing between the T1 and S1 minima and a noticeable dependence of the S1→S0 oscillator strength on molecular deformations from low-frequency antisymmetric vibrational modes. These conclusions can be useful in targeted design of efficient TADF emitters.

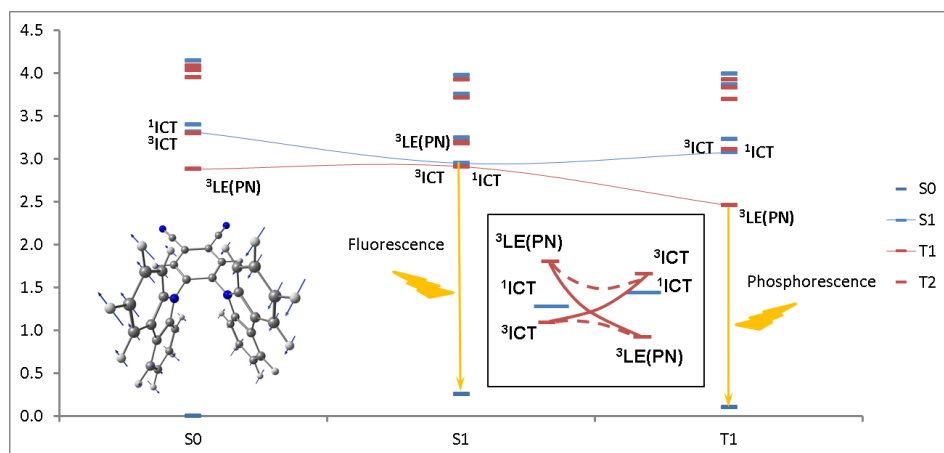


Figure 1. Proposed mechanism of TADF in 2CzPN

This work was supported by the Russian Science Foundation (project no. 19-13-00383), the Ministry of Science and Higher Education within the State assignment FSRC Crystallography and Photonics RAS, Russia (State Registration Number 115092170003), and by the Competitiveness Program of the National Research Nuclear University "MEPhI".

A Kinetic Monte Carlo Study of Triplet-triplet Annihilation in Conjugated Luminescent Materials

R. Saxena^{1*}, *T. Meier*¹, *S. Athanasopoulos*², *H. Bässler*³, *A. Köhler*^{1,3}

¹ Soft Matter Optoelectronics and Bavarian Polymer Institute (BPS), University of Bayreuth

² Departamento de Física, Universidad Carlos III de Madrid

³ Bayreuth Institute of Macromolecular Research (BIMF), University of Bayreuth

*e-mail: rishabh.saxena@uni-bayreuth.de

It is well known that in organic solids the collision of two excitons can give rise to delayed fluorescence (DF). Revived interest in this topic is stimulated by the current endeavor towards the development of efficient organic opto-electronic devices such as OLEDs and solar cells, or sensitizers used in photodynamic therapy. In such devices, triplet excitations are ubiquitously present but their annihilations can be either detrimental, e.g. giving rise to a roll-off of intensity in an OLED, or mandatory, e.g. if the sensitizer relies on up-conversion of long-lived low energy triplet excitations. Since the employed materials are usually non-crystalline, optical excitations migrate via non-coherent hopping. The method of choice to unravel the complex pattern of individual elements in the hopping process is kinetic Monte Carlo simulation (kMC). In the current work we employ kMC to study the interplay of triplet-triplet annihilation (TTA) and quenching of the triplet excitations by impurities in a single component system featuring a Gaussian energy landscape. Our simulation results are in agreement with the experimental observations of Hoffmann *et al.* for oligomers and polymers with different conjugation length.¹ By examining the material parameters, we find that enhanced room temperature DF requires:

- (i) a transport morphology that allows triplets to access many different energy sites
- (ii) materials with a long conjugation length
- (iii) materials that are well purified so that they have a defect concentration $\leq 10^{17} \text{ cm}^{-3}$, and
- (iv) materials that show a high degree of energetic disorder ($\sigma \geq 70 \text{ meV}$).

We also explore the effect of replacing Miller-Abrahams hopping rates by Marcus rates. An essential message is that the DF features a maximum at a temperature that scales as or similar to $\sigma/K_B T$ as shown in Fig.1; observing a maximum at $\sigma/K_B T \approx 3$.

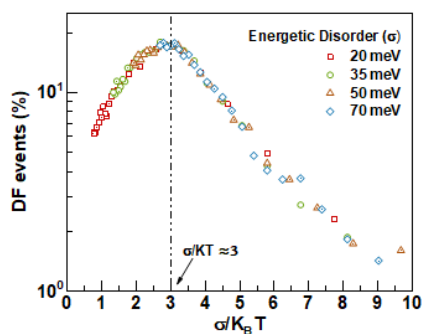


Figure 1. Delayed fluorescence peaks at $\sigma/K_B T \approx 3$ for all the disorder values.

¹ Hoffmann, S. T.; Koenen, J. M.; Scherf, U.; Bauer, I.; Strohriegel, P.; Bassler, H.; Köhler, A., *J. Phys. Chem. B* 2011, **115**(26), 8417-23.

Interplay Between RISC and TTA in Exciplex-based TADF OLEDs

J. Grüne^{1*}, *N. Bunzmann*¹, *A. Sperlich*¹, *V. Dyakonov*¹

¹Experimental Physics VI, Julius Maximilian University of Würzburg

*e-mail: jeannine.gruene@physik.uni-wuerzburg.de

Organic light emitting diodes (OLEDs) based on thermally activated delayed fluorescence (TADF) show increased efficiencies due to effective upconversion from non-emissive triplet states to emissive singlet states via reverse intersystem crossing (RISC)¹. Several promising concepts are under consideration where an exciton is formed between donor and acceptor, either as an intramolecular exciton on the same molecule or as an intermolecular exciton at the interface between two molecules, also called exciplex. A suitable model material combination for the investigation of exciplex-based OLEDs, which still attracts much attention in literature, is 4,4',4''-Tris[(3-methylphenyl)phenylamino]triphenylamine (m-MTDATA), as donor and Tris(2,4,6-trimethyl-3-(pyridin-3-yl)phenyl)borane (3TPYMB), as acceptor. To assess the influence of the characteristic efficiency-enhancing RISC process as well as possible efficiency-limiting effects on device performance, we carried out temperature-dependent measurements of transient electroluminescence (trEL)². With kinetic modeling, we quantified and separated the impact of different time- and temperature-dependent contributions to the EL. The underlying rate equations adapted for EL measurements on TADF systems include radiative and non-radiative first- and second-order effects. In this way, we were able to evaluate the non-radiative recombination and annihilation processes with respect to their efficiency-limiting effects on these OLEDs. On the one hand, we evaluated the depopulation of intermolecular exciplex triplet states via non-radiative direct triplet decay, RISC and triplet-triplet annihilation (TTA). On the other hand, we determined the contribution to EL from the formation of singlet exciplex states via polarons, RISC and TTA. Our results show that triplet depopulation by TTA outcompetes RISC and thus contributes significantly to EL while, however, limiting the overall device quantum efficiency.

This work was supported by GRK2112.

¹ Goushi, A., Yoshida, K., Sato, K., Adachi, C. *Nature Photonics* 2012, **6**(4), 253-258.

² Grüne, J., Bunzmann, N., Dyakonov, V., Sperlich, A. *arXiv:2007.08862*, 2020.

Organic Nanoelectronics Inside Us: Charge Transport and Localization Within tRNA Could Orchestrate Ribosome Operation

A.Yu. Sosorev¹, O.G. Kharlanov²

¹Shemyakin and Ovchinnikov Institute of Bioorganic Chemistry RAS

²Moscow State University, Faculty of Physics

*e-mail: sosorev@physics.msu.ru

Ribonucleic acid (RNA) molecules are in the heart of various molecular machines, one kind of which – the ribosome – produces all the proteins in all the organisms and is thus essential for life. However, the physics underlying the protein synthesis at the ribosome – translation – lacks appropriate understanding despite of several decades of research. Specifically, during translation, ribosome undergoes large-scale conformational changes of its distant parts, but the mechanism synchronizing these motions is unknown.

In this study, we suggest that such a mechanism is based on charge (hole) transport along and between the RNA molecules, localization of these charges in certain sites and successive conformational changes. Taking transfer RNAs as an example, we show theoretically that nucleotides are strongly electronically coupled to each other, i.e., have large charge transfer integrals, so that extended π -conjugated system is formed (Fig. 1a). We then monitor holes motion within this molecule and find that they localize at functionally important sites – guanine nucleotides G10, G27 and G63 (Fig. 1b,c). Finally, we show that charge localization induces significant geometrical changes, justifying our suggestion. We anticipate that our findings can qualitatively advance the understanding of the key biological processes at the nanoscale and facilitate formulation of novel approaches to the treatment of various diseases.

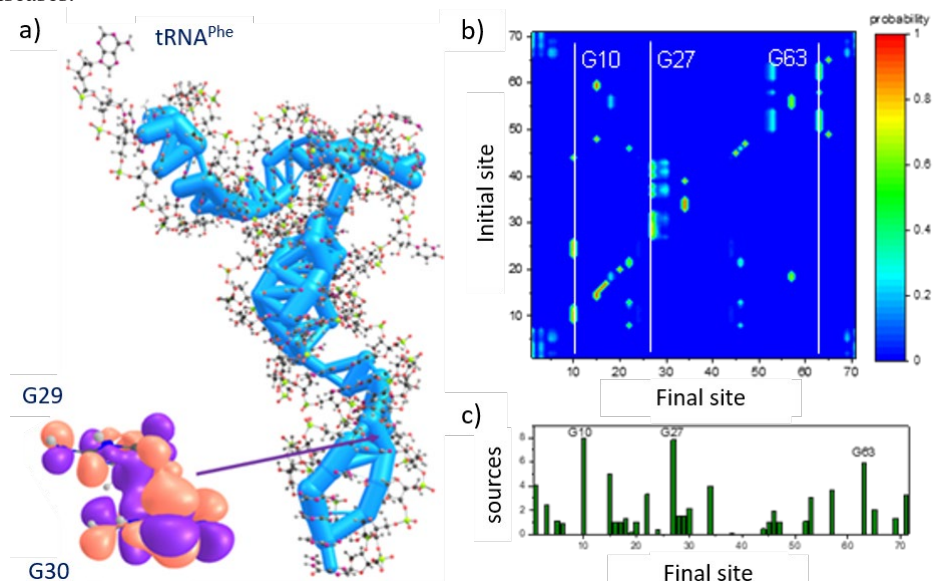


Figure 1. (a) Hole transfer integrals, J , for the studied tRNA. The thickness of the cylinders represents the magnitude of J . Inset depicts HOMO delocalization between nucleotides illustrating large J . (b) Probability of finding the hole from various initial sites at various final sites. (c) Average number of initial sites from which the hole localizes at given final site.

This work was supported by RFBR (project № 19-32-60081).

Novel Star-shaped Donor-acceptor Molecules for Bulk Heterojunction and Single-material Organic Solar Cells

Yu.N. Luponosov^{1*}, A.N. Solodukhin¹, D.O. Balakirev¹, A.L. Mannanov^{1,2}, P.S. Savchenko^{1,2}, D.Yu. Paraschuk^{1,2}, S.A. Ponomarenko¹

¹Enikolopov Institute of Synthetic Polymeric Materials of the Russian Academy of Sciences

²International Laser Center and Faculty of Physics, Moscow State University

*e-mail: luponosov@ispm.ru

During the past two decades, 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 such as PET and PEN 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. Among OSCs the single-material organic solar cells (SMOSC) are greatly attracted by their simple structure and ease of fabrication so that they are virtually free from a number of drawbacks of heterojunction organic solar cells. In this work, we report on the design, synthesis and comprehensive study of star-shaped donor-acceptor molecules having either triphenylamine or benzotriindole core as a donor fragment linked through oligothiophene π -spacer to either dicyanovinyl or cyanoester acceptor groups [1-5].^{1,....5} Some of these molecules have shown record high efficiency among the star-shaped molecules in fullerene bulk heterojunction organic solar cells.⁴ Besides that, these rather simple molecules have been utilized as an active layer in SMOSC achieving high open-circuit voltage up to 1.19 V and the power conversion efficiency up to 1.22%, which are among the highest for SMOSC based on conjugated donor-acceptor small molecules.³ In addition, successful application of these molecules in single-material organic photodetectors revealed their high perspective for mimicking biological photoreceptors of human retina eyes.

The work was supported by Russian Science Foundation (RSF) (19-73-10198), whereas the work in the part of single-component photodetectors was supported by RSF (19-73-30028).

¹ J. Min, Y.N. Luponosov, A. Gerl, M.S. Polinskaya, S.M. Peregudova, P.V. Dmitryakov, A.V. Bakirov, M.A. Shcherbina, S.N. Chvalun, S. Grigorian, N. Kausch-Busies, S.A. Ponomarenko, T. Ameri, C.J. Brabec. *Advanced Energy Materials*, 2014, **4**, 1301234.

² Yu. N. Luponosov, A. N. Solodukhin, A. L. Mannanov, V. A. Trukhanov, S. M. Peregudova, S. A. Pisarev, A. V. Bakirov, M. A. Shcherbina, S. N. Chvalun, D. Yu Paraschuk, S. A. Ponomarenko, *Organic Electronics*, 2017, **51**, 180-189.

³ A. L. Mannanov, P. S. Savchenko, Yu. N. Luponosov, A. N. Solodukhin, S. A. Ponomarenko, D. Yu. Paraschuk, *Organic Electronics* 2020, **78**, 105588.

⁴ Yu. N. Luponosov, A. N. Solodukhin, A.L. Mannanov, P. S. Savchenko, Yury Minenkov, D. Yu. Paraschuk, S. A. Ponomarenko, *Dyes and Pigments*, 2020, **177**, 108260.

⁵ D.O. Balakirev, Yu. N. Luponosov, A.L. Mannanov, P. S. Savchenko, Yury Minenkov, D. Yu. Paraschuk, S. A. Ponomarenko, *Dyes and Pigments*, 2020, **181**, 108523

Charge Carrier Recombination in Amorphous Organic Semiconductors

S.V. Novikov^{1,2*}

¹A.N. Frumkin Institute of Physical Chemistry and Electrochemistry RAS

²National Research University Higher School of Economics

*e-mail: novikov@elchem.ac.ru

Recombination of electrons and holes is one of the basic processes in electronic and optoelectronic organic devices. Properties of the recombination process are important for the reliable prediction of the overall performance of the devices. Recombination of charge carriers in amorphous organic materials is still not fully understood. For example, it is unclear to what extent the recombination rate constant γ differs from the corresponding Langevin rate constant $\gamma_L = 4\pi e(\mu_p + \mu_n)/\varepsilon$, here $\mu_{n,p}$ are mobilities of electrons and holes and ε is the dielectric constant.

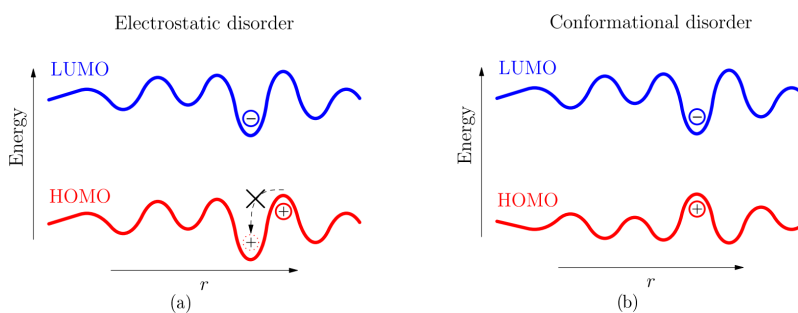


Figure 1. Typical spatial profiles of HOMO and LUMO for electrostatic (a) and conformational (b) disorder.

Recently we demonstrated that the most important reason for the deviation of γ from γ_L is the spatial correlation in the random energy landscape which is ubiquitous in organic materials.^{1,2} Energy landscape is arranged as a set of hills and valleys. If the energetic relaxation is over, then carriers are trapped at the bottom of valleys. When the carrier of the opposite sign is approaching, it interacts with other carrier by the Coulomb attraction and, additionally, is under the action of the random energy landscape, surrounding the trapped carrier. There is the principal difference between materials where the dominant part of the energetic disorder comes from electrostatic sources (dipoles and quadrupoles)¹ and materials where the disorder comes from the conformation fluctuations² (see Figs. 1a, b for typical HOMO and LUMO profiles). For materials with electrostatic disorder energy profiles of electrons and holes vary in the opposite directions and a hill for the electron is a valley for the hole (Fig. 1a), while for the conformation disorder they quite frequently vary in the same direction (Fig. 1b). First case leads to the additional effective repulsion between carriers (and in that case $\gamma < \gamma_L$), while the second one gives the additional attraction (and, hence, $\gamma > \gamma_L$). Calculation shows that the decrease of γ could be up to several orders of magnitude, while the increase of γ is typically rather moderate, about 50-100%. Such effects significantly influence the performance of electronic organic devices.

¹ S.V. Novikov, *J. Phys. Chem. C* 2018, **122**(40), 22856-22863.

² S.V. Novikov, *J. Phys. Chem. C* 2019, **123**(31), 18854-18860.

Extended Description of Hopping Transport by the Multiple Trapping Model

V.R. Nikitenko^{1*}

¹National Research Nuclear University “MEPhI” (Moscow Engineering Physics Institute)

e-mail: vladronik@yandex.ru

Analytic methods are important for description of charge transport in disordered organic semiconductors,¹ which is one of the key physical processes, responsible for the operation of organic electronic devices. In organics, all electronic states are localized,² nevertheless one can use the relatively simple formalism of the multiple trapping and release model (MTR) to describe the hopping transport. Up to now, an application of the MTR formalism rests upon the concept of the transport level, which is the formal analog of the mobility edge. As a rule, the numerous variants of the transport level concept rest upon the Miller-Abraham’s (MA) model of hopping rates.^{1,3} Meanwhile, other models of hopping rates are in use, in particular – the Marcus model, which accounts for the polaron effect. Fortunately, we don’t need to introduce the transport level explicitly, in order to use a MTR formalism. One has only pick out some fraction of states, which make a principal contribution to transport. These states work as “conductive”, in analogy with MTR. This idea has been proposed many years ago,⁴ but the rather general way of transport parameters calculation was not developed. In this work, the MTR approach, which is suitable for the description of hopping transport in a very general scope, is developed and applied to the analysis of the temperature dependence of small-concentration diffusivity (and of the small-field mobility μ), providing both MA and Marcus hopping rates.

Under certain rather broad assumptions, one can reduce the well-known master equation of the hopping transport to the balance equation of the MTR model, irrespective to the concrete model of hopping rates. Operationally, the “conductive” states ordered by the condition, that the escape time of a carrier from this state does not exceed some value, this quantity is not important, if it is rather small. The mobility determined by the mean release rate of a carrier from a state of a given energy, which is founded by the mean hopping parameter method.⁵ An important modification is that the return jumps excluded from the consideration, i.e. the percolation effects included. One can consider the well-known methods of effective transport level^{1,3} and mean hopping parameter^{5,6} as simplified and special versions of this formalism.

Results of calculations confirm the validity of the well-known law², $\mu = \mu_0 \exp[-C(\sigma/kT)^2]$. The coefficient C varieties from 0.40 to 0.48 (in agreement with previous results¹), and from 0.34 to 0.43 for the case of MA and Marcus model, respectively, if the localization parameter varieties from 6 to 20. In addition, the value of C reduces slightly, if the reorganization energy in Marcus model increases. These results are useful for the extraction of the value of C from experiments and can help to resolve the long-standing discrepancy in literature⁷ about this value, providing Marcus hopping rates.

This work was supported by the Volkswagen foundation, grant “Understanding the dependence of charge transport on the morphology of organic semiconductor films”.

¹ Baranovskii S.D., *Phys. Stat. Sol. A* 2018 **215**, 1700676 1-12

² Bäessler H., *Phys. Stat. Sol. B* 1993 **175**, 15-56

³ Arkhipov V. I., Emelianova E. V., Adriaenssens G. J., *Phys. Rev. B* 2001, **64**, 125125.

⁴ Schmidlin F.W. *Phys. Rev. B* 1977, **16**, 2362-2384.

⁵ Arkhipov V.I., Emelianova E.V., Bäessler H. *Phil. Mag. B* 2001, **81**, 985-996.

⁶ Apsley N. and Hughes H.P. *Phil. Mag. B* 1975, **31**, 1327-1339.

⁷ Fishchuk I. I., Kadashchuk A., Hoffmann S. T., Athanasopoulos S., Genoe J., Bäessler H., and Köhler A. *Phys. Rev. B* 2013, **88**, 125202.

Poster presentations

Portable device for measuring of OFETs array parameters allowing detection and determination of various gases.

A.A. Abramov^{1,2}, D.S. Anisimov¹, V.P. Chekusova¹, A.A. Trul¹, E.V. Agina¹, S.A. Ponomarenko¹.*

¹Enikolopov Institute of Synthetic Polymeric Materials of the Russian Academy of Sciences

²Bauman Moscow State Technical University

*e-mail: abramov@ispm.ru

Thin-film organic field-effect transistors (OFETs) based sensors are promising for many sensing applications in the field of detection of small quantities of different kinds of volatile substances. The ease of manufacturing of multiple sensors on a single substrate promotes the usage of an array of sensors for higher measurement reliability by means of response averaging and machine-learning based signal conditioning.

There are several types of sensors, arrays of which may be used for gas sensing, but they have disadvantages, obstructing the creation of a small inexpensive and portable device: quartz crystal microbalance sensors are comparatively large and require complicated driving and measurement circuitry, electrochemical sensors are complicated and bulky, metal-oxide-semiconductor sensors need high power for heating the sensor up to 300°C.^{1,2} Conducting polymer sensors are less sensitive than OFETs and provide less measurable parameters.^{3,4,5} OFETs have a non-linear current-voltage dependence, there are many different OFETs characteristics, such as mobility, threshold voltage and subthreshold slope which could be considered as a sensor response. Each case requires proper measurement technique.

In our work characterization of an array of receptor-covered OFET sensors, placed on a single substrate, was needed. For this purpose a portable 20-channel source-meter was designed, which technical characteristics are discussed further. Mixed-signal microcontrollers (MCU) incorporate a rich set of analog and communicating peripherals and a powerful computing core, which allows minimizing the number of external components, reducing size, power consumption, and device cost. MCU selected incorporates three 16-bit sigma-delta analog-to-digital converters with analog multiplexers, a digital-to-analog converter (DAC), a floating-point computation unit, and numerous communicating interfaces. To convert the OFETs channel current to voltage, a transimpedance amplifier was used. Theoretical resolution is 0,2 nA with upper limit of 13 µA. The source part consists of high-voltage operational amplifiers, supplied from a double-channel DC-DC converter, and DACs of the MCU. A gas chamber with a sensor array is placed on a separate board, connected to the mainboard via a board-to-board connector, which allows using different gas chambers and auxiliary sensors.

The device developed opens up a range of applications of OFET gas sensors and arrays of them, which can detect toxic gases in the sub-ppm concentration range and to efficiently discriminate them in wide relative humidity range. With appropriate sensor board evaluation of other types of current-response sensors is possible. Small dimensions, portability and extensibility allow using the device for environmental control and embedding in health monitoring or food spoilage detection systems.

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

¹ M. Baietto et al, *Sensors*, 2010, **10**(2);

² A.D. Wilson et al, *Sensors*, 2009, **9**(7);

³ S. Freddi et al, *Advanced Healthcare Materials*, 2020, **9**(12);

⁴ B. Li et al, *Sensors and Actuators B: Chemical*, 2007, **123**(2).

⁵ J. B. Chang, *Journal of Applied Physics* 2006, **100**.

Revealing the impact of small molecular hole-transport materials on the performance of perovskite solar cells

E.E. Agafonova^{1*}, *M.M. Tepliakova*^{1,2}, *Y.N. Luponosov*³, *E.I. Romadina*^{1,2}, *A.N. Soloduhin*³,
*S.A. Ponomarenko*³, *K. Stevenson*¹, *P.A. Troshin*^{1,2}

¹Skolkovo Institute of Science and Technology, Moscow, Russia

²Institute for Problems of Chemical Physics of RAS, Chernogolovka, Russia

³Enikolopov Institute of Synthetic Polymeric Materials RAS, Moscow, Russia

*e-mail: ek.e.agafonova@gmail.com

Perovskite solar cells (PSCs) represent now rapidly emerging and highly promising photovoltaic technology with the best laboratory device efficiencies surpassing 25% threshold.¹ While the efficiencies of PSCs come close to that of crystalline silicon solar cells, there is a severe gap in operation stability of these two types of photovoltaic devices. Silicon solar cells can operate for 25-40 years, while most of perovskite solar cells degrade within few thousand hours under continuous illumination.² There is a growing evidence that stability of PSCs is strongly impacted by interfacial charge transport layers.³

In particular, hole transport layer (HTL) is responsible for multiple degradation pathways discovered for PSCs. State-of-art HTLs require additional p-doping with oxygen and hydrosopic Li-salts, which impairs ambient stability of PSCs. Moreover, doped HTLs are intrinsically unstable in combination with complex lead halides since cationic species tend to oxidize I⁻ to molecular iodine. Therefore, designing new p-type materials enabling decent transport of positive charge carriers without additional doping is crucially important.

In this work, we present a systematic study of a big series of p-type organic small-molecular semiconductors as HTL materials in PSCs. These materials represented triazatruxene-, triphenylamine- and dithiophenol- derivatives with various solubilizing chains. Highest occupied molecular orbital (HOMO) energies of these materials varied from -5.06 to -6.00 eV, thus providing excellent screening library for matching the perovskite valence band. All materials were evaluated in PSCs with n-i-p configuration and HTL film thickness and deposition conditions were thoroughly optimized. The best devices showed power conversion efficiencies approaching 20% thus suggesting efficient hole extraction from the device active layer.

Most importantly, we revealed a relationship between HOMO energies of HTL materials and open circuit voltage (and also efficiency) of perovskite solar cells. The obtained results establish guidelines for designing new dopant-free HTL materials for efficient perovskite solar cells.

¹ <https://www.nrel.gov/pv/assets/pdfs/best-research-cell-efficiencies.20190923.pdf> cited on 14.10.2019

² Han, Y., Meyer, S., Dkhissi, Y., Weber, K., Pringle, J. M., Bach, U., Cheng, Y.-B. *Journal of Materials Chemistry A*, 2015, **3**, 8139–8147.

³ Akbulatov, A. F., Frolova, L. A., Griffin, M. P., Gearba, I. R., Dolocan, A., Vanden Bout, D. A., Tsarev, S., Katz, E. A., Shestakov, A. F., Stevenson, K. J., Troshin, P. A. *Adv. Energy Mater.* 2017, **7**, 1700476.

Intrinsic stability challenges in design of absorber materials for lead halide perovskite solar cells

Azat F. Akbulatov¹, Lyubov A. Frolova^{1,2}, Nadezhda N. Dremova¹, Ivan Zhidkov³, Vyacheslav M. Martynenko¹, Sergey A. Tsarev², Sergey Yu. Luchkin², Ernst Z. Kurmaev^{3,4}, Sergey M. Aldoshin¹, Keith J. Stevenson², Pavel A. Troshin^{2,1}

¹ The Institute for Problems of Chemical Physics of the Russian Academy of Sciences, Semenov Prospect 1, Chernogolovka, 141432, Russia

² Skolkovo Institute of Science and Technology, Nobel St. 3, Moscow, 143026, Russia

³ Institute of Physics and Technology, Ural Federal University, Mira st. 19, Yekaterinburg, 620002, Russia

⁴ M. N. Mikheev Institute of Metal Physics of Ural Branch of Russian Academy of Sciences, S. Kovalevskoi st. 18, Yekaterinburg, 620990, Russia

E-mail: qweas89@mail.ru

We report the first systematic assessment of intrinsic thermal and photochemical stability of a large panel of complex lead halides APbX₃ incorporating different univalent cations (A=CH₃NH₃⁺, [NH₂CHNH₂]⁺, Cs⁺) and halogen anions (X=Br, I) using a series of complementary analytical techniques such as UV-vis spectroscopy, x-ray diffraction, x-ray photoelectron spectroscopy, EDX chemical analysis, atomic force and scanning electron microscopy, electron spin resonance spectroscopy and mass spectrometry. We show that both heat stress and light soaking can induce a severe degradation of perovskite films even under well-controlled inert atmosphere in the absence of oxygen and moisture. The stability of complex lead halides increases in the order MAPbBr₃<MAPbI₃<FAPbI₃<FAPbBr₃<CsPbI₃<CsPbBr₃, thus featuring all-inorganic perovskites as the most promising absorbers for stable perovskite solar cells.

An important correlation was found between the stability of the complex lead halides and the volatility of univalent cation halides (AX) incorporated in their structure. In particular, MAPbBr₃ has the lowest stability since it is comprised of PbBr₂ and the most volatile MABr. On the contrary, all-inorganic CsPbX₃ compounds show remarkable stability since CsBr and CsI are non-volatile under the solar cell operation conditions. The established relationship provides useful guidelines for designing new complex metal halides with immensely improved stability.

This work was supported by Russian Science Foundation (project 19-73-30020).

Electrochemical reduction of polyfluorinated quinoxalines

Avrorov P. A.^{1,2}, Irtegov I. G.¹, Makarov A. Yu.¹, Shundrin L. A.¹, Zibarev A. V.¹.

¹ N.N. Vorozhtsov Institute of Organic Chemistry, Russia

² The Scientific Institute of Clinical and Experimental Lymphology, Russia

*e-mail: pavel.avrorov@gmail.com

Despite the fact that quinoxalines (benzopyrazines) are well-studied classes of aza-aromatics [1], only a few number of polyfluorinated quinoxalines are known [2], and their redox properties are poorly studied. We studied the electrochemical reduction (ECR) of 5,6,7,8-tetrafluoroquinoxaline (**1**) and its derivatives bearing substituents R: (7-H (**2**), 7,8-H₂ (**3**), 6-CF₃ (**4**), 6-Cl (**5**), 5,7-Cl₂ (**6**), 5-NH₂ (**7**), 6-OCH₃ (**8**), 6,7-(OCH₃)₂ (**9**), 6,7,8-(OCH₃)₃ (**10**), 5,6,7,8-(OCH₃)₄ (**11**), 6-OCH₃,7-N(CH₃)₂ (**12**), 6-N(CH₃)₂ (**13**), 6,7-(N(CH₃)₂)₂ (**14**), 5,6,7-(N(CH₃)₂)₃ (**15**), and 7,8-*cyclo*-(=CF-CF=CF-CF=) (**16**)) in the carbocycle by cyclic voltammetry in MeCN on Pt-electrode.

The first stage of ECR **2–3** and **7–15** is one-electron and diffusion-controlled reversible process. Corresponding radical anions (RAs) are long-lived and characterized by EPR spectroscopy together with DFT calculations. A good linear correlation between calculated gas-phase adiabatic electron affinities (A_{ad}) and experimental values of the first reduction peak potentials (E_p^{1C}) was observed covering all compounds studied (Figure 1a), thus indicating the one-electron nature of the ECR. The corresponding changes in free energies of solvation under one-electron transfer, $\Delta\Delta G_{solv}^0$, calculated using the known value for unsubstituted quinoxaline (**17**) [3], form a good linear dependence on the topological indices, I , whose values reflect the nature of the substituents and the type of substitution (Figure 1b).

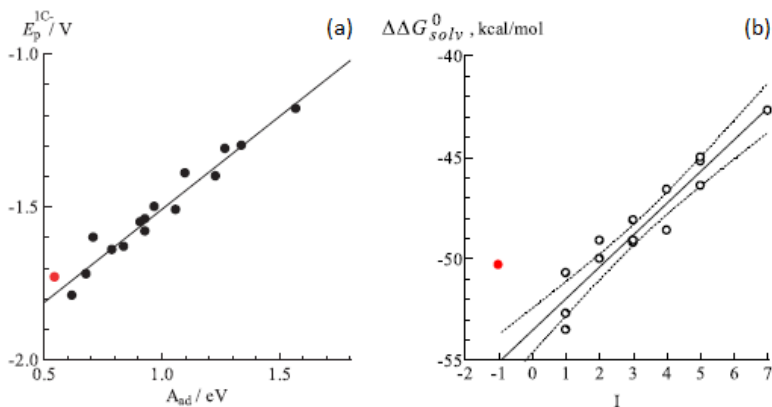


Figure 1. a): Correlation between DFT-calculated adiabatic electron affinities of substituted quinoxalines and their first peak reduction potentials; b): resolution energies for compounds **1–15** versus topological indices I (red points correspond the compounds: **17** (a) and **15** (b)).

The first ECR stage of chlorinated quinoxalines **5**, **6** is well-described by EC-process indicating the instability of RAs **5**, **6**, which leads to dechlorination. The corresponding RA's decay rate constants were found to be 2.37 s^{-1} and 0.19 s^{-1} , respectively.

Literature:

1. J. Alvarez-Builla, J. J. Vaquero, J. Barluengo (Eds) // *Modern Heterocyclic Chemistry*, Wiley-VCH. 2011.
2. A. G. Makarov, N. Y. Selikhova, A. Y. Makarov, V. S. Malkov, I. Y Bagryanskaya, Y. V. Gatilov, A. S. Knyazev, Y. G. Slizhov, A. V. Zibarev // *J. Fluorine Chem.* 2014. V. 165. P. 123.
3. G. W. Dillow, P. Kebarle // *Can. J. Chem.* 1989. V. 67. P. 1628.

Electrochemical reduction of fluorinated/chlorinated 2,1,3-benzothia/selenadiazoles

Avrorov P. A.^{1,2}, Irtegov I. G.¹, Makarov A. Yu.¹, Shundrin L. A.¹, Zibarev A. V.¹

¹ N.N. Vorozhtsov Institute of Organic Chemistry, Russia

² The Scientific Institute of Clinical and Experimental Lymphology, Russia

*e-mail: pavel.avrorov@gmail.com

2,1,3-benzothia/selenadiazoles possess positive electron affinity (EA_1) making them effective electron acceptors [1] – precursors of stable radical anions (RAs). For this reason they found applications as building blocks of molecular functional materials for organic electronics and optoelectronics. Electrochemical redaction (ECR) of new fluorinated 2,1,3-benzothia/selenadiazoles bearing also chlorine and some other electron-donating/withdrawing substituents was studied by cyclic voltammetry in DMF. The first stage of the ECR for all studied compounds is one-electron, diffusion-controlled and reversible process. Radical anions formed at the first stage of ECR were characterized by EPR-spectroscopy together with DFT calculations at the (U)B3LYP/6-31+G(d) level of theory.

The first peak potentials, E_p^{1c} , of selenadiazoles are *ca.* 0.1 ± 0.03 V less negative, and gas-phase calculated EA_1 *ca.* 0.17 eV more positive, than those of thiadiazoles with the same substitution patterns. The values E_p^{1c} for thiadiazoles and selenadiazoles correlate well with the corresponding EA_1 , forming two independent linear regressions: $EA_1 = a E_p^{1c} + b$ with a , b and r^2 equal to $1.79 \text{ eV}\cdot\text{V}^{-1}$, 3.50 eV and 0.972 , respectively, for thiadiazoles (Figure 1a); and to $1.61 \text{ eV}\cdot\text{V}^{-1}$, 3.30 eV and 0.948 for selenadiazoles (Figure 1b).

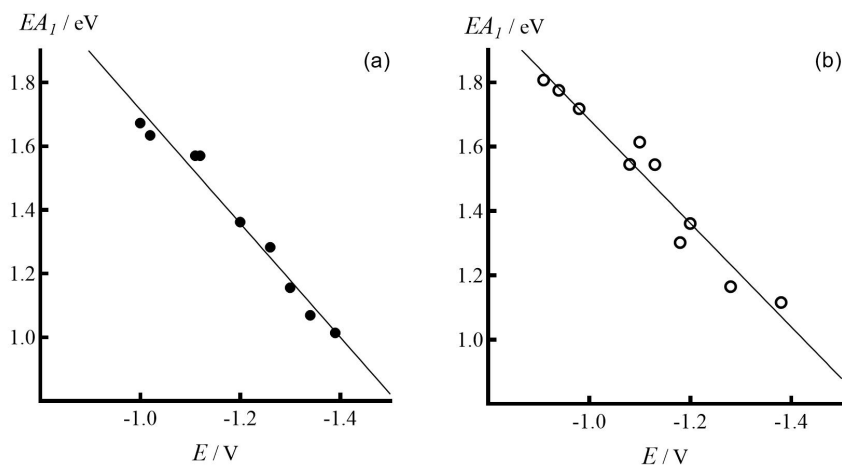


Figure 1. Correlations between EA_1 and E_p^{1c} for thiadiazoles (a) and selenadiazoles (b).

These findings indicate that selenadiazoles are better electron acceptors than their *S* congeners in spite of lesser atomic EA_1 and Allen electronegativity of *Se* vs. *S*. This feature may be used in the design and synthesis of molecular functional materials.

Literature:

1. A. V. Lonchakov, O. A. Rakin, N. P. Gritsan, A. V. Zibarev // *Molecules*. 2013. V. 18. P. 9850.

**Novel donor small molecules based on benzotriindole and benzodithiophene cores:
synthesis, properties and application in organic solar cells**

D.O. Balakirev^{1}, Yu.N. Luponosov¹, E.A. Svidchenko¹, S.M. Peregodova², Artur L.
Mannanov^{1,3}, Petr S. Savchenko¹, Dmitry Yu. Paraschuk^{1,3},
S.A. Ponomarenko¹*

¹Enikolopov Institute of Synthetic Polymeric Materials, RAS

²Nesmeyanov Institute of Organoelement Compounds, RAS

³Moscow State University, Faculty of Physics & International Laser Center

*e-mail: balakirev@ispm.ru

Organic photovoltaics (OPV) is one of the main science and technology part, which have been developed rapidly in the last decade. Despite the pessimistic forecasts earlier, nowadays, with well-designed and optimized molecular structure, the performance of organic solar cells (OSCs) have achieved the power conversion efficiency (PCE) to over 17%, which in turn makes OPVs more close to the theoretical prediction PCEs maximum. However, the search of novel structural blocks and evaluating of the “structure-property” relationships for OPV materials remains an urgent task, timely solving of which will help to increase PCE values for OSCs even more.

Here we report on an efficient synthesis and complex properties studies of novel Donor- π -Acceptor benzotriindole-based and benzodithiophene-based p-type organic semiconductor molecules for the OSCs application. These molecules, which containing different electron-withdrawing groups, linked through bithiophene or terthiophene π -spacer with electron-donating either benzotriindole or benzodithiophene cores were synthesized in high yields. The electrochemical, thermal and optical properties of these compounds were investigated by cyclic voltammetry, differential scanning calorimetry, thermogravimetric analysis and UV-Vis spectroscopy with interesting optical and thermal properties exhibition. In addition, fullerene OSCs prototypes in case of benzotriindole-based molecules and non-fullerene OSCs prototypes in case of benzodithiophene-based molecules were designed and showed competitive results.

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

Carboxyl-Containing Asphaltenes as Promising Acceptor Materials for Bulk Heterojunction Solar Cells

N.I. Borzdun^{1}, R.R. Ramazanov¹, A.D. Glova¹, S.V. Lyulin¹, S.V. Larin¹*

¹ Institute of Macromolecular Compounds, Russian Academy of Sciences
*e-mail: natalia.borzdun@gmail.com

Nowadays an active search for new donor and acceptor materials for bulk heterojunction (BHJ) solar cells is underway with a view to improve their efficiency, mechanical properties and stability, as well as to reduce production costs. Of high interest as new acceptors are graphene-like particles capable of forming stacked structures due to π - π -interactions that ensures efficient charge transportⁱ. Asphaltenes are natural carbon nanoparticles resembling graphene. Their architecture usually includes polyaromatic core, heteroatoms and side aliphatic groupsⁱⁱ. Since asphaltenes are side products of deep oil refining, they cost significantly less than analogous synthesized carbon particles. In addition, via simple chemical modifications it is possible to remove or substitute aliphatic groups in asphaltene molecules. Such rational modifications might influence both electronic properties and interactions with the donor material, potentially favoring the properties of an active layer of BHJ solar cellⁱⁱⁱ.

In this work, we probe carboxyl-containing asphaltenes as a novel low-cost acceptor material for BHJ solar cells. To this end, we studied a mixture of asphaltenes modified with carboxyl groups and poly(3-hexylthiophene) (P3HT) as a model polymer-donor material using density functional theory calculations (DFT) and all-atom molecular dynamics simulations (MD). The results of DFT calculations show that the chemical modification of asphaltenes with carboxyl groups allows modulating their energy levels and thereby obtaining the distance between the lowest unoccupied molecular orbital (LUMO) levels of the acceptor and donor materials required for efficient charge transfer. MD simulations allow us to predict the heterophase structure of P3HT/asphaltenes mixtures, as well as the formation of stacks of asphaltenes via π - π -stacking and the alignment of P3HT chains, all of these being important for the formation of an active layer with required morphology and electronic properties. Overall, the results obtained allow us to conclude that asphaltenes modified with carboxyl groups represent a promising low-cost acceptor material for BHJ solar cells.

This work is supported by RFBR (project № 19-33-90259). The simulations were performed using the computational resources of the Institute of Macromolecular Compounds and the equipment of the shared research facilities of HPC computing resources at Lomonosov Moscow State University, as well as the resources of the Federal collective usage center “Complex for Simulation and Data Processing for Mega-science Facilities” at NRC “Kurchatov Institute” (ministry subvention under agreement RFMEFI62117X0016), <http://ckp.nrcki.ru/>.

ⁱ Bottari G., Herranz M.Á., Wibmer L., Volland M., Rodríguez-Pérez L., Guldi D.M., Hirsch A., Martín N., D'Souza F., Torres T. *Chem. Soc. Rev.* 2017, **46**, 4464-4500.

ⁱⁱ Lyulin S.V., Glova A.D., Falkovich S.G., Ivanov V.A., Nazarychev V.M., Lyulin A.V., Larin S.V., Antonov S.V., Ganan P., Kenny J.M. *Petroleum Chemistry*. 2018, **58**(12), 983-1004.

ⁱⁱⁱ Begue D., Guille E., Metz S., Arnaud M.A., Santos Silva H., Seck M., Fayon P., Dagrón-Lartigau C., Iratcabal P., Hiorns R.C. *RSC Adv.* 2016, **6**, 13653.

Biocompatibility assessment of organic semiconductors in the context of their application in wearable and on-skin electronics

M.R. Chetyrkina^{1,3*}, F.S. Talalaev^{1,2}, S.V. Kostyuk³, P.A. Troshin^{1,2}

¹Skolkovo Institute of Science and Technology

² Institute for Problems of Chemical Physics of Russian Academy of Sciences (IPCP RAS)

³ Research Centre for Medical Genetics (RCMG)

*e-mail: margarita.chetyrkina@yandex.ru

The preventive and personalized medicine strategy for disease treatment stands apart from traditional medicine therapy. Nowadays, non-invasive monitoring and diagnostic systems based on wearable electronics and e-skin are considered as crucially important for implementation of smart healthcare technologies. However, materials for such devices should fulfill specific requirements, e.g. have a good combination of charge-transport properties, mechanical flexibility, and biocompatibility. In this work, we explored the biological effects of a series of different organic semiconductors on *in vitro* living system. Human embryo lung fibroblasts were incubated at standard conditions with thin films of studied materials. Cells were fixed at different time points in order to find out acute and long-term effects on fibroblasts (30 hours, 96 hours, 14 days). Flow cytometry and immunofluorescence microscopy techniques were performed with antibodies to H2A histone family member X and 8-oxoguanine for DNA damages evaluation. The occurred changes in cell metabolism were detected by real-time polymerase chain reaction, which was carried out with primers to the genes involved in apoptosis regulation and oxidative stress in cells. Results of our study demonstrated that some of the studied organic semiconductors represent biocompatible materials suitable for wearable and on-skin electronics.

Simple interfacial passivation for HTL-free perovskite solar cells with carbon top electrodes

E.A. Dolzhikova^{1,2*}, *S.A. Tsarev*², *P.A. Troshin*^{2,3}

¹D. Mendeleev University of Chemical Technology of Russia

²Skolkovo Institute of Science and Technology

³Institute for Problems of Chemical Physics of the Russian Academy of Sciences

*e-mail: dolzhikova01@list.ru

Perovskite solar cells (PSCs) represent a promising photovoltaic technology that has a great potential to surpass crystalline silicon photovoltaics (PV). The main advantages of the perovskite solar cells are related to the simplicity of their fabrication, tunable optical properties, and low-cost of the active materials [1]. Electrodes are essential components of perovskite solar cells. Typically, the top electrode is formed by a thin evaporated metal film, whereas carbon electrodes gained more popularity recently as a low-cost and environmentally friendly alternative [2]. However, the power conversion efficiency (PCE) of PSCs with carbon electrodes is still lagging behind the conventional solar cell architectures.

Highly conductive carbon films are normally deposited by blading a suspension of carbon particles and an organic polymer binder in some appropriate solvent directly on the perovskite absorber layer. Herein, we present a new approach to increase the PCE of PSCs by deposition of the carbon electrodes on a pre-passivated perovskite layer, followed by the passivation of the perovskite/electrode interface. The origin of the PCE improvement was attributed to the passivation of defects on the perovskite/carbon interface and improving electrical contact between the electrode and the active layer. After some optimization of the interfacial passivation, we obtained PCE of 8.2% in HTL-free n-i-p solar cell configuration, thus almost doubling the initial efficiency of the non-passivated devices.

To summarize, it is evident that the passivation of the perovskite/carbon interface can lead to a substantial improvement in the performance of PSCs with carbon top electrodes. The method presented in this work is especially attractive for large-area applications since the solar cells were produced using scalable electrode deposition techniques and without application of expensive vacuum deposition techniques or organic hole-transport materials.

1. Green, M. A., Ho-Baillie, A., & Snaith, H. J. The emergence of perovskite solar cells. *Nature Photonics*, 2014.

2. G. Yue, D. Chen, P. Wang, J. Zhang, Z. Hu, Y. Zhu, Low-temperature prepared carbon electrodes for hole-conductor-free mesoscopic perovskite solar cells, *Electrochimica Acta*, 2016.

Neuro-like oscillators system based on PANI/PVDF-TrFE memristor

R.N. Belenkov, K.I. Puchenkov, V.E. Melnichenko, A.V. Budaev, N.A. Emelianov*

Kursk State University
*e-mail: emelianov@kursksu.ru

Broad perspectives of practical implementation of neural networks in information processing technologies lead to the necessity of active study of neuronal and neural-like networks consisting of active elements capable of being in different dynamic states, for example, oscillations, bistability and excitability. The ion channels providing the transmission of an electrical signal between neurons have the characteristics of memristive systems from the physical point of view. The pulse frequency and its amplitude corresponding to the relaxation of self-sustained oscillations directly depend on the change in the conductivity of electrical contacts. This leads to the appearance of various dynamic patterns. An important method of research in this area is the construction of substitute electric circuits with elements which dynamics simulate neural ones. The principal element of this type of circuit is a memristor with hysteresis current-voltage characteristic, changing the value of its conductivity depending on the value of the passed charge. Previously, the system of neuro-like generators with simulated synaptic coupling on the base of inorganic memristor was discovered and modes of oscillation synchronization were studiedⁱ.

The paper presents the results of investigation of oscillation modes of the system of two FitzHugh-Nagumo oscillators with synaptic coupling on the base of PANI/PVDF-TrFE memristor obtained earlier by the authorsⁱⁱ. The following frequency synchronization modes were implemented: 1:1, 1:2, 1:3.

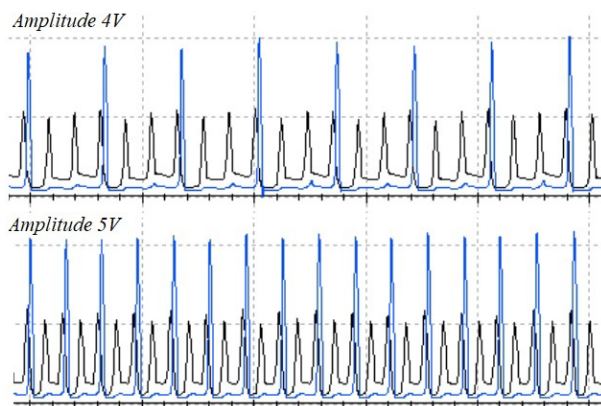


Fig. 1. Synchronization of frequencies depending on the amplitude of the driving oscillator

Moreover, the frequency shift at constant voltage of the pulses of the driving oscillator was observed. And this can be caused by the degradation of the memristive properties of PANI/PVDF-TrFE interface with an increasing number of resistive switching cycles.

ⁱ Gerasimova S.A., Mikhaylov A.N., Belov A.I., Korolev D.S., Gorshkov O.N. and Kazantsev V.B. *Technical Physics* 2017, 62, 1259–1265.

ⁱⁱ Budaev A.V., Belenkov R.N., Emelianov N.A. *Condensed Matter* 2019, 4, 56.

Poly-(N-methylaniline) and dihydrophenazine-based copolymers as promising cathode materials for dual-ion batteries

A.I. Somova^{1,2}, *E.S. Fedina*^{1,2}, *F.A. Obrezkov*², *P.A. Troshin*^{2,3}

¹D. Mendeleev University of Chemical Technology of Russia

²Skolkovo Institute of Science and Technology

³Institute for Problems of Chemical Physics of the Russian Academy of Sciences

*e-mail: fedinalenn@mail.ru

Over the past decades, the growing demand for portable electronics dictated new performance requirements for energy storage devices such as high energy and power densities and good charge-discharge cycling stability. Despite the huge success of lithium-ion batteries on the market of high-performance energy storage devices, there are several concerns regarding their further development associated mainly with their recyclability and limited resources of lithium available in the Earth crust and ocean.

Within the last years, a number of post-lithium technologies have been emerging. The dual-ion batteries based on organic electrode materials deserved a special attention due to a number of reasons. In particular, organic materials are comprised of only naturally abundant chemical elements (C, H, N, O, S), they undergo simple redox chemistry and hence usually operate equally well in combination with any metal ion (Li^+ , Na^+ , K^+ etc.).^[1,2]

Polymeric aromatic amines are among the most promising organic cathodes for dual-ion batteries. However, cathodes based on polyaniline (PAni), which is among the most extensively studied materials of this type, demonstrate poor rate capabilities and retention characteristics. Polytriphenylamine (PTPA), which is another frequently used polyamine-based cathode, is devoid of such disadvantages but provides relatively low theoretical capacity (110 mAh/g).^[3]

Herein, we report aromatic polyamines with high theoretical capacity, good cycling stability and rate capabilities. In particular, poly-(N-methylaniline) (**PNMA**) was designed as a more stable analogue of polyaniline.^[4] In addition, two novel copolymers of dihydrophenazine with diphenylamine (**PDPAPZ**) and phenothiazine (**PPTZPZ**) were synthesized and investigated as cathode materials for dual-ion batteries. Lithium cells with all designed polymeric cathodes demonstrated high average discharge potentials of $> 3\text{V}$. Being galvanostatically charged and discharged at the current density of 5 A g^{-1} , **PNMA** cathodes provided the specific capacity of 137 mAh g^{-1} , while **PDPAPZ** showed the capacity of 101 mAh g^{-1} with 86% and 34% retention after 100 and 25000 cycles, respectively. Still impressive discharge capacity of 82 mAh g^{-1} was reached in lithium half-cells at the high current density of 20 A g^{-1} , which corresponds to complete battery charge in 20-30 seconds. Furthermore, encouraging energy density of 398 Wh kg^{-1} was obtained in potassium half-cells. Thus, the obtained results feature **PDPAPZ** as one of the best organic cathode materials designed so far for ultrafast lithium and potassium dual-ion batteries.

This study was supported by RFBR (project 19-33-90233) and RSF (project 16-13-00111).

1. W. Deng, X. Liang, X. Wu, J. Qian, Y. Cao, X. Ai, J. Feng, H. Yang, *Sci. Rep.* **2013**, 3, 2671.

2. L. Fan, Q. Liu, Z. Xu, B. Lu, *ACS Energy Lett.* **2017**, 2, 1614.

3. J. K. Feng, Y. L. Cao, X. P. Ai, H. X. Yang, *J. Power Sources* **2008**, 177, 199.

4. H. Gao, L. Xue, S. Xin, J. B. Goodenough, *Angew. Chemie - Int. Ed.* **2018**, 57, 5449.

High performance 2D field-effect transistors based on novel tetrathienothiophene derivatives

R. S. Fedorenko^{*1,2}, *V. A. Trukhanov*^{1,2}, *M. S. Skorotetcky*², *O.V.Borshchev*², *S.A. Ponomarenko*², *D.Yu. Paraschuk*^{1,2}

¹Faculty of Physics & International Laser Centre, Lomonosov Moscow State University

²Institute of Synthetic Polymer Materials RAS

*e-mail: roman96233@yandex.ru

Recent progress in organic field-effect transistors (OFET) based on ultrathin (mono- or a few layer) single crystals stimulates the interest to ultrathin (2D) organic light-emitting transistors (OLET). The combination of high semiconducting and luminescent properties makes it possible to create an efficient OLET. Tetrathienothiophene (TTA)-based small molecules show high carrier mobilities in OFET^[1], but they are weakly luminescent. Therefore, it is highly desirable to combine good electrical performance of TTA-based semiconductors with efficient luminescence.

In this work, we synthesize tetrathienoacene (TTA) as the central core end-capped with hexyl phenyl ((Hex-Ph)₂-TTA). For (Hex-P)₂-TTA the photoluminescence quantum yield (PLQY) in diluted THF solution is 52%^[2]. Ultrathin films with lateral dimensions in the range of 300–500 μm were grown on silicon substrates. Figure 1 (a,b) shows an image of a typical OFET fabricated on a silicon substrate and its transfer characteristic. The hole mobility in OFETs based on few-layer films was in the range 0.5–0.7 cm²/Vs in the linear regime. Using (Hex-Ph)₂-TTA as active layers, we fabricated polycrystalline OFET samples with low and high-work function electrodes to study ambipolar charge transport and light emission in devices. The device geometry and optical image of an operating OLET are shown in Figure 1c. Our study shows that (Hex-Ph)₂-TTA support a high charge-carrier mobility, ambipolar charge transport and electroluminescence, and therefore could be a promising platform for OLETs.

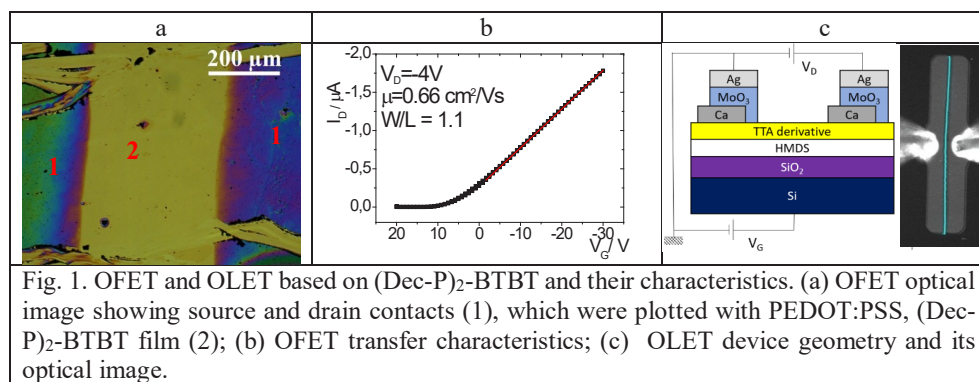


Fig. 1. OFET and OLET based on (Dec-P)₂-BTBT and their characteristics. (a) OFET optical image showing source and drain contacts (1), which were plotted with PEDOT:PSS, (Dec-P)₂-BTBT film (2); (b) OFET transfer characteristics; (c) OLET device geometry and its optical image.

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

¹Liu Y., et al., *Adv Funct Mater* 19, 2009, 772-778.

²Borshchev O., et al., *Dyes and Pigments*., submitted.

Methoxycarbazolyl-substituted oxygafluorenes as bipolar hosts for PhOLED and TADF-based OLEDs

Dalius Gudeika^{1,2}, *Dmytro Volyniuk*¹, *Juozas V. Grazulevicius*¹

¹Department of Polymer Chemistry and Technology, Kaunas University of Technology

²Institute of Solid State Physics, University of Latvia

*e-mail: gudeika.dalius@gmail.com

Many host materials were reported for either phosphorescent or TADF OLEDs [1¹]. However, incomparably less research was done on the search for versatile host materials, which can be applied both for PhOLEDs and TADF OLEDs. In most cases, carbazole is selected due to high triplet energy, good thermal stability and useful optical and charge-transporting properties of carbazole derivatives. To our knowledge, no derivatives of methoxy-substituted carbazole capable of effectively transporting both holes and electrons were reported. Therefore, it is of interest to further study structure-properties relationship of methoxy-substituted carbazoles.

In this study, three donor-acceptor-donor compounds were designed and synthesized as bipolar host materials containing electron-donating methoxycarbazole and electron-accepting dibenzofuran units as versatile host materials for both PhOLEDs and TADF-based OLEDs. Photophysical, thermal, electrochemical electrooptical and charge transporting properties of the compounds were investigated. The synthesized compounds exhibited relatively high thermal stability with 5% weight loss temperatures exceeding 378 °C and formed molecular glasses with high glass-transition temperatures ranging from 120 to 148 °C. High triplet energy values of 2.86-2.96 eV were estimated for dilute THF solutions at 77 K. Hole and electron drift mobilities estimated using time-of-flight technique in solid layers approached $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at high electric fields exceeding $3.6 \times 10^5 \text{ V cm}^{-1}$. Taking into account the results of investigations, the hosts were utilized in phosphorescent and TADF OLEDs discussing effects of substitution patterns on device performances. The synthesized methoxy-carbazole based compounds were tested as hosts in electrophosphorescent and TADF organic light-emitting diodes reaching luminance of 53000 cd m^{-2} and external quantum efficiency of 12.5% in the best case.

This work was supported by ERDF PostDoc (project № 1.1.1.2/VIAA/1/16/177).

¹ Jia B., Lian H., Sun T., Wei J., Yang J., Zhou H., Huang J., Dong Q. *Dyes Pigments* 2019, **168**, 212-218.

**Synthesis and study of properties of linear oligothiophenes end-capped with
methyldicyanovinyl and ethyl cyanoacetate groups**

N.K. Kalinichenko^{1}, D.O. Balakirev¹, Yu.N. Luponosov¹, S.A. Ponomarenko¹*

¹ Enikolopov Institute of Synthetic Polymeric Materials of the Russian Academy of Sciences,
Moscow, Russia

*e-mail: kalinichenko@ispm.ru

Oligothiophenes are widely used π -conjugated compounds for organic electronics and photonics devices because of their high stability, good semiconducting and optical properties and relatively simple and well-studied synthesis [1,2].

The donor-acceptor approach allows to fine-tune physical and chemical characteristics of the organic conjugated systems by varying the donor and acceptor units, the length of the π -conjugated spacer between them, and by introducing additional solubilizing alkyl groups [3-5].

Here a series of oligomers containing 5 and 7 conjugated thiophene units with and terminal electron withdrawing methyldicyanovinyl and ethyl cyanoacetate groups on each side of the central core were synthesized. All precursors and the target compounds were characterized by ¹H and ¹³C NMR spectroscopy and size exclusion chromatography in an individual state. Optical, thermal and electrochemical properties of molecules were studied and compared. The obtained oligothiophenes are promising candidates for organic photovoltaics.

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

¹ A. Mishra, C. Ma, P. Baurele, *Chem. Rev.*, **2009**, 109 (3),1141.

² L. Zhang, N.S. Coella, B.P. Cherniawski, et al., *ACS APPL MATER INTER*, **2014**, 6 (8), 5327.

³ J. E. Coughlin, Z. B. Henson, G. C. Welch, et al., *Acc. Chem. Res.*, **2014**, 47, 257.

⁴ S. Athanasopoulos, L. A. Hernandez, D. Beljonne, et al., *J. Phys. Chem. Lett.*, **2017**, 8 (7), 1688.

⁵ O.V. Kozlov, Yu.N. Luponosov, A.N. Luponosov, et al., *Org. Electron.*, **2018**, 53, 185.

New ladder-type conjugated polymer with hexaazatriphenylene fragments as a cathode material for Li-, Na- and K-based batteries

R.R Kapaev^{1,2,3}, P.A. Troshin^{1,2}*

¹Center for Energy Science and Technology, Skolkovo Institute of Science and Technology

²Institute for Problems of Chemical Physics RAS

³D.I. Mendeleev University of Chemical Technology of Russia

*e-mail: roman.kapaev@skoltech.ru

Organic compounds have recently attracted much attention as active materials for energy storage devices. Their main advantages include great versatility, tunability and absence of transition metals, such as cobalt or nickel, which makes them friendlier to the environment and easier to dispose. Molecules with hexaazatriphenylene (HAT) moieties are one of the promising types of organic cathode battery materials since they combine excellent cycling stability (up to tens of thousands of cycles), high capacities and high rate capabilities. However, HAT-based materials remain poorly studied in energy storage devices, especially in post-lithium batteries.

In this study, we propose a novel ladder-type conjugated polymer with HAT redox-active fragments as a promising cathode material for lithium, sodium and potassium batteries. In a potential range of 1.2-3.8 V vs. Li⁺/Li, the proposed material showed a specific capacity of 170-180 mA h g⁻¹ at a current density of 0.1 A g⁻¹, possessing an average discharge potential of 2.0 V vs. Li⁺/Li. At the current density of 5 A g⁻¹ (charging/discharging in 1-1.5 minutes), the capacity reached 90-110 mA h g⁻¹. The polymer was stable in all three types of batteries with Li⁺, Na⁺ or K⁺ ions. In K-based cells, no capacity fading was observed over 4000 charge-discharge cycles at 5 A g⁻¹, which makes it one of the most stable cathode materials for anhydrous potassium batteries reported so far.

This work was supported by RFBR (project № 19-33-90034).

Novel Anolyte Material for High Voltage Non-Aqueous Organic Redox Flow Batteries

E. I. Romadina^{1,2}, *D. S. Komarov*^{1,3*}, *K. J. Stevenson*¹, *P. A. Troshin*^{1,2}

¹ Skolkovo Institute of Science and Technology,

² Institute of Problems of Chemical Physics of Russian Academy of Sciences,

³ D. Mendeleev University of Chemical Technology of Russia,

*e-mail: komarov.d.s.24@gmail.com

The widespread implementation of eco-friendly renewable energy sources, such as geothermal power, solar, or wind energy, requires the development of next-generation energy storage technologyⁱ. Redox flow batteries (RFB) deserved special attention for their excellent scalability, flexible design capabilities, and low costⁱⁱ. These features are arising from the construction of the batteries: energy storage system (electrolyte tanks) and electrochemical cell are isolated from each other in the RFBs (Fig. 1). This aspect distinguishes redox flow batteries from lithium-ion systems, where an electrochemically active substance is located inside the electrode.

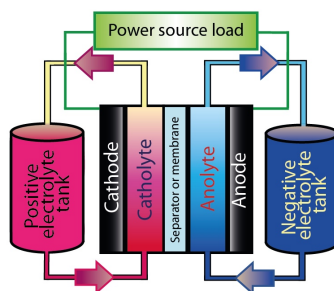


Fig. 1. Schematic view of a redox flow battery system

However, RFB still exhibited the lowest specific capacity among the electrochemical energy storage technologies and it is an obstacle for massive commercialization of the batteries. Replacement of the classical inorganic materials (such as vanadium) to the organic redox-active molecules and implementation of the organic solvents with wide electrochemical stability window (>5 V) could lead to a significant improvement of the all battery parametersⁱⁱⁱ.

In this work, we made a step forward to increasing specific capacity and power of RFBs. For this purpose, we focused on the modification of the well-known phenazine molecule for its application as an anolyte material for non-aqueous organic RFBs. Investigated molecule exhibits reversible and stable redox reaction at -1.72 V vs. Ag/AgNO_3 and 2.5 M solubility in acetonitrile. A non-aqueous organic RFB based on modified phenazine molecule as an anolyte exhibited high charge capacities ($\sim 93\%$ from the theoretical value) on the first cycles; more than 95% coulombic efficiency and 65% utilization of active materials with no capacity decay from 20th to 50th cycles. The obtained results feature the designed phenazine derivative as a promising anolyte material for emerging organic redox-flow batteries.

ⁱ Panwar N. L., Kaushik S. C., Kothari S., *Renew. Sustain. Energy Rev.*, 2011, **15**(3), 1513–1524

ⁱⁱ Placke T., Heckmann A., Schmuck R., Meister P., Beltrop K., Winter M., *Joule*, 2018, **2**, 2528–2550

ⁱⁱⁱ Chen H., Cong G., Lu Yi. C., *Journal of Energy Chemistry*, 2018, **27**, 1304–1325

New organic semiconductors for organic electronics

Oleg Borshchev¹, Maxim Skorotetcky¹, Marina Polinskaya¹, Elena Agina¹, Askold Trul¹,
Victoria Chekusova¹, Sergey Ponomarenko^{1,2}

¹ Institute of Synthetic Polymer Materials RAS

² Moscow State University, Department of Chemistry

*e-mail: borshchev@ispm.ru

Organic electronics has been actively developed in recent years due to their advantages such as ease of processing, low manufacturing cost, and mechanical flexibility. Nowadays development of efficient field-effect transistors is a great challenge of organic electronics.¹⁻³ As it was reported earlier, the charge transport in organic field-effect transistors (OFETs) mainly occurs in 1-2 molecular layers close to the gate dielectrics.^{4,5} Recently we reported organosilicon derivatives of oligothiophenes allowing monolayer formation at the water-air interface, which were used for fast and efficient SAMFETs fabrication by Langmuir-Blodgett (LB) and Langmuir-Schaefer (LS) techniques.⁶⁻⁹ In this work we synthesized several novel derivatives of dialkyl substituted [1]benzothieno[3,2-b][1]-benzothiophene (BTBT) containing flexible aliphatic spacers of various length linked to disiloxane anchor groups via bromine protection-deprotection of the terminal alkenyl double bonds in combination with Friedel-Crafts acylation, Wolff-Kishner reduction and hydrosilylation reactions.¹⁰ They were successfully used in monolayer OFETs with the charge carrier mobilities up to 0.02 cm²/Vs, threshold voltage close to 0 V and On/Off ratio up to 10,000. Influence of the chemical structure of the molecules synthesized on the morphology, molecular 2D ordering in the monolayers and their semiconducting properties is considered.¹¹ Also we designed and synthesized several novel derivatives of [3,2-b]thieno[2',3':4,5]thieno[2,3-d]thiophene (TTA). We report on a new design of highly sensitive gas sensors based on Langmuir-Blodgett, Langmuir-Schaefer and spin-coating monolayer organic field-effect transistors (OFETs).^{12,13} The devices fabricated are able to operate in air and allow an ultrafast detection of different analytes at low concentrations down to tens of parts per billion. The results reported open new perspectives for the OFET-based gas-sensing technology and pave the way for easy detection of the many types of gases, enabling the development of complex air analysis systems based on a single sensor.

This work was supported by Russian Science Foundation (grants № 18-73-10182).

1 R. Kagan, *Top. Curr. Chem.* 2012, **312**, 213-238.

2 O. V. Borshchev, S. A. Ponomarenko, *Polym. Sci. C.* 2014, **56(1)**, 32-46.

3 F. Gholamrezaie et al, *Nano Lett.* 2010, **10(6)**, 1998-2002.

4 C. Tanase et al, *Org. Electron.* 2003, **4(1)**, 33-37

5 M. Mottaghi et al, *Adv. Funct. Mater.* 2007, **17(4)**, 597-604

6 A.S. Sizov et al, *Langmuir* 2014, **30(50)**, 15327-15334

7 E.V. Agina et al, *Langmuir* 2012, **28(46)**, 16186-16195.

8 A.S. Sizov et al, *Appl. Phys. Lett.* 2013, **103**, 043310.

9 E.V. Agina et al, *ACS Appl. Mater. Interfaces* 2017, **9(21)**, 18078-18086.

10 O.V. Borshchev et al, *Chem. Commun.*, 2017, **53**, 885-888.

11 E.V. Agina et al, *Proc. SPIE Organic Field-Effect Transistors XVI*, 2017, 1036500

12 A.S. Sizov et al, *ACS Appl. Mater. Interfaces* 2018, **10(50)**, 43831-43841

13 A.A. Trul et al, *J. Mater. Chem. C*, 2018, **6**, 9649-9659

New organic luminophores for scintillation and wavelength shifting fibers

*O.V. Borshchev**¹, *M.S. Skorotetcky*¹, *N.M. Surin*¹, *S.A. Ponomarenko*^{1,2}

¹ Enikolopov Institute of Synthetic Polymeric Materials RAS

² Moscow State University, Department of Chemistry

*e-mail: borshchev@ispm.ru

During the last years, the number of light-harvesting luminescent dendritic molecules has increased rapidly. One of the most interesting features of these molecules is a possibility of incorporation of different chromophores within one molecule that can lead to an intramolecular directional energy transfer from their peripheries to the center. Recently we have developed a new class of highly efficient luminescent materials with unique properties - nanostructured organosilicon luminophores (NOLs).^{1,2,3} 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.^{4,5,6} 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. Photoluminescence study of the NOLs has shown an intramolecular energy transfer with the efficiency up to 99% and luminescence quantum yield up to 95% in various spectral regions. Optical and thermal properties of the NOLs were compared with the properties of the model linear oligomers.⁷ It should be noted that combination of different chromophores in NOLs allows tuning their emission wavelengths in a wide spectral region, which open possibilities for their wide application as spectral shifters – converters of the emission with the energy of high frequency photons (140–400 nm) into emission in the visible spectral range (400–700 nm).⁸

We applied NOLs as organic luminophores for manufacturing scintillation and wavelength shifting polymer fibers.⁹ A blue and a green emitting prototype fibre were produced and characterised in terms of attenuation length, ionisation light yield, decay time and tolerance to x-ray irradiation. Both the blue and the green prototype fibres show a very short decay time constant and mark to our knowledge new records. The GPF-19-1 prototype fibre is about a factor 6 faster than the SCSF-3HF fibre produced by Kuraray and about two times faster than the green BCF-20 fibre produced by Saint-Gobain Crystals.

The new NOLs used in various devices of organic photonics and electronics, such as spectral shifting fibers⁹, organic light-emitting diodes (OLEDs)¹⁰, CIGS photovoltaic devices¹¹. NOLs are commercialized by a startup Limited Liability Company "Luminescent Innovative Technologies" (LumInnoTech LLC). All the details can be found on www.luminnotech.com

This work was supported by RFBR (№18-29-17006MK).

¹ S.A. Ponomarenko, N.M. Surin, O.V. Borshchev, at. al. *Scientific Reports* 2014, **4**, 6549.

² T.Yu. Starikova, N.M. Surin, O.V. Borshchev, at. al., *J. Mater. Chem. C*, 2016, **4**, 4699.

³ S.A. Ponomarenko, N.M. Surin, O.V. Borshchev, at. al., *Proc. SPIE*, 9545, 2015, 954509-1.

⁴ O.V. Borshchev, S.A. Ponomarenko, at. al., *Organometallics*, 2007, **26**, 5165.

⁵ Yu.N. Luponosov, S.A. Ponomarenko, N.M. Surin, O.V. Borshchev, E.A. Shumilkina, A.M. Muzafarov, *Chem. Mater.* 2009, **21**, 447.

⁶ O.V. Borshchev, Y.N. Luponosov, E.A. Kleymyuk, N.M. Surin, S.A. Ponomarenko, A.M. Muzafarov *Russ. Chem. Bull.*, 2010, **4**, 781.

⁷ M.S. Skorotetcky, E.D. Krivtsova, O.V. Borshchev at. al., *Dyes and Pigments* 2018, **155**, 284–291.

⁸ D.Y. Akimov, O.V. Borshchev, S.A. Ponomarenko, at. al., *NIM A*, 2012, **695**, 403-406.

⁹ O. Borshchev, A.B.R. Cavalcante, L. Gavardi, O. Shinjie et. al., *JINST* 2017. **12**. P05013

¹⁰ Y.N. Luponosov, N.M. Surin, at. al., *Org. Photonics Photovolt.*, 2015, **3**, 148-155

¹¹ T. Uekert, A. Solodovnyk, S. Ponomarenko at. al., *Sol. Energy Mat. Sol. Cells*, 2016, **155**, 1-8.

Design of multiscale simulation models of photovoltaic polymeric nanocomposites

Komarov P.V.^{1,2}, Guseva D.V.¹, Rudyak V.Yu.³, Gavrilov A.A.³,
Ivanov V.A.³, Tung S.-H.⁴

¹A.N. Nesmeyanov Institute of Organoelement Compounds RAS, Moscow, Russia
²Tver State University, Tver, Russia

³M. V. Lomonosov Moscow State University, Moscow, Russia

⁴National Taiwan University, Taipei, Taiwan

*e-mail: pv_komarov@mail.ru

Polymer-based solar cells (PSC) have attracted great interest as a perspective replacement for inorganic solar cells due to their lightweight, low-cost, and easy manufacturing. Single-layer PSC are made by sandwiching of an organic photoactive layer (PhL) between two conductors. The efficiency of PSC can be increased by incorporating suitable pair of electron donor and acceptor materials with offset energy levels of about 0.3 eV. The electron donor could be organic molecules or polymer, and the electron acceptor could be organic molecules, fullerenes, carbon nanotubes, inorganic nanoparticles, or quantum dots. The forming morphology of PhL is crucial for performance of PSC. Therefore, it is important to carry out a preliminary study of photovoltaic polymeric nanocomposites for the subsequent engineering of the active layer with high-energy conversion efficiency.

This report discusses the problems of design of computer models for simulations of the photoactive layer of polymer solar cells. There are several challenges here. Crystalline domains, which strongly influence PhL properties, are formed in conjugated polymers due to π - π stacking interactions. However, at present, computer simulation methods have very limited possibilities for constructing models of polymeric materials, taking into account π - π interactions driven self-assembly processes. This problem is especially acute for mesoscopic methods that allow the study of polymeric materials at relatively large length and time scales. In this report, we propose a method for taking into account π - π stacking interactions in mesoscale models and check it in the framework of the dissipative particle dynamics method. As prototypes of polymer model, we use poly(3-hexylthiophene-2,5-diyl) (P3HT), poly(3-2-methylbutylthiophene) (P3MBT), poly(3-2-methylpentylthiophene) (P3MPT).

We also constructed the reverse-mapping procedure that makes it possible to create models of atomistic samples of PhL based on the final states of the mesoscopic models. This creates possibilities to construct the multiscale schemes for simulation of the nanocomposites based on the conjugated polymers with various fillers for prediction of their thermophysical properties and thermal stability.

The research is carried out using the equipment of the shared research facilities of HPC computing resources at Lomonosov Moscow State University with financial support from the Russian Foundation for Basic Research (Project No. 19-53-52004) and the Ministry of Science and Technology of Taiwan (Project MOST 108-2923-E-002-001-MY3).

Hole hopping in dimers of N,N' di(1-naphthyl)-N,N'-diphenyl-4,4'-diamine (α -NPD): a theoretical study

I.D. Krysko^{1,2}, A.Y. Freidzon^{1,2}, A.A. Bagaturants^{1,2}

¹National Research Nuclear University MEPhI (Moscow Engineering Physics Institute)

²Federal Research Center "Crystallography and Photonics" Photochemistry Center RAS

*e-mail: ilya_krysko@mail.ru

Hole-hopping parameters for Marcus-like charge transport, Marcus hole hopping rates, and hole mobilities are calculated for a series of model dimers of a typical hole-transporting material α -NPD using multireference quantum chemistry methods. The parameters are extracted from the two-state energy profiles built for charge hopping between two states with a hole localized on each of the monomers. Energy profiles of intermolecular hole migration are plotted by linear interpolation procedure in internal molecular coordinates. Script for automating preparatory calculations for the linear interpolation procedure was written. The dependence of the hopping integral on the intermolecular arrangement in the dimer is studied. It is shown that at short intermolecular distances strong orbital interactions between molecules cause a drastic increase in the hopping integral and, therefore, in the hopping rate.

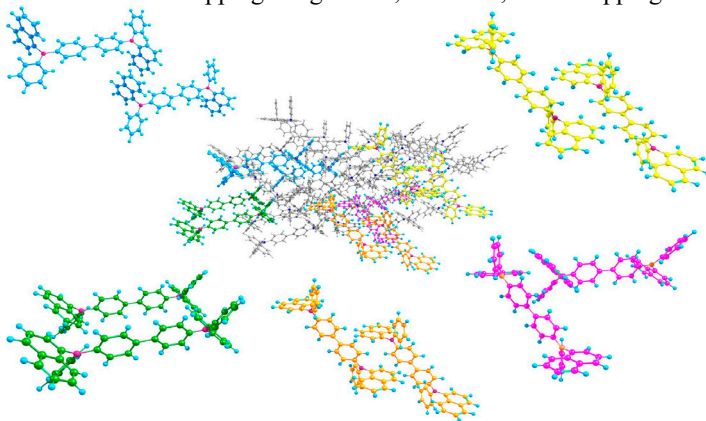


Fig. 1. Closest contact dimers in crystal α -NPD

This work was supported by RSF (project № 19-13-00383).

Novel organic metal BEDO₄Dy(OH)₆ 4(H₂O) (H₂OW3-H-OW3H₂). based on π -donor BEDO and [Dy(NO₃)₅]²⁻ anion: synthesis, structural peculiarities and conductivity.

N. D. Kushch^{1}, G. V. Shilov¹, L.I. Buravov¹, V.N. Zverev^{2,3}*

¹Institute of Problems of Chemical Physics RAS

²Institute of Solid State Physics, RAS

³Moscow Institute of Physics and Technology

*e-mail: kushch@icp.ac.ru

The design and synthesis of new polyfunctional compounds is one of the top priorities in the chemistry of modern materials. In particular, compounds with electrical conductivity and magnetism in the same crystal lattice are objects of intensive study, which is associated with the possible synergism of these properties and the appearance of new phenomena in them. Recently, we synthesized the first conductive single monomolecular magnet (SMM), (BEDO)₄[ReF₆]·6H₂O, (BEDO – bis(ethylenedioxo)tetrathiafulvalene) and studied its structure, conducting and magnetic properties. This complex is characterized by high conductivity (up to 4.2 K) and monomolecular magnetism coexist in the same temperature range. This result demonstrates the possibility of the creation of SMMs based on cation radical salts with highly conductive at helium temperatures. In this work BEDO was used as a π -donor and the (Bu₄N)₅Dy(NO₃)₅ salt as supporting electrolyte. Previously we defined the structure of the (Bu₄N)₅Dy(NO₃)₅ electrolyte as well as magnetic properties and discovered that it possessing the properties of SMM.

However, instead the presuppose salt BEDO with counter-ion [Dy(NO₃)₅]²⁻, BEDO electrocrystallization in a chlorobenzene-96% ethanol (9:1) mixture solvent resulted in the synthesis of novel radical cation salt BEDO₄Dy(OH)₆ 4(H₂O) (H₂OW3-H-OW3H₂). No N atoms in the crystal was the great surprise for us. The salt composition was analyzed by full X-ray diffraction analysis. The complex crystallizes in a triclinic cell with the parameters $a = 7,9590(8) \text{ \AA}$, $b = 10,5564(9) \text{ \AA}$, $c = 17,2309(18) \text{ \AA}$, $\alpha = 77,310(8)^\circ$, $\beta = 88,573(8)^\circ$, $\gamma = 82,160(7)^\circ$, $V = 1399,13 \text{ \AA}^3$, space group $P(-1)$, $Z=1$, $R_1=0,0930$. From differential syntheses near oxygen atoms involved in the coordination of Dy and solvate water molecules, weak electron density peaks were detected, which were taken as hydrogen atoms. They were refined with restrictions on bond lengths and thermal parameters. Near the OW3 water molecule, three hydrogen atoms were identified, two in general position and one in the center of inversion. When propagated by the inversion center, the dioxonium cation H₂OW3-H-OW3H₂ is obtained. One unit cell contains one [Dy(OH)₆]³⁻-octahedral anion, four organic cations with a total charge of +2, one dioxonium cation with charge +1 and fore water molecules. As a result of a total charge molecule is 0, i.e. electroneutrality is observed. The salt has a layered structure, which is characterized by alternation of conducting β^{π} -type cation-radical layer and 2D anion net involving magnetic Dy atoms. Radical cation layers build up the stacks consist of the crystallographically independent A and B molecules with a charge of $\approx +0,5$ and have a "twist" conformation. The dihedral angle between the neighboring A and B radical cations is $3,47^\circ$. The terminal ethylene groups both BEDO molecules are ordered. Radical cations in the conductive layers are bonded by the short contacts S ... S and O ... S and hydrogen bonds O... HC. The anion layers have the complicate structure. Thus, fore oxygen atom of octahedron in the equatorial positions are bonded with water molecules while two apical those are linked, respectively, with two O atoms belong to the radical cation A. In addition, H₂O molecules are linked to each other and the H₂OW3-H-OW3H₂ ion by hydrogen bonds. Between the cationic and anionic layers there are also notable shortened contacts of the type O... S and O...C and several hydrogen bonds O...HC. The crystals exhibit a metallic behavior of resistance up to $\sim 4,5 \text{ K}$. The sample resistivity's in the conducting plane and to it are $1,4 \cdot 10^{-3}$ and $94,4 \text{ \Omega cm}$, respectively at 300 and 4,5 K. Resistance anisotropy is $1,5 \cdot 10^{-5}$.

The work was done on the topic of the State task № AAAA-A19-11902390079-8 and in part supported by the RFBR grant N 18-02-00280.

Synthesis of novel (X-DADAD)_n polymers with fluorene and phenylene X blocks and their application in organic solar cells

I.E. Kuznetsov^{1*}, P.M. Kuznetsov,¹ D.V.Revina,¹ P.A. Troshin,^{2,1} A.V.Akkuratov¹

¹ Institute for Problems of Chemical Physics, Russian Academy of Sciences

² Skolkovo Institute of Science and Technology

*e-mail: kusnetsovilja@gmail.com

Organic solar cells (OSCs) based on polymer-based electron donor and fullerene or non-fullerene acceptors have attracted a considerable attention because of such their characteristics as lightweight, semitransparency, low cost, and simple fabrication by solution processing.ⁱ Numerous conjugated polymers with advanced functional properties have been already developed thus leading to a steady improvement in the performance of OSCs.

We recently proposed and implemented an approach to design novel conjugated polymers with an extended system of alternating donor and acceptor blocks (X-DADAD)_n.ⁱⁱ Novel carbazole-based PCDTBTBT polymer demonstrated improved optoelectronic properties in comparison with the well-known PCDTBT analogue. However, low solubility of PCDTBTBT did not allow us to utilize it in fabrication of solar cells.

Herein, we present two (X-DADAD)_n polymers incorporating fluorene (**P1**) or phenylene (**P2**) moieties bearing long-chain branched alkyl substituents. Both conjugated polymers are highly soluble in common organic solvents.

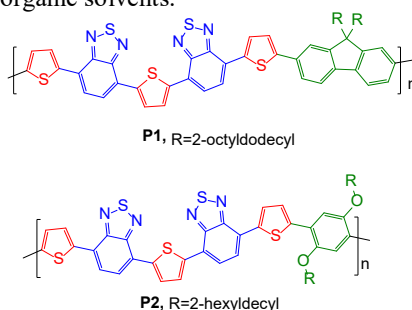


Figure 1. Molecular structure of conjugated polymers **P1** and **P2**.

Polymer **P2** with bis(alkoxy)phenylene X unit exhibited an impressive bathochromic shift of 150 nm in optical absorption spectra when going from solution to thin films, which indicates efficient intermolecular electronic interactions of polymer chains in solid state. Such supramolecular ordering of the material is usually very beneficial for its performance in OSCs. The fluorene-based polymer **P1** showed low HOMO energy of -5.76 eV, which can enable high open circuit voltages (V_{OC}) of OSCs.

Preliminary experiments with polymers **P1** and **P2** in OSCs delivered efficiencies of $>4\%$ when using [60]PCBM as acceptor. Further optimization as well as application of improved fullerene-based and non-fullerene acceptors is expected to lead to improved device efficiencies.

This work was supported by the Russian Foundation for Basic Research (grant No. 20-03-00309).

i Q. Liu, Y. Jiang, K. Jin, J. Qin, J. Xu, W. Li, J. Xiong, J. Liu, Z. Xiao, K. Sun, S. Yang, X. Zhang and L. Ding, *Science Bulletin*, 2020, **65**, 272–275.

Organic field-effect transistors-based flexible temperature sensor for healthcare applications

S.Mandal¹, D.K. Goswami^{1,2}

¹Indian Institute of Technology Kharagpur, Department of Physics

² Indian Institute of Technology Kharagpur, School of Nanoscience and Technology

*e-mail: mandal.suman84@gmail.com

The design simplicity, larger areal integration to the integrated circuit and amplification capability of inferior signal make organic field-effect transistors (OFETs) are more engaging for physical, chemical or biological sensing applications, where active and dielectric materials are chosen in such a way that one of them or both are sensitive to a specific stimulus and the immediate effect of it can be extracted easily. In this work, we are going to present a flexible OFETs based temperature sensor suitable for wearable medical applications. Here, we have used Alumina (Al_2O_3) and barium titanate (BTO) to make a suitable bilayer dielectric system where barium titanate (BTO) film used as temperature-sensitive materials. The low-cost solution process has been used to prepare BTO based dielectric ink. This ink can be spin-coated or screen printed on top of Al_2O_3 layer to make a suitable bilayer dielectric combination. We have fabricated OFETs on top of ultra-thin (10 μm) flexible substrate which is working around 1.2V with the highest observed mobility of 1.4 cm^2/Vs . The temperature sensing properties in these devices have been attributed to the variation of capacitance of our bilayer dielectric system with temperature. As temperature increases, the capacitance of the dielectric system increases. As a result, the charge accumulation at the dielectric/semiconductor interfaces enhances due to the applied gate field and also enhances the sensitivity of temperature measurement. We have found the response and recovery time of our device 24 ms and 51 ms, respectively. The devices were tested to monitor the changes in the body temperature of mice under anesthesia doses. The sensitivity measured in these devices is about 4 milli-Kelvin.

Reference: Mandal, S. *et al. Acs. Appl. Mater. Interfaces* **11**, 4193-4202 (2019).

Incorporation of vanadium (V) oxide in hybrid hole transport layer enables long-term operational stability of perovskite solar cells

Marina M. Tepliakova^{1,2}, Aleksandra N. Mikheeva^{3*}, Lyubov A. Frolova^{1,2}, Aleksandra G. Boldyreva¹, Aly Elakshar¹, Artyom V. Novikov^{1,2}, Sergei A. Tsarev¹, Marina I. Ustinova^{1,2}, Olga R. Yamilova^{1,2}, Albert G. Nasibullin^{1,4}, Sergey M. Aldoshin², Keith J. Stevenson¹, and Pavel A. Troshin^{1,2}

¹Skolkovo Institute of Science and Technology, Moscow, Russia

²Institute for Problems of Chemical Physics of RAS, Chernogolovka, Russia

³D.Mendeleev University of Chemical Technology, Moscow, Russia

⁴Department of Applied Physics of Aalto University School of Science, Espoo, Finland

*e-mail: sashulya-miheeva@mail.ru

In the modern world energy demand grows exponentially. Therefore, the development of renewable energy sources is a major challenge for humanity. Among technologies for solar energy conversion, the strongest rivals to silicon photovoltaics are perovskite solar cells (PSCs) with their efficiency exceeding 25%.ⁱ The main obstacle for technology commercialization is the insufficient stability of devices under realistic operational conditions.

Standard PSC configuration comprises a photoactive layer with perovskite structure sandwiched between hole and electron transport layers. Under the action of stress factors such as elevated temperature, light and/or electric bias perovskite layer reversibly decomposes with the formation of volatile by-products. It was recently shown that these decomposition products can recombine and regenerate perovskite absorber layer.ⁱⁱ However, all degradation products should be maintained inside the absorber layer, so some low gas-permeability charge-transport layers should be implemented at the interfaces with the perovskite photoactive layer.ⁱⁱⁱ

In this work, we developed a hybrid hole-transport layer (HTL) comprised of organic p-type polymer PTAA (polytriarylamine) and vanadium (V) oxide. Devices assembled in n-i-p configuration with PTAA/VO_x as HTL demonstrate high efficiencies up to 20% while using various perovskite materials and metal oxide electron transport layers. Furthermore, solar cells with the designed hybrid PTAA/VO_x hole-transport layer show no significant degradation over 4500 h of continuous light soaking. On the contrary, reference cells comprising PTAA/MoO_x as HTL lose ~50% of their initial efficiency under the same aging conditions. This improvement in device stability associated with the use of VO_x is related to its better compatibility with complex lead halides, whereas MoO_x undergoes severe chemical interactions with the perovskite absorbers.

To summarize, the proposed hybrid HTL utilizing vanadium (V) oxide and PTAA spectacularly improved the operational stability of PSCs, which is essential for future practical implementation of this exciting PV technology.

This work was supported by Russian Science Foundation (project No. 19-73-30020) at IPCP RAS and Skolkovo Foundation grant at Skoltech.

ⁱ NREL Best Research-Cell Photovoltaic Efficiency Chart, <https://www.nrel.gov/pv/cell-efficiency.html>, accessed: august, 2020.

ⁱⁱ E. J. Juarez-Perez, L. K. Ono, M. Maeda, Y. Jiang, Z. Hawash, Y. Qi. *J. Mater. Chem. A* 2018, **6**, 9604.

ⁱⁱⁱ T. H. Schloemer, T. S. Gehan, J. A. Christians, D. G. Mitchell, A. Dixon, Z. Li, K. Zhu, J. J. Berry, J. M. Luther, A. Sellinger. *ACS Energy Lett.* 2019, **4**, 473.

Exploring the substitution of Pb^{2+} with Ca^{2+} in the CsPbI_3 perovskite system

M.M. Mikheeva^{1,2*}, *M.I. Ustinova*^{2,3}, *N.N. Dremova*³, *K.J. Stevenson*², and *P.A. Troshin*^{2,3}

¹*D. Mendeleev University of Chemical Technology of Russia,
Institute for Problems of Chemistry and Sustainable Development*

²*Skolkovo Institute of Science and Technology*

³*Institute for Problems of Chemical Physics of RAS*

**e-mail: maria210900@gmail.com*

The power conversion efficiency (PCE) of perovskite solar cells has crossed the threshold of 25%, thereby giving serious hopes for their commercialization. This rapid progress is associated to a large extent with the development of new compositions of photoactive layer. However, the presence of organic cations in the structure of the most efficient hybrid lead halide perovskite materials usually leads to their rapid thermal or photochemical degradation. On the contrary, less studied all-inorganic α - CsPbI_3 stable at high temperatures of 300-350°C is an attractive alternative to hybrid perovskites. The major obstacle of CsPbI_3 application is its rapid phase transition to the yellow not photoactive δ -phase under standard solar cell operational conditions.¹

Herein, we present an approach to stabilize the black perovskite-like phase of this all-inorganic material by partial substitution of Pb^{2+} with Ca^{2+} in CsPbI_3 . It was shown that Ca^{2+} cations introduced in concentrations ranging from 5 to 30% enable the formation of the desired black polymorph at significantly reduced temperatures of 100-150°C. The designed $\text{CsPb}_{1-x}\text{Ca}_x\text{I}_3$ compositions were explored as absorber materials in perovskite solar cells. Preliminary experiments showed that n-i-p devices based on all-inorganic $\text{CsPb}_{0.92}\text{Ca}_{0.08}\text{I}_3$ material demonstrate encouraging PCE of 7.5% and EQE of ~85% (Fig. 1). The $\text{CsPb}_{0.9}\text{Ca}_{0.1}\text{I}_3$ films showed promising stability and do not undergo conversion to yellow δ -phase under exposure to light and elevated temperatures.

Thus, the obtained results feature a partial substitution of Pb^{2+} in CsPbI_3 as a promising strategy to design all-inorganic absorber materials for efficient and stable perovskite solar cells.

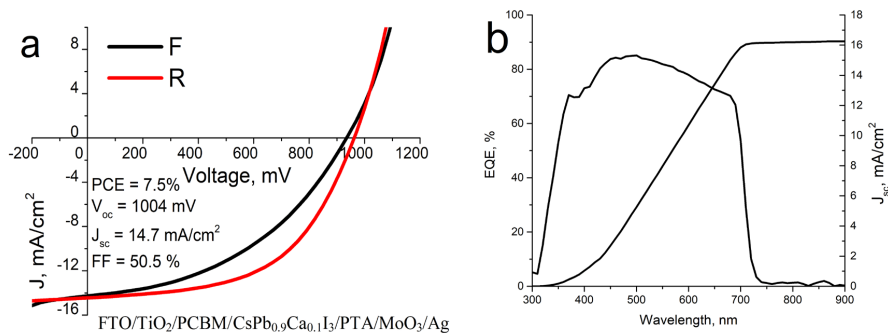


Figure 1. J-V curves (a) and EQE spectrum (b) of perovskite solar cells with $\text{CsPb}_{0.92}\text{Ca}_{0.08}\text{I}_3$ absorber layer.

¹ C. Lau et al. *Journal of Materials Chemistry A*. 2018, **6**, 5580-5586.

Benzodiazine derivatives: synthesis and fluorescence sensory ability

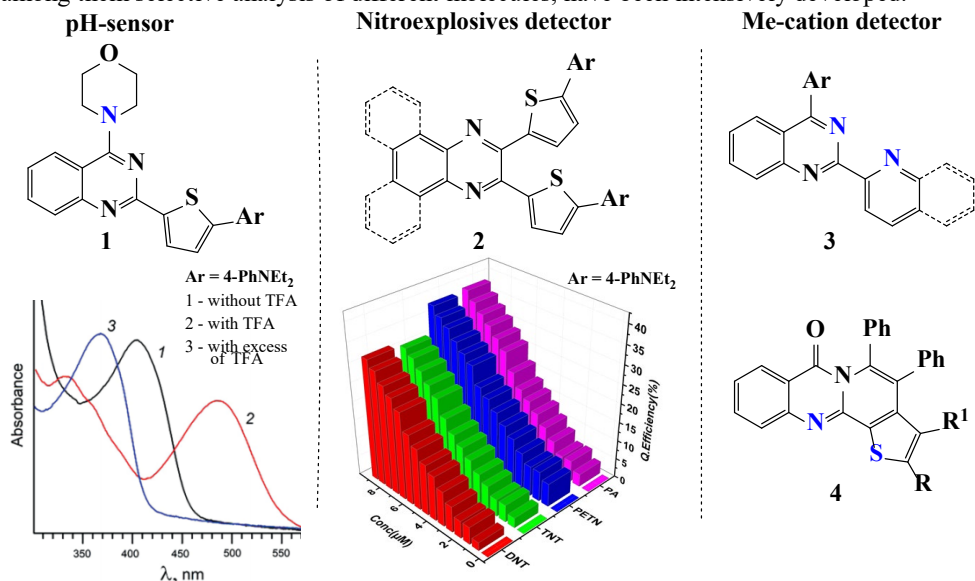
T.N. Moshkina^{1*}, *A.E. Kopotilova*¹, *E.V. Nosova*^{1,2}, *G.N. Lipunova*^{1,2}, *V.N. Charushin*^{1,2}

¹ Department of Organic and Biomolecular Chemistry Ural Federal University

² Postovsky Institute of Organic Synthesis Ural Division of the Russian Academy of Sciences

*e-mail: tan.moshckina@yandex.ru

Through the past few decades, compounds of benzodiazine type for diverse applications, among them selective analysis of different molecules, have been intensively developed.^{i,ii}



Ar = 4-(diethylamino)phenyl, 4-(diphenylamino)phenyl, 4-(9*H*-carbazol-9-yl)phenyl
 Fig. 1. Benzodiazine derivatives with perspective sensory ability.

The ability of compounds **1** to function as colorimetric and luminescent pH sensors was demonstrated by pH triggered color changes and luminescence switching.ⁱⁱⁱ V-shaped 2,3-bis(5-arylthiophen-2-yl)-quinoxaline derivatives **2** displayed fluorescence quenching upon addition of nitro-containing explosives; diethylaminophenyl substituted derivative is the most representative chemosensor ($K_{sv} = 48400\text{--}57800\text{ M}^{-1}$ and LOD = 32–216 ppb).^{iv} The novel 2-pyridinyl- and 2-quinolinyl-substituted quinazolines **3** and polycyclic quinazolinone derivatives **4** were synthesized. The presence of additional hetero atom affords to detect Me-cations in medium^v and this ability will be checked.

This work was supported by the Russian Foundation for Basic Research (grant number 19-33-90014).

ⁱ Lipunova G.N., Nosova E.V., Charushin V.N., Chupakhin O.N., *Curr. Org. Synth.* 2018, **15**, 793–814.

ⁱⁱ Patil A., Salunke-Gawali S., *Inorganica Chimica Acta*, 2018, **482**, 99–112.

ⁱⁱⁱ Nosova E.V., Moshkina T.N., Lipunova G.N. et al, *Eur. J. Org. Chem.* 2016, **2016**, 2876–2881.

^{iv} Moshkina T.N., Nosova E.V., Kopotilova A.E. et al, *Asian J. Org. Chem.* 2020, **9**, 673–681.

^v Zheng L., Hua R., *J. Org. Chem.* 2014, **79**, 3930–3936.

Design of hybrid hole-transport layers for efficient and stable perovskite solar cells

E. V. Mosina^{1,2*}, *M. M. Tepliakova*^{2,3}, *I. K. Yakushchenko*³, *P. A. Troshin*^{2,3}

¹D. Mendeleev University of Chemical Technology

²Center of Energy Science and Technology, Skolkovo Institute of Science and Technology

³Institute for Problems of Chemical Physics of the Russian Academy of Science

*e-mail: katya.3@bk.ru

In the context of sustainable development of our society, there is a growing interest in renewable energy sources, among which perovskite solar cells (PSCs) are of particular interest. First of all, PSCs demonstrate power conversion efficiencies above 25%ⁱ, which is comparable to that of solar cells based on crystalline silicon. In addition, scalability of the perovskite PV technology and availability of all raw materials suggest a potential for substantial decreasing the cost of the produced electric energy. The important obstacle for PSC real-life applications is insufficient device operational lifetime.

It is known that complex lead halides readily decompose under the influence of such stress factors as light or elevated temperature. The following migration of the volatile decomposition products from the absorber layer to other device components causes severe PSCs degradation. It has been reported recently that the stability of PSCs can be improved by utilizing a hole-transport layer (HTL) based on the combination of organic polymer polytriarylamine (PTAA) and metal oxide providing good encapsulation properties.ⁱⁱ It should be noted, that the organic polymeric counterpart is expensive due to the costly synthesis, therefore there is an urgent demand for development of some alternative and more available materials to be applied in the hybrid HTL.

In this work, we fabricated PSCs in standard n-i-p configuration containing hybrid HTL based on the combination of vanadium (V) oxide and various inexpensive organic small molecules with triarylamine and pyrene moieties. In the preliminary experiments, decent solar cell efficiencies of up to 16.4% were demonstrated along with the substantially improved stability of the devices under continuous light soaking.

ⁱNREL Best Research-Cell Photovoltaic Efficiency Chart, <https://www.nrel.gov/pv/cell-efficiency.html>, accessed: august, 2020.

ⁱⁱM. M. Tepliakova, A. N. Mikheeva, L. A. Frolova, A. G. Boldyreva, A. Elakshar, A. V. Novikov, S. A. Tsarev, M. I. Ustinova, O. R. Yamilova, A. G. Nasibulin, S. M. Aldoshin, K. J. Stevenson, P. A. Troshin. *J. Phys. Chem. Lett.* 2020, **11**, 5563.

Polydiphenylamine-based cathodes for dual-ion batteries

F.A. Obrezkov¹, A.F. Shestakov², P.A. Troshin^{1,2}

¹Skolkovo Institute of Science and Technology

²Institute for Problems of Chemical Physics of the Russian Academy of Sciences

*e-mail: filipp.obrezkov@skoltech.ru

The constantly growing demand for electric vehicles, portable devices and smart grids dictates new requirements for energy storage devices.^[1] To achieve the required cost and performance metrics, several post-lithium technologies have been actively explored. Among them, dual-ion batteries (DIB) might be considered as one of the most promising types of energy storage devices due to their optimal combination of considerably high energy and power densities, which makes them suitable for multiple portable and stationary applications.

The most well-studied type of DIB is represented by dual-carbon batteries due to the relatively low price of such electrode materials. Despite this, they have several significant drawbacks, such as low specific capacity (typically less than 110 mAh g⁻¹),^[2] and excessively high operational voltages going beyond stability windows of common electrolytes thus causing their degradation.^[2,3] We believe that implementation of organic cathodes in DIB is one of the most promising ways to solve the aforementioned issues.

A serious drawback of the vast majority of known organic cathodes for metal-ion and dual-ion batteries is a relatively low content of the active material in the electrode composites dictated by the need for substantial (40-50%) loadings of the conductive carbon filler.

In this work, we studied for the first time the non-doped polydiphenylamine (PDPA) as an active positive electrode material for lithium and potassium dual-ion batteries. Intrinsically high electronic conductivity of PDPA allowed us to fabricate electrodes comprising appreciably high (up to 80%) concentrations of the active material. Such high loading of PDPA was reached using two different types of conductive additives: super-P carbon and multi-walled carbon nanotubes (MWCNTs). The performance of PDPA-based cathodes was compared with other previously reported cathode materials: polyaniline (PAni) and polytriphenylamine (PTPA). It should be emphasized that PDPA cathodes with the active material content of 80% delivered impressive energy densities of ~ 523 Wh kg⁻¹ in lithium- and ~462 Wh kg⁻¹ in potassium batteries. These results outperform the characteristics reached for both PAni and PTPA cathodes processed in a similar way. The analysis of the reported to date literature data indicated that PDPA demonstrated the highest energy density of 418 Wh kg⁻¹ calculated for the total cathode mass among all organic polymer cathodes reported to date for dual-ion batteries. Thus, the obtained results feature PDPA as a highly promising and readily available organic cathode material for efficient and low-cost dual-ion batteries.

This study was supported by RFBR (project 19-33-90233) and RSF (project 16-13-00111).

-
1. D. Larcher and J. M. Tarascon, *Nat. Chem.* **2015**, 7, 19.
 2. M. Wang and Y. Tang, *Adv. Energy Mater.* **2018**, 8, 1703320.
 3. T. Placke, A. Heckmann, R. Schmich, P. Meister, K. Beltrop and M. Winter, *Joule* **2018**, 2, 2528.

Impact of surface passivation coatings on intrinsic photochemical and thermal stability of lead halide perovskites

V. V. Ozerova^{1,2}, L. A. Frolova^{3,2}, S. M. Aldoshin², and P. A. Troshin^{3,2}

¹D.Mendeleev University of Chemical Technology, Moscow, Russia

²Institute for Problems of Chemical Physics of RAS, Chernogolovka, Russia

³Skolkovo Institute of Science and Technology, Moscow, Russia

*e-mail: podsolnuz@gmail.com

Low operational stability of perovskite solar cells represents a bottleneck issue hampering commercialization of this exciting photovoltaic technology. Among different approaches proposed to tackle this problem, a particular promising is the application of so called passivation coatings for modification of perovskite films. Typically, these are very thin (some times even monomolecular layers) films of some reagents that are introduced atop the absorber films or at the grain boundaries to decrease the density of defects and improve photovoltaic performance and/or operational stability of perovskite solar cells. There are hundreds of various additives or passivation coatings tested directly in photovoltaic cells, whereas the information on their action mechanisms is very scarce and controversial. One of the reasons is that these passivation coatings were mostly screened towards improving ambient stability of perovskite solar cells, which is probably not the best approach since efficient encapsulation should solve the extrinsic stability problem. Surprisingly, there are almost no studies on the effect of such passivation coatings on the intrinsic photochemical and thermal stability of perovskite films. Obviously, having no such fundamental information it is hardly possible to draw any reliable conclusions about action mechanisms of certain passivation coatings or processing additives.

Herein, we performed a systematic study in order to fill the aforementioned gap in the knowledge. In particular, we investigated the impact of a broad range of passivation coatings (>30 compounds) on intrinsic photochemical and thermal stability of MAPbI₃ thin films under well-controlled anoxic conditions. The influence of such parameters as loading of passivation additives in the perovskite ink, processing of passivation coatings above the absorber films and their thickness were studied. The obtained results allowed us to (1) identify the most promising passivation coatings, (2) elaborate the appropriate procedures for passivation of perovskite films, (3) establish correlations between the molecular structures of the additives and their stabilization effect induced in MAPbI₃ films and (4) draw some conclusions about the action mechanisms of the most promising passivation coatings.

The performed studies featured a tremendous potential of rationally designed passivation coatings to be used for blocking main intrinsic degradation pathways in complex lead halides and boosting spectacularly the operational stability of perovskite solar cells.

This work was supported by Russian Science Foundation (project 19-73-30020) at IPCP RAS.

Highly sensitive and selective ammonia gas sensor based on FAPbCl₃ lead halide perovskite

A. A. Parfenov^a, O. R. Yamilova^{a, b}, L. G. Gutsev^{a, c}, D. K. Sagdullina^a, A. V. Novikov^{a, b}, B. R. Ramachandran^c, K. J. Stevenson^b, S. M. Aldoshin^a and P. A. Troshin^{a, b}

^a IPCP RAS, Semenov Ave 1, Chernogolovka, Moscow Region, 142432, Russian Federation.

^b Skolkovo Institute of Science and Technology, Skolkovo Innovation Center, Building 3, Moscow, 143026, Russian Federation.

^c Institute for Micromanufacturing, Louisiana Tech University, Ruston, LA 71272, United States.

*e-mail: diana-susarova@yandex.ru

Organic–inorganic hybrid lead halide perovskites exhibit a wide range of unique optoelectronic properties that can be utilized in a variety of semiconducting photoelectronic devices. There is also an increasing interest in using metal halide perovskites as sensor materials for detecting various gas-phase analytes.

In this work, we report the design and investigation of a gas sensor based on formamidinium lead chloride (FAPbCl₃), which demonstrated strong and outstandingly selective response towards ammonia. Using a standard two-terminal resistor-type device geometry with FAPbCl₃ semiconductor films, we designed sensors demonstrating fast (within 0.83 s) and record-high response towards ammonia exceeding 300% for 1 ppm of the analyte. The NH₃ detection threshold was estimated to be as low as 50 ppb and can be further improved via rational sensor design engineering. Most importantly, the fabricated sensors showed excellent selectivity with respect to NH₃ even in comparison with other typically interfering analytes of similar chemical nature (EtNH₂, Et₂NH, Me₃N) and molecular size (H₂S). A good reversibility and operational stability of the devices at room temperature was also observed thus featuring complex lead halides as highly promising family of materials for gas sensor and electronic nose applications.

These observations were confirmed by our calculations to be due to a “lock-and-key” mechanism of the ammonia filling the chlorine-vacancy defect, which effectively healed the carrier trap created by such a defect. The obtained results clearly feature a tremendous potential of lead halide perovskites for advancing the current gas sensing technology and emphasize a need for further systematic exploration of this exciting family of materials.

This work was supported by the Russian Foundation for Basic Research (project No. 18-33-20222) at IPCP RAS and Next Generation Skoltech-MIT program at Skoltech. The computational parts of this research were conducted with high-performance computational resources provided by the Louisiana Optical Network Infrastructure (<http://www.loni.org>).

Design and synthesis of functional derivatives of [1]benzothieno[3,2-B][1]-benzothiophene for use in organic electronic

M.S. Polinskaya^{1*}, *O.V. Borshchev*¹, *M.S. Skorotetcky*¹, *S.A. Ponomarenko*¹

¹ Institute of Synthetic Polymer Materials RAS

*e-mail: polinskaya@ispm.ru

In recent years, an approach to creating various elements and devices of soft robotics, such as an electronic nose, based on organic field-effect transistors has been gaining popularity. In such sensors, instead of the resistive principle, field effect registration is used – gas sorption on the active layer of transistors changes the field distribution in the channel and allows registering significantly lower concentrations. Printed methods of manufacturing organic field-effect transistors (OFETs) allow us to create arrays of sensors on flexible polymer substrates. The use of organic materials allows to flexibly change the properties of functional layers at the stages of synthesis of substances, which ensures the selectivity of sensors based on them. The development of this approach requires the creation of both new organic semiconductors capable of forming ultra-thin films with high mobility of charge carriers, and new receptor molecules. Ones of the most efficient OFETs which can be used for such sensors are based on [1]benzothieno[3,2-B][1]-benzothiophene (BTBT) due to its high charge carrier mobility and stability of the molecules¹.

We have synthesized a number of new conjugated compounds-symmetric and asymmetric mono-and disubstituted derivatives of BTBT with a 6-bromhexane substituent, from which the target alkyne/azide precursors were obtained at the last stage. (Fig. 1).

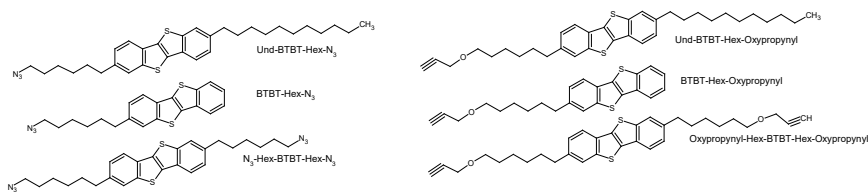


Fig. 1. Structural formula of synthesized molecules

The synthetic rout was based on a combination of Friedel-Crafts acylation of the initial BTBT and reduction of keto groups to alkyl groups. For the synthesis of an unsymmetrical compound **Und-BTBT-Hex-Br**, at first **Und-BTBT** was synthesized as described in literatureⁱⁱ. Then, by subsequent acylation of this product with 6-bromhexanoic acid chlorangydride and the reduction of the ketone, the target compound **Und-BTBT-Hex-Br** was obtained with a good yield. To obtain mono - and disubstituted derivatives **Br-Hex-BTBT** and **Br-Hex-BTBT-Hex-Br**, BTBT reacted by Friedel-Crafts with 6-bromhexanoic acid chlorangydride. Depending on the temperature of the reaction and the taken excess of the chlorangydride precursor, the required mono- or disubstituted BTBT derivative is formed. Then the reduction of the keto group using NaBH₄ and AlCl₃ as a Lewis acid resulted in the formation of **Br-Hex-BTBT** and **Br-Hex-BTBT-Hex-Br** molecules. At the final stage, the resulting brominated compounds were converted to functional azides and alkynes. Interaction with sodium azide allowed practically quantitative synthesis of azide derivatives. While the Williamson reaction of formation of esters resulted in the formation of target alkynes with yields about 34-66%.

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

ⁱ Takimiya K., at.al. *Thin Solid Films*, 2014, **554**, 13.

ⁱⁱ H. Minemawari, at. al., *Chem. Mater.*, 2017, **29** (3), 1245-1254.

Design of a Novel Tetrapodal Self-Assembled Monolayer for Functional Engineering of Interfaces

Valentina Rohnacher^{1,2}, *Frank S. Benneckendorf*^{2,4}, *Sabina Hillebrandt*^{1,2}, *Jan Freudenberg*^{2,4}
Wolfram Jaegermann^{2,3}, *Paolo Samori*⁵, *Michael Zharnikov*⁶, *Uwe H. F. Bunz*⁴,
Annemarie Pucci^{1,2} and *Klaus Müllen*^{2,8}

¹Kirchhoff Institute for Physics, Heidelberg University, Germany

²Innovationlab, Heidelberg, Germany

³Surface Science Division, TU Darmstadt, Germany

⁴Organisch-Chemisches Institut, Uni Heidelberg

⁵CNRS, ISIS, University of Strasbourg, France

⁶Applied Physical Chemistry, Heidelberg University, Germany

⁷Max Plack Insitute for Polymer Research, Mainz, Germany

*e-mail: valentina.rohnacher@kip.uni-heidelberg.de

Conformationally rigid multipodal molecules should control the orientation and packing density of functional head groups upon self-assembly on solid supports. Common tripods frequently fail in this regard, because of inhomogeneous bonding configuration and stochastic orientation. These issues are circumvented by a suitable tetrapodal diazatriptycene (DAT) moiety, bearing four thiol-anchoring groupⁱ.

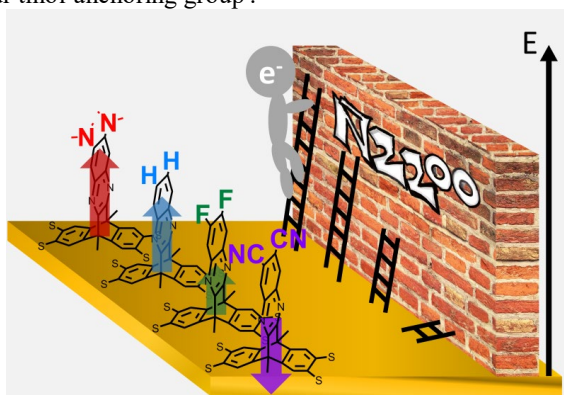


Fig. 1. Functionalized tetrapodal SAMs with various dipole moments for interface tuningⁱⁱ

We perform infrared reflection-absorption spectroscopy (IRRAS) measurements on DAT molecules on gold substrates to probe the orientation and quality of the SAMs. Combining the IR results with the contact angle goniometry, scanning tunneling microscopy, and NEXAFS and photoelectron spectroscopy data, a deep understanding of the SAM structure and organization was achieved. We found out that the DAT molecule form defined self-assembled monolayers (SAMs) on Au(111) substrates, whereby the tetrapodal scaffold enforces a nearly upright orientation of the terminal head group with respect to the substrate. Functionalization by condensation chemistry allows a large variety of functional head groups to be introduced to the tetrapod, paving the path towards advanced surface engineering and sensor fabrication.

ⁱ F.S.Benneckendorf et al. *ACS Applied Materials & Interfaces*. 2019, **12**(5), 6565-6572.

ⁱⁱ V.Rohnacher et al. *Advanced Materials Technologies*. published: 08 June 2020

Synthesis and properties of novel nanostructured organosilicon luminophores for scintillation and wavelength shifting fibers

Evgeniy A. Zaborin^{1*}, *Oleg V. Borshchev*¹, *Maxim S. Skorotetcky*¹, *Sergey A. Ponomarenko*^{1,2}

¹Institute of Synthetic Polymer Materials RAS
²Moscow State University, Department of Chemistry
 *e-mail: zaborin@ispm.ru

Organosilicon oligomers and polymers take an immense place among the luminescent materials^{1–3}. Silicon is an effective conjugation breaker due to its electronic structure and the relatively weak p–d interactions. It allows to create luminescent macromolecules of branched and dendritic architecture with unique characteristics such as high luminescence and efficient charge transport^{4–8}. Lately we synthesized nanostructured organosilicon luminophores (NOLs)⁹ with different pairs of donor and acceptor moieties and described their properties and application as highly-efficient plastic scintillators. Here we show synthesis and properties of 2 lines of novel NOLs with different acceptor moieties: 4,7-diphenyl-2,1,3-benzothiadiazole (PhBtdPh) and 1,4-bis(5-phenylthienyl-2-yl)-phenylene (AC5). It is known that both acceptors show good optic properties in different donor-acceptor frameworks^{10,11}. As for donors moieties - 2,5-diphenyloxazole (PPO), 4-(2-ethylhexyl)-p-terphenyl (EH-3Ph) and 2',5',4-trimethyl-p-terphenyl (3Me3Ph) were used (fig.1).

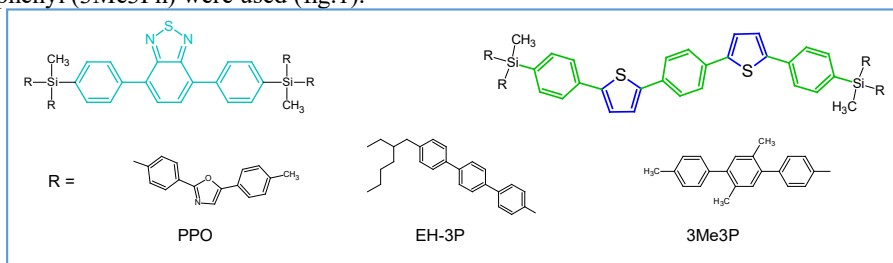


Figure 1. Novel NOLs

The structures of the synthesized compounds were confirmed by ¹H NMR spectroscopic data. Thermostability of new oligoarylenevinylenes was determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Optic properties (absorption and emission spectra) were examined in diluted solution and thin film.

This work was supported by the Russian Foundation for Basic Research (project no. 18-29-17006).

¹ M.-Y. Yeh et al., *Macromolecules*, 2007, **40**, 9238.

² J. Ohshita et al., *Polym. Chem.*, 2014, **5**, 346.

³ J. Ohshita, *Org. Photonics Photovolt.*, 2016, **4**, 52.

⁴ T.-Y. Luh and Y.-J. Cheng, *Chem. Commun.*, 2006, **45**, 4669.

⁵ E. A. Shumilkina, O. V. et al., *Mendeleev Commun.*, 2007, **17**, 34.

⁶ S. A. Ponomarenko and S. Kirchmeyer, 2011, *Adv. Polym. Sci.*, **33**, 235.

⁷ S. A. Ponomarenko et al., *Macromolecules*, 2012, **45**(14), 2014–2024.

⁸ J. Ohshita, et al., *Asian J. Org. Chem.*, 2014, **3**, 170.

⁹ Ponomarenko, S. A. et al., *Scientific Reports*, 2014, **4**(1).

¹⁰ Borshchev, O. V. et al., *Organic Photonics and Photovoltaics*, 2017, **5**(1), 1–8.

¹¹ Skorotetcky, M. S., et al., *Mendeleev Communications*, 2017, **27**(4), 377–379.

Predicting properties of OFET-based sensors by their electrical characteristics

D.S. Anisimov^{1}, A.A. Trul¹, V.P. Chekusova¹, A.A. Abramov¹, E.V. Agina¹,
S.A. Ponomarenko¹*

¹Enikolopov Institute of Synthetic Polymeric Materials of Russian Academy of Sciences

*e-mail: anisimov@ispm.ru

Thin film organic field effect transistors (TF-OFETs) are known to be very sensitive to different polar gases due to direct contact of a charge transporting layer with the environment. Since major transport occurs in the monomolecular layer close to the semiconductor-dielectric interface, sorption of polar analytes directly to the current-carrying layer strongly affects the charge density.¹ Single OFETs and array of them are widely used to solve a great variety of practical problems.² However, general model describing sensor properties in relation with device electrical characteristics is still lacking, embarrassing sensor properties prediction. Just a few correlations of transistor properties with sensitivity for certain type materials and device architectures were shown,^{3,4} however they fail if approximated to a more general case.

It is known that charge traps of any origin influence both electrical and sensory properties of OFETs.⁵ In this work we aim to unravel correlation of basic FET parameters such as charge carrier mobility, threshold voltage, subthreshold slope, hysteresis and bias stress characteristic time with OFETs sensor properties such as limit of detection and sensitivity. To do so we have fabricated an array of FETs based on monolayer Langmuir-Blodgett films on top of different polymer dielectrics and fully characterized their electrical properties. Furthermore, we have studied array sensor response to nitrogen dioxide and considered sensitivity dispersion among samples and its relation to electrical parameters. We have also analysed response cross-sensitivity to variety of volatile organic compounds and have found a great inconsistency with existing model of sensitivity to polar molecules through interaction of dipole with semiconductor. We show substances having 3 orders of magnitude difference in sensitivity, such as water and hydrogen disulphide, while having very close dipole moment.

This work takes the first steps towards predicting sensor properties based on electrical ones, which are much easier to be measured. We also show inconsistency of existing sensitivity model and propose its modification with consideration of charge transfer during sensing process.

This work was supported by RFBR (project № 20-03-00810).

¹ Andringa, A.-M., et al., *Advanced Functional Materials*, 2011. **21**(1): p. 100-107.

² Zhang, S., et al., *Small*, 2019. **15**(12): p. 1805196.

³ Duarte, D. and A. Dodabalapur, *Journal of Applied Physics*, 2012. **111**(4): p. 044509.

⁴ Lv, A., et al., *Chemistry – A European Journal*, 2016. **22**(11): p. 3654-3659.

⁵ Huang, W., et al., *Advanced Materials*, 2017. **29**(31): p. 1701706.

Study of charge injection in thiophene-phenylene co-oligomers via their terminal substitution

*D.I. Dominskiy**^{1,3}, *V.A. Trukhanov*^{1,3}, *A.Yu. Sosorev*^{1,3}, *Oleg G. Kharlanov*¹, *L.E. Yakushkin*^{1,3}, *A.S. Komolov*², *O.V. Borshchev*³, *S.A. Ponomarenko*³, *D.Yu. Paraschuk*^{1,3}

¹Faculty of Physics & International Laser Centre of Lomonosov Moscow State University, Leninskiye gory 1/62, 119991 Moscow, Russia

²St. Petersburg State University, Universitetskaya nab. 7/9, St. Petersburg, Russia.

³Enikolopov Institute of Synthetic Polymeric Materials of Russian Academy of Sciences, Profsoyuznaya Str. 70, 117393 Moscow, Russia

Moscow, Russia

*e-mail: di.dominskiy@physics.msu.ru

Commonly organic semiconducting materials are divided by the charge transport type into the so-called n-type and p-type groups¹. In practice, the type of charge transport in material is not easily switched. Fluorination is a well-known approach to alter the electronic properties of p-conductive semiconductors. For example, common p-conductive organic semiconductors such as pentacene, copper phthalocyanine, diethynyl naphthalene and oligophenylenevinyls can be converted to the n-conductive ones via fluoro-substituents^{2,3}. This can be attributed to the change of energy level alignment at the metal/organic interface favoring electron over hole injection.

Here, we study the impact of fluorination of the methyl terminal group on the structural and electronic properties of single- and polycrystals of thiophene-phenylene co-oligomers (TPCO) with the phenylene-thiophene-thiophene-phenylene (PTTP) conjugated core using x-ray diffraction, DFT, GW and dipole moment calculations, ultra-violet photoelectron spectroscopy (UPS) and field-effect transistor (FET) measurements.

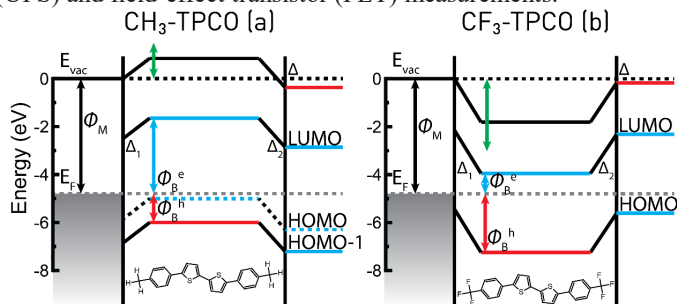


Fig. 1. Schematic energy-level diagram at an electrode/TPCO interface in organic electronic devices: a) CH₃-TPCO and b) CF₃-TPCO.

Our experimental data show that fluorination of the methyl terminal group in CH₃-TPCO results in an insignificant impact on the crystal habit and on the molecular orientation vs their basal plane but switches the conductivity from the p-type to the n-type. The extensive calculations and UPS data strongly support the key role of the terminal groups in charge injection. We argue that the terminal groups control the charge transport type in the FET active layer and present a model to explain observed phenomenon (Fig. 1).

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

¹ C. Zhang et al., *Small*, 2016, **12**(10), 1252-1294

² T. Yasuda et al., *Applied Physics Letters*, 2006, **89**(18), 182108

³ T. Yasuda et al., *Journal of Physics D: Applied Physics*, 2007, **40**(15), 4471

Hydrophilic organo-inorganic composite systems based on ZrO₂ nanopowders –the promising materials for adsorption electronics and power engineering

A.S. Doroshkevich^{1,2}, *A.V. Shylo*², *A.I. Lyubchyk*³, *T.Yu. Zelenyak*¹, *V.A. Aleksandrov*^{1,4}, *M. Lacusta*², *A. Stanculescu*⁵, *M. Balasoiu*^{1,6}, *E.B. Asgerov*^{1,7}, *A.I. Madadzada*^{1,7}, *D. Chicea*⁸

¹ Joint Institute for Nuclear Research, Russia

² Donetsk Institute for Physics and Engineering named after A.A. Galkin NAS of Ukraine

³i3N/CENIMAT, Department of Materials Science, Faculty of Science and Technology, New University of Lisbon and CEMOP/UNINOVA, Portugal

⁴Dubna International University, st. Universitetskay, 19, Dubna-141980, Russia.

⁵ National Institute for Materials Physics, Romania

⁶Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering, Romania

⁷National Nuclear Research Center, Azerbaijan

⁸University "LUCIAN BLAGA" of SIBIU, Romania

*E-mail:doroh@jinr.ru

Dispersed systems based on ZrO₂ nanopowders and organic polymers are promising materials for adsorption power energetics and electronics [1]. Water adsorption leads to changing the structure of the energy zones of the nanoscale crystal, in particular, to the formation of additional impurity or to compensation of its own localized electronic states in the forbidden zone [2]. This allows to controlled changes of energy, optical and electrical properties of the surface of nanoparticles as part of an organo-inorganic functional material.

Sorbed on the surface of ZrO₂ water molecules as a rule dissociates into protons and OH groups that are localized mainly on di- and tricoordinated bridged oxygen atoms [3, 4] (the adsorption energy is 95±20 kJ/mol [5, 6]). Both the OH group and the proton combine almost instantly with molecular water to form H₃O⁺ hydrates. By means of hydrates, electrical conductivity is achieved in the interparticle space, i.e., continuity of electrical properties is ensured [7- 8].

In general, a composite system in the form of ZrO₂ nanoparticles distributed in a hydrophilic polymer can be considered as a medium with nonlinear electrical properties that can be controlled by an adsorption process. On the basis of such systems, it is possible to obtain not only humidity sensors [9] but active elements: adsorption capacitors [10] and electric generating devices [11].

The study was performed in the scope of the H2020/MSCA/RISE/SSHARE number 871284 and the RO-JINR Projects No. 267/2020 item 25 and 268/2020 item 57 and No.268/2020 item 58.

1 V.A. Aleksandrov, A.S. doroshkevich, A.I. lyubchyk, and all. // IBWAP-2019, 182 -183.

2 Koutecky J. // *Phys. Rev.* 1957. Vol.10, N1. P. 13-22.

Blumenthal U. B. *Chemistry of Zirconium*. - M: PH of foreign literature, 1963. - 345 p.

4 Evarestov R.A., Bandura A.V. // *Rus. chem. Zh.*, 2007, V. L1, №.5, 150-158.

5 Raz S., Sasaki K., Maier J., Riess I. *Solid State Ionics*, 2001, V.143, 181.

6 Hofmann A., Sauer J. // *J.Phys. Chem. B*, 2004, V.108, p. 14652.

7 B. V. Martynenko *Acids and bases*. M: Enlightenment. 1985, 159p.

8 O. S. Doroshkevych, A. V. Shylo, O. V. Saprukina, and all. // *WJCMF*. 2012. №2, 1-9.

9 E.A. Gridina, A.S. Doroshkevich, A.I. Lyubchyk, and all. // *Adv Ph Res*. 2019, T.1, №2, 70-80.

10 Doroshkevich A. S., Shilo A.V., Zelenyak et al. Nanoionic capacitor based on nano-powders of dielectrics Rospatent No. 2019135580 (070225).

11 A.S. Doroshkevich, E.B. Askerov, A.I. lyubchyk, and all. // *Applied Nanoscience*. 9(8), 1603-1609 DOI 10.1007/s13204-019-00979-6.

Dielectric properties of polymer composites based on polydimethylsiloxane and carbon fillers

Khmelnitskaya A.G.¹, Kalinina A.A.¹, Agina E.V.¹, Ponomarenko S.A.¹, Muzafarov A.M.^{1,2}

¹Institute of Synthetic Polymer Materials RAS

²A.N.Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences
*e-mail: akazaeva95@gmail.com

Currently, the creation of electromechanically active polymers (EAP) is a rapidly developing and promising field of research and development. [1] Electroactive polymers are a new class of materials that are capable of converting electrical energy into mechanical work and vice versa, what allows them to be used in robotics, electronics, biomechanical prostheses and various kinds of drives.

The main characteristics of the dielectric EAP, which is a part of the energy converter, are dielectric constant, dielectric breakdown strength and linear deformation. Silicone elastomers are one of the most used dielectric EAPs for energy converters due to the reproducibility of cycles, a slight tendency to the Mullins effect and aging, the ability to work over a wide temperature range.[2] The creation of silicone composite materials with special electrophysical properties is achieved by introducing fillers into the polymer matrix. This work is devoted to the study of the effect of carbon fillers on the properties of a composite material based on polydimethylsiloxane (PDMS).

The results of a study of the effect of processing fillers (carbon black, graphite, carbon nanotubes and their mixtures) on the dielectric and mechanical characteristics of composites will present in the work.

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

References

[1] P. Brochu, Q. Pei, *Macromol. Rapid Commun.* 2010, **31**, 10.

[2] L. Maffi, S. Rosset, M. Ghilardi, F. Carpi, H. Shea, *Adv. Funct. Mater.* 2015, **25**, 1656.

Novel thiazolothiazole-based donor-acceptor conjugated polymers for large-area organic solar cells

P.I Proshin^{1*}, *S.L. Nikitenko*¹, *P.A. Troshin*^{2,1} and *A.V. Akkuratov*¹

¹Institute for Problems of Chemical Physics of the RAS

²Skolkovo Institute of Science and Technology

*E-mail: pavel8pro@gmail.com

Solution-processed organic solar cells (OSCs) have attracted tremendous attention because of their advantages such as low cost, lightweight, mechanical flexibility and easy manufacturing process. The efficiencies of OSCs were remarkably improved in the last decade up to 18%. This progress is mainly due to the development of new semiconductor materials with advanced propertiesⁱ.

Nevertheless, we are still far from real commercialization of OSCs since the large-area panels are usually processed from toxic and halogenated solvents and demonstrate low efficiencies due non-optimal morphology of photoactive filmsⁱⁱ. To address this problem, some novel materials with improved properties are required for industry-scale production of efficient large-area OSCs using “green” non-toxic solvents.

Recently, we showed that thiazolothiazole-based (TzTz) polymers are promising absorber materials for environment friendly and large-area photovoltaicsⁱⁱⁱ. In this work, we report the synthesis of novel TzTz-based conjugated polymers **P1** and **P2** incorporating ADA moieties composed of benzothiadiazole (A) and thiophene (D) alternating blocks (Fig.1). We introduced thioalkyl side chains into thiophene rings in order to improve the polymer crystallinity and thereby increase charge carrier mobilities^{iv}. Additionally, incorporation of thioalkyl side chains results in decreased HOMO energy levels that enhances the open circuit voltage in polymer solar cells. The photovoltaic properties of the designed polymers were investigated in solar cells and larger area modules.

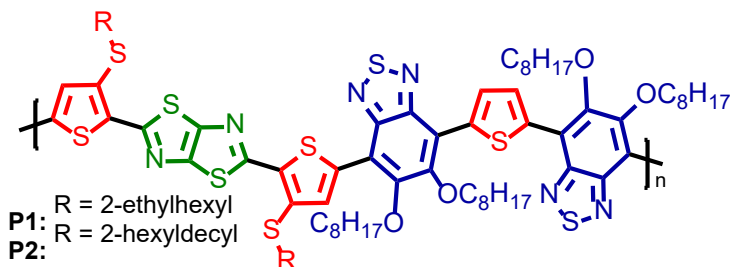


Fig. 1. Molecular structures of conjugated polymers **P1** and **P2**

The reported study was funded by Russian President Science Foundation MK-1103.2020.3

ⁱ Liu, Q. et al. *Sci. Bull.*, 2020, **65**, 4, 272–275.

ⁱⁱ Agrawal, N. et. al., *Sol. Energ. Mat. Sol. Cells*, 2016, **157**, 960-965

ⁱⁱⁱ Kuznetsov, P. et al. *Tetrahedron Lett.*, 2020, **61**, 152037.

^{iv} Genee, Z. et al., *Org. Electron.*, 2020, **77**, 105572

New Low Bandgap Polymer for Self-Powered Organic Near-Infrared Photodetectors

E. I. Romadina^{1,2*}, *A.V. Akkuratov*², *S. D. Babenko*³, *P. M. Kuznetsov*², *P. A. Troshin*^{1,2}

¹ Skolkovo Institute of Science and Technology

² Institute for Problems of Chemical Physics of RAS

³ The Branch of Talrose Institute for Energy Problems of Chemical Physics of RAS

*e-mail: romadina-lena@mail.ru

Organic photodetectors are promising thin-film devices that could be applied for a range of innovative applications, for example, in remote control devices such as artificial eyes, chemical or biological sensors, medical devices, etcⁱ. Organic photodetectors are good candidates for potential replacement of well-known inorganic analogs: they have such inherent advantages as low fabrication cost, flexibility, lightweight, and tunability of the spectral responseⁱⁱ. Considerable attention now is paid to organic photodetectors operating in the near-infrared spectral region (NIR photodetectors), which can find many important civil and military applications.

As part of this work, novel low bandgap (~1.29 eV) conjugated polymer comprising benzodithiophene and diketopyrrolopyrrole units was designed and synthesized (Fig. 1). The obtained polymer exhibited strong absorption in the near-infrared region with the absorption maximum at 816 nm and the edge of the absorption band at 961 nm. The optoelectronic properties of **P1** polymer indicate the prospects for its application in NIR organic photodetectors.

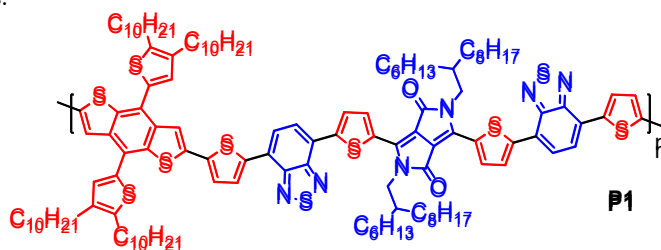


Fig. 1. Structure of conjugated polymer **P1**

Photodetectors based on the polymer/fullerene derivative blends were fabricated and their electrical behaviour was investigated. The devices demonstrated rapid response in a broad spectral range from visible ($\lambda = 470$ nm) to infrared ($\lambda = 850$ nm) wavelengths. Photodetectors can be operated in up to 5.0×10^5 Hz frequency regime with responsibility of 42 mA W^{-1} and detectivity of 1.26×10^{12} Jones at $\lambda = 470$ nm and zero applied potential. These results point towards the prospects of application of conjugated polymers as materials for advanced optoelectronic devices such as NIR light detectors.

This work was supported by Russian Science Foundation (grant No. 18-13-00205).

ⁱ Zhou X., Yang D., Ma D., *Adv. Opt. Mater.* 2015, **3**, 1570–1576.

ⁱⁱ (a) Yao Y., Liang Y., Shrotriya V., Xiao S., Yu L., Yang Y. *Adv. Mater.* 2007, **19**, 3979–3983; (b) Baeg K.J., Binda M., Natali D., Caironi M., Noh Y.Y. *Adv. Mater.* 2013, **25**, 4267–4295; (c) Rauch T., Böberl M., Tedde S.F., Fürst J., Kovalenko M. V., Hesser G., Lemmer U., Heiss W., Hayden O. *Nat. Photonics.* 2009, **3**, 332–336.

Enhanced non-volatile attribute of FeFET based Memory Device via tuning of ferroelectric microstructure

Dhrubojyoti Roy^{1*}, Partho S. G. Pattader¹, Dipankar Bandyopadhyay¹

¹Indian Institute of Technology Guwahati, Department of Chemical Engineering
*e-mail: dhrubojyoti2@iitg.ac.in

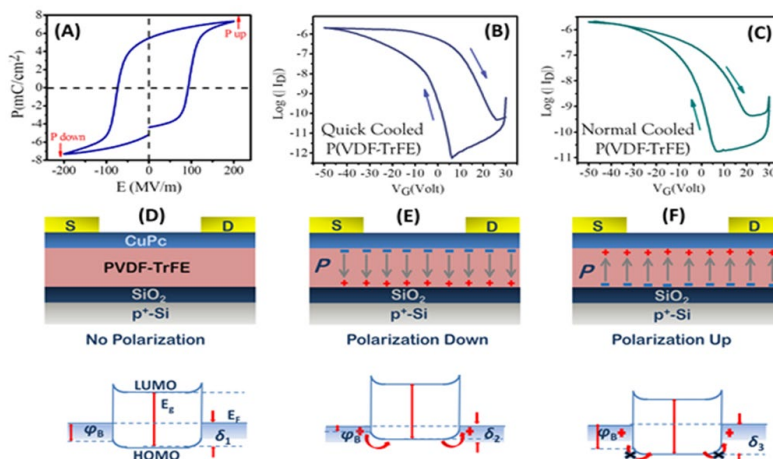


Fig. 1. Ferroelectric electrical properties of P(VDF-TrFE)/CuPc hybrid structure. A) The ferroelectric hysteresis plot of 380 nm P(VDF-TrFE) thin film capacitor. The transfer curve at room temperature of CuPc active channel based FE-FET with b) quick cooled and (c) normal cooled P(VDF-TrFE) ferroelectric polymer as gate dielectric. D-F) Depict the schematic cross section structure of Fe-FET in three different polarization state of PVDF-TrFE ferroelectric gate dielectric and correspondingly the energy band diagrams represent the ease of charge flow process that occur from source to drain at three different ferroelectric polarization state.

Fundamental relationships exist between alignment of ferroelectric dipoles in the gate dielectric layer and its effect on the channel mobilityⁱ and non-volatile characteristic of the Fe-FET deviceⁱⁱ. Tuning of the ferroelectric microstructure which promoted better alignment of electric dipole moments in the dielectric layer, was achieved by adopting different cooling procedure after annealing the spin coated ferroelectric polymer P(VDF-TrFE) substrates. Higher degree of alignment of ferroelectric polymer chains along substrate surface and thus the C-F- dipoles was obtained for fast quenched sample. The result was justified by the observed reduction in localized states in the semiconductor and facile switching of C-F- dipole moments in ferroelectric gate dielectric close to semiconductor-dielectric interface.

This work was supported by DST SERB (project № EMR/2016/001824).

ⁱ Senanayak P., Guha S., Narayan K. S. *Phy. Rev. B* 2012, **85**, 1153.

ⁱⁱ Houili H., Picon J. D., Zuppiroli L., Bussac M. N. *J. Appl. Phys.* 2006, **100**, 023702.

An analysis of J-V characteristics of QD-based photovoltaic cells from a theoretical model

A.Yu. Saunina^{1*}, *V.R. Nikitenko*¹, *A.A. Chistyakov*¹, *M.A. Zvaizgne*¹, *A.R. Tameev*²
and *A.E. Aleksandrov*²

¹National Research Nuclear University “MEPhI” (Moscow Engineering Physics Institute)

² A.N. Frumkin Institute of Physical Chemistry and Electrochemistry RAS

*e-mail: ayus03@mail.ru

Quantum dot (QD) solids have unique optical properties and high photostability, which seem very promising for optoelectronic applicationsⁱ. However, the increase of the power conversion efficiency (PCE) remains a challenging problem of the QD-based photovoltaics, one of the reasons being the transport of charge carriers. Experimental and theoretical studies imply the hopping regime of transport with better mobilities corresponding to shorter surface ligands. Recently, the usage of halide ligands such as tetrabutylammonium iodide (TBAI) demonstrated the enhanced mobilities and PCE values of QD-based cellsⁱⁱ. The basic Shockley-Queisser modelⁱⁱⁱ for the calculation of the PCE does not include characteristics of the charge carriers and exciton transport, and thus, could not provide the deeper understanding of the effects of such characteristics on the cell performance.

An analytic model of J-V characteristics of QD-based solar cells is developed, including drift and diffusion of electrons and holes, as well as diffusion of excitons. Analytical expressions for the J-V characteristics and the PCE are obtained for the case of neglected recombination. The model discusses the effective parameters, such as exciton diffusion length, exciton boundary conditions and charge mobilities, and their effect on the PCE and the J-V characteristics.

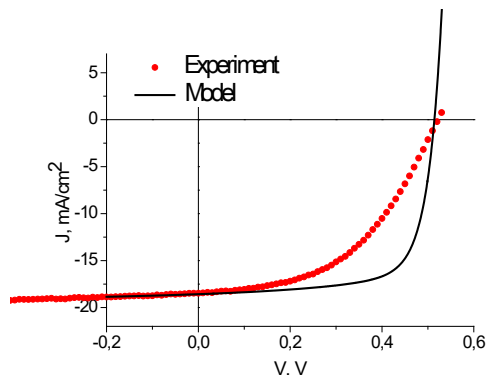


Fig. 1. Experimental (symbols) and calculated according to the presented model (solid line) J-V characteristics of a QD-based solar cell.

Fig. 1 illustrates the experimental and calculated J-V characteristics for ITO/PEDOT:PSS/PbS_{TBAI}/ZnO/Al cell based on 2.9 nm PbS QDs with TBAI ligands. The experimental PCE is 4.7% and the calculated (without recombination) PCE is 5.7%. The parameters are chosen in order to fit the experimental values of the open-circuit voltage and short-circuit current.

ⁱ Chistyakov A.A. *et al.*, *J. Phys. Chem. Lett.* 2017, **8**, 4129.

ⁱⁱ Lan X. *et al.*, *Nano Lett.* 2016, **16**(7), 4630.

ⁱⁱⁱ Shockley W., Queisser H.J., *J. Appl. Phys.* 1961, **32**, 510.

A Kinetic Monte Carlo Study of Triplet-triplet Annihilation in Conjugated Luminescent Materials

R. Saxena^{1*}, *T. Meier*¹, *S. Athanasopoulos*², *H. Bässler*³, *A. Köhler*^{1,3}

¹ Soft Matter Optoelectronics and Bavarian Polymer Institute (BPS), University of Bayreuth

² Departamento de Física, Universidad Carlos III de Madrid

³ Bayreuth Institute of Macromolecular Research (BIMF), University of Bayreuth

*e-mail: rishabh.saxena@uni-bayreuth.de

It is well known that in organic solids the collision of two excitons can give rise to delayed fluorescence (DF). Revived interest in this topic is stimulated by the current endeavor towards the development of efficient organic opto-electronic devices such as OLEDs and solar cells, or sensitizers used in photodynamic therapy. In such devices, triplet excitations are ubiquitously present but their annihilations can be either detrimental, e.g. giving rise to a roll-off of intensity in an OLED, or mandatory, e.g. if the sensitizer relies on up-conversion of long-lived low energy triplet excitations. Since the employed materials are usually non-crystalline, optical excitations migrate via non-coherent hopping. The method of choice to unravel the complex pattern of individual elements in the hopping process is kinetic Monte Carlo simulation (kMC). In the current work we employ kMC to study the interplay of triplet-triplet annihilation (TTA) and quenching of the triplet excitations by impurities in a single component system featuring a Gaussian energy landscape. Our simulation results are in agreement with the experimental observations of Hoffmann *et al.* for oligomers and polymers with different conjugation length.¹ By examining the material parameters, we find that enhanced room temperature DF requires:

- (i) a transport morphology that allows triplets to access many different energy sites
- (ii) materials with a long conjugation length
- (iii) materials that are well purified so that they have a defect concentration $\leq 10^{17} \text{ cm}^{-3}$, and
- (iv) materials that show a high degree of energetic disorder ($\sigma \geq 70 \text{ meV}$).

We also explore the effect of replacing Miller-Abrahams hopping rates by Marcus rates. An essential message is that the DF features a maximum at a temperature that scales as or similar to $\sigma/K_B T$ as shown in Fig.1; observing a maximum at $\sigma/K_B T \approx 3$.

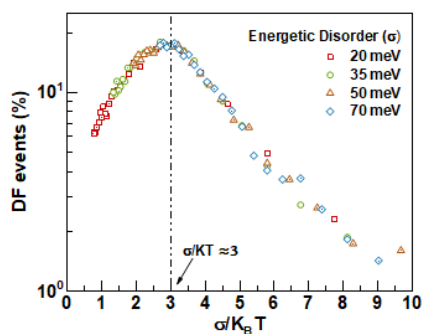


Figure 1. Delayed fluorescence peaks at $\sigma/K_B T \approx 3$ for all the disorder values.

¹ Hoffmann, S. T.; Koenen, J. M.; Scherf, U.; Bauer, I.; Strohrriegel, P.; Bassler, H.; Köhler, A., *J. Phys. Chem. B* 2011, **115**(26), 8417-23.

Polyimides based on NTCDA and *p*- or *m*-phenylenediamines as cathode materials for potassium batteries

A.G. Scherbakov^{1,2}, *R.R. Kapaev*^{2,3*}, *A.F. Shestakov*³, *K.J. Stevenson*², *P.A. Troshin*^{2,3}

¹D.I. Mendeleev Russian University of chemical technology, Institute of chemistry and sustainable development

²Center for Energy Science and Technology, Skolkovo Institute of Science and Technology

³Institute for Problems of Chemical Physics RAS

*e-mail: roman.kapaev@skoltech.ru

Li-ion batteries (LIBs) are very popular in various aspects of modern life. However, lithium is a rare element that is mined in only a few countries, which makes the battery industry dependent on exports. Potassium is one of the most promising sustainable alternatives to lithium in the batteries. It has a low reduction potential ($E_0 = -2.93$ V), which is good for achieving high voltages. Moreover, K^+ has a smaller Stokes radius compared to Li^+ in the battery electrolytes, which is beneficial for fast charge/discharge of the batteries. Organic molecules are one of the perspective classes of active materials for potassium batteries. These compounds contain no expensive and toxic transition metals, which makes them more sustainable and friendly to the environment.

In this study, we compared two isomeric polyimides, **mPI** and **pPI** (Fig. 1a), as cathode materials for potassium batteries. We showed that **mPI** has significantly higher capacities and high rate capabilities compared to **pPI** (Fig. 1b), as well as slightly higher redox potentials. The higher capacities of **mPI** are likely associated with its significantly larger specific surface area and smaller particle size, which were evidenced *via* low-temperature nitrogen adsorption experiments and scanning electron microscopy. We also suggest that the redox potential increase is related to coordination of K^+ ions by two adjacent imide units, which is more sterically favorable for **mPI** than for **pPI**. These results render *m*-phenylenediamine as a more suitable building block for polyimide-based battery materials.

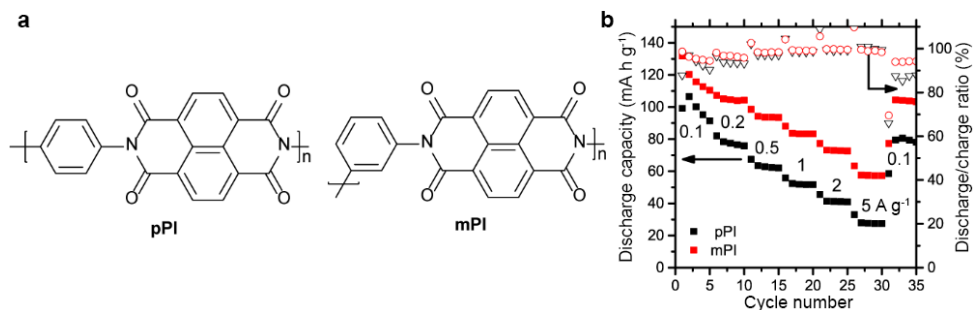


Fig. 1. Structures of **mPI** and **pPI** polymers (a) and the dependence of the specific capacity and Coulombic efficiency on the current density (b).

This work was supported by Russian Science Foundation (project 16-13-00111P).

Ambipolar polyimides with pendant groups based on 9H-thioxanthene-9-one derivatives: synthesis, thermostability, electrochemical and electrochromic properties

D. S. Odintsov¹, I. K. Shundrina¹, I. A. Os'kina¹, I. V. Oleynik¹, J. Beckman², L. A. Shundrin¹

¹ N.N. Vorozhtsov Institute of Organic Chemistry, Russia

² Institute for Inorganic Chemistry and Crystallography, University of Bremen, Germany

*e-mail: shundrin@nioch.nsc.ru

New electro-active polyimides (PI) with pendant groups based on 9H-thioxanthene-9-one (Th(O)S) and its S,S-dioxide derivative (Th(O)SO₂) have been synthesized on the basis of 2-[[bis(4-aminophenyl)aminomethyl]-9H-Th(O)S/Th(O)SO₂] by the route including the synthesis of the corresponding polyamidoacids followed by their chemical imidization¹. The synthesized polyimides demonstrated thermal stability up to 400 °C without a noticeable weight loss. Thin-layer cyclic voltammetry showed the polyimides to be capable of reversible electron transfer at low negative potentials, their values depending on the nature of the pendant groups.

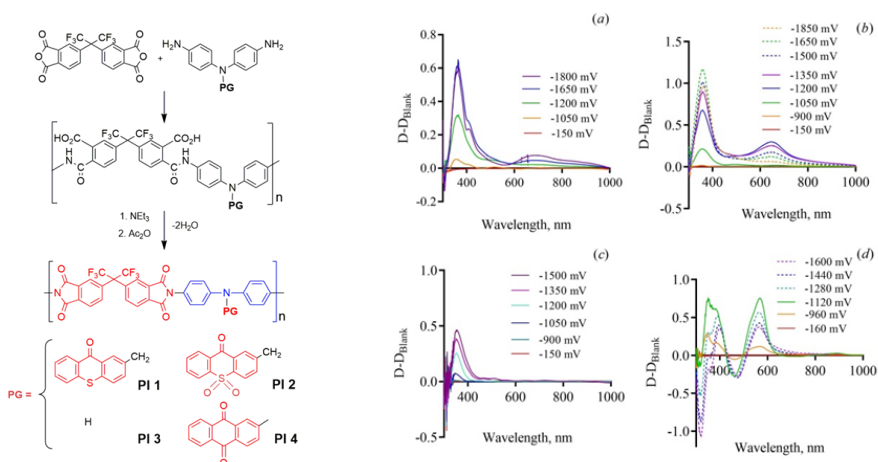


Figure 1. *Left:* Synthesis of polyimides. Red color indicates the electron-acceptor moieties of the PIs, blue color relates to the electron-donor fragment; *Right:* Differential optical spectra of the PI films on ITO working electrode under electrochemical reduction at various potentials (indicated by color): (a) PI 1, (b) PI 2, (c) PI 3, (d) PI 4.

The electrochromic behavior of the polyimides showed absorption bands at 363, 409, 683 nm for the PI with the Th(O)S pendant group and 355, 644 nm for the PI with the Th(O)SO₂ in the potential sweep range 0 > E > -2.1 V. Optical absorption bands under electrochemical reduction conditions are associated with the formation of radical anion states of the pendant groups inside the PI layer as well as reversible electron transfer to the electron-acceptor moiety of the polymer chain. The synthesized PIs are promising as electro-active materials for use in polymer based resistive memory devices.

This work was supported by RFBR (project № 18-03-00596-a), DFG, project BE 3616/6-2

¹ Danila S. Odintsov, Inna K. Shundrina, Irina A. Os'kina, Irina V. Oleynik, Jens Beckmann, Leonid A. Shundrin. *Polymer Chemistry*. 2020, **11**, 2243-2251

Tetrathienoacene derivatives for monolayer field-effect transistors

Skorotetcky M.S.¹, Chekusova V.P.¹, Borshchev O.V.¹, Ponomarenko S.A.^{1,2}

¹Enikolopov Institute of Synthetic Polymeric Materials of RAS

² Moscow State University, Chemistry Department

*e-mail: skoroteckiy@ispm.ru

Tetrathienoacene (TTA) derivatives are known for their good semiconducting properties in organic field-effect transistors (OFETs) and high stability under ambient conditions [1,2]. However, due to their high crystallinity and low solubility, it is difficult to obtain thin films of acceptable quality. It is known, however, that only the first two molecular layers next to the dielectric interface dominate the charge transport in OFETs. That is why we developed new symmetrical TTA derivatives with disiloxane group and investigated their semiconducting properties in the monolayer.

This work describes a method for preparation of thieno[3,2-b]thieno[2',3'':4,5]thieno[2,3-d]thiophene (TTA) with disiloxane group and new semiconductors on their basis. The synthesis route involves the preparation of 3-bromothieno[3,2-b]thiophene from 3,4-dibromothiophene, followed by the preparation of the corresponding disulfide and oxidative ring closure to produce TTA. The combination and adaptation of various literature methods [3,4] allowed to increase the total reaction yields in the case of 3-bromothieno[3,2-b]thiophene from 54% to 72% and TTA from 27% to 45%. The results of the TTA acylation reaction are presented for the first time. At the last stage, the Suzuki-Miyaura coupling reaction was used to obtain the final materials (Fig.1).

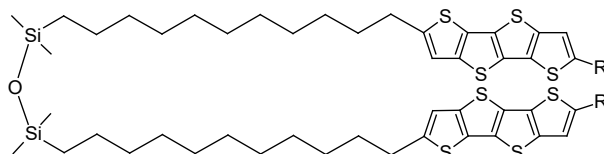


Fig. 1. Represented structure of TTA derivatives with disiloxane group

This work was supported by Russian Science Foundation (grant 18-73-10182).

¹ Skorotetcky M.S.; Borshchev O.V.; Ponomarenko S.A *IOP Conf. Ser.: Mater. Sci. Eng.*, 2019, 525

² Borshchev O.V., Skorotetcky M.S., Vasily A. Trukhanov V.A. et. al. *Dyes Pigm.* 2020 in press

Effects of thiophene π -spacer length and fused triphenylamine core on properties of star-shaped molecules for organic solar cells and photodetectors

Alexander N. Solodukhin^{1*}, *Yuriy N. Luponosov*¹, *Artur L. Mannanov*^{1,2}, *Dmitry Yu. Paraschuk*^{1,2}, *Sergey A. Ponomarenko*¹

¹Institute of Synthetic Polymer Materials RAS

²Faculty of Physics and International Laser Center, Lomonosov Moscow State University

*e-mail: solodukhin@ispm.ru

Star-shaped donor-acceptor oligomers based on electron-donating triphenylamine are promising semiconductor materials for organic electronics^{i-iv}. In this work the first star-shaped donor-acceptor triphenylamine-based molecule **4T** with quathiothiophene conjugated π -spacers and hexyldicyanovinyl electron-withdrawing groups and novel analogues **0T** and **1T** were synthesized (Fig. 1a). Their physicochemical and photovoltaic properties were studied and compared to those of molecule **2T**^v and **3T**^v (Fig. 1a). An influence of the length of π -conjugated oligothiophene spacers from 0 to 4 thiophene units on the material properties has been revealed.

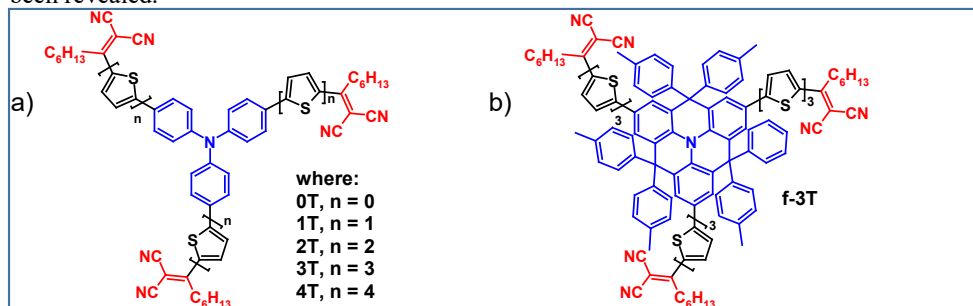


Fig. 1. Schematic representation of donor-acceptor oligomers **0T**, **1T**, **2T**, **3T**, **4T** based on triphenylamine (a) and **f-3T** based on fused triphenylamine core

Also the synthesis of a novel star-shaped donor-acceptor molecule **f-3T** with acridine-based core being a fused derivative of triphenylamine is reported in this work^{vi}. Its physicochemical and photovoltaic properties were comprehensively studied and compared to those of molecule **3T** (structural analog but with a pristine propeller-like triphenylamine core).

The work in the part of synthesis and investigations of star-shaped oligomers 0T, 1T, 4T was supported by Russian Science Foundation (№19-73-30028), whereas the work on synthesis and investigation of f-3T oligomer was supported by Russian Science Foundation (19-73-10198).

ⁱ Luponosov Y.N., Solodukhin A.N., Ponomarenko S.A. *Polymer Science, Ser. C*, 2014, **56**(1), 105–135.

ⁱⁱ Ponomarenko S.A., Luponosov Y.N., Min J. et al. *Faraday Discuss.*, 2014, **174**, 313-339.

ⁱⁱⁱ Chang C.-Y., Solodukhin A.N., Liao S.-Y. et al. *J. Mater. Chem. C*, 2019, **7**, 8634-8642.

^{iv} Mannanov A.L., Savchenko P.S., Luponosov Y.N. et al. *Organic Electronics*, 2020, **78**, 105558.

^v Min J., Luponosov Y.N., Baran D. et al. *Mater. Chem. A*, 2014, **38**(2), 16135-16147.

^{vi} Luponosov Y.N., Solodukhin A.N., Mannanov A.L. et al. *Dyes and Pigments*, 2020, **177**, 108260.

Novel star-shaped benzotriindole-based donor-acceptor molecule for organic photovoltaics

P.K. Sukhorukova^{1,2}, D.O. Balakirev¹, Yu.N. Luponosov¹, E.A. Svidchenko¹, S.M. Peregodova², Artur L. Mannanov^{1,3}, Petr S. Savchenko¹, Dmitry Yu. Paraschuk^{1,3}, S.A. Ponomarenko¹*

¹Enikolopov Institute of Synthetic Polymeric Materials, RAS

²Moscow State University, Department of Chemistry

³Nesmeyanov Institute of Organoelement Compounds, RAS

⁴Moscow State University, Faculty of Physics & International Laser Center

*e-mail: spollet@mail.ru

Organic photovoltaics, the one of the most promising branches of science, contribute the development of alternative energy. Improvement of the structure and conductive properties of materials for organic solar cells (OSC) has led to an increase in their power conversion efficiency and an improvement in their current-voltage characteristics. However, the theoretical maximum of power conversion efficiency has not yet been reached, so today's challenge is to research and design new molecular structures in order to increase the efficiency of organic solar cells.

Here we report on an efficient synthesis and complex properties studies of novel conjugated benzotriindole-based oligomer for OSCs application. This molecule, which contains 2-ethylhexylcyanoacetate electron-withdrawing groups, linked through terthiophene π -spacers with electron-donating benzotriindole core was synthesized in high yields. The electrochemical, thermal and optical properties of these compounds were investigated by cyclic voltammetry, differential scanning calorimetry, thermogravimetric analysis and UV-Vis absorption spectroscopy. In addition, OSCs prototypes were designed and tested, and demonstrated promising results.

The work was performed with financial support by a grant from the Russian Science Foundation (project № 19-73-10198).

Strength of Attraction: Pyrene-based Hole-transport Materials with Effective π - π Stacking for Dopant-free Perovskite Solar Cells

M.M. Tepliakova^{1,2*}, *I.K. Yakushenko*², *P.A. Troshin*^{1,2}

¹Center of Energy Science and Technology, Skolkovo Institute of Science and Technology

²Institute for Problems of Chemical Physics of the Russian Academy of Science

*e-mail: Marina.Tepliakova@skoltech.ru

Perovskite solar cells (PSCs) is a rapidly emerging photovoltaic technology, which demonstrates high power conversion efficiencies along with the potential for low-cost due to cheap perovskite layer deposition methods, and compatibility with roll-to-roll fabrication.¹

In a planar PSC configuration, the active layer is sandwiched between charge transport layers, which selectively extract and transport charge carriers to the electrodes. Currently, the most commonly used hole-transport materials (HTMs) are based on organic small molecules. These materials generally require doping to compensate for their low hole mobility, which leads to the increase in the cost and compromises device operational stability.

An alternative approach is based on using compounds with large aromatic moieties enabling strong intermolecular interactions in solid state thus boosting the charge carrier transport. In particular, pyrene derivatives with arylamine substituents are of a great interest as they can be easily synthesized in a few steps², their energy levels are well aligned with the perovskite valence band providing efficient hole extraction, and the presence of heteroatoms and aromatic blocks is leading to defect passivation at the perovskite grain boundaries.³ Finally, high glass transition temperatures suppress recrystallization and hence should improve the operational stability of the devices.

In this work, four pyrene derivatives were investigated as HTMs in PSCs. We demonstrated that devices assembled with thermally evaporated pyrene derivatives deliver superior power conversion efficiency as compared to the devices with solution-processed HTMs with a similar structure. The device efficiency of 17.9% was obtained using the best material, which corresponds to the state-of-the-art values reported for dopant-free small molecular HTMs.

The obtained results support our belief that HTMs based on pyrene derivatives hold a great promise for the development of inexpensive and highly efficient dopant-free perovskite solar cells.

This work was supported by RFBR project number 19-33-90294

¹ M. Saliba, J.-P. Correa-Baena, M. Grätzel, A. Hagfeldt, A. Abate. *Angew. Chem. Int.* 2018, **57**, 2554.

² M. G. Kaplunov, I. K. Yakushchenko, S. S. Krasnikova, S. B. Echmaev. *Mendeleev Commun.* 2016, **26**, 437.

³ L. Zhang, C. Liu, J. Zhang, X. Li, C. Cheng, Y. Tian, A. K.-Y. Jen, B. Xu. *Adv. Mater.* 2018, **30**, 1804028.

Inkjet printed OFETs for gas sensing of toxic gases

A.A. Trul^{1}, E.V. Agina¹, K.Y. Mitra², S. Kapadia², M. Polomoshnov², S.A. Ponomarenko¹*

¹Enikolopov Institute of Synthetic Polymeric Materials RAS

²Technische Universitaet Chemnitz, Institute for Print and Media Technology

*e-mail: trul@ispm.ru

Printed organic field effect transistors (OFETs) are promising platform for gas sensing since potentially they can combine both OFETs high sensitivity to the presence of toxic gases in the atmosphere¹ and low-cost device fabrication. In the present work, we investigated sensory properties of fully printed OFETs fabricated by inkjet printing. To estimate sensory properties the drain current was measured in air atmosphere containing toxic gases. The current values were collected during 35 seconds in order to increase the accuracy. Since change of the current in time represents the charge transferred through semiconducting layer, the relative change of the charge value was used as a response parameter. Printed devices were found to be highly sensitive to extremely low concentrations of NH₃, H₂S, NO₂ (Figure 1a). Similarly to chemo-resistive inorganic sensors, the current and relative change of the charge values of printed OFETs increases in the atmosphere containing oxidizing gases such as NO₂ and decreases in the atmosphere containing reducing gases such as NH₃ and H₂S. The limit of detection was found to be 50-200 ppb depending on toxic gas, that is almost the same value as for the sensors based on monolayer Langmuir-Schaefer OFETs recently developed by our group.²

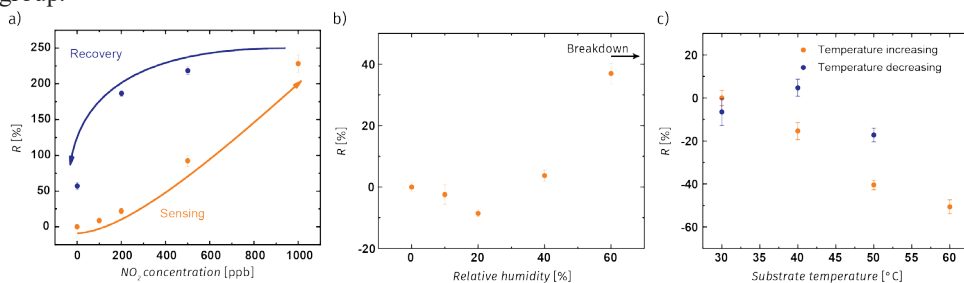


Figure 1. The device response to nitrogen dioxide (a). Dependence of the response parameter on relative air humidity (b) and substrate temperature (c).

However, unlike monolayer devices printed OFETs are not completely recovered even within 12-20 hours after surcease of toxic gases exposure. In addition, it was found that the response parameter depends on relative air humidity (RH) (Figure 1b) and substrate temperature (Figure 1c). At first, it decreases with RH increasing, but after RH reaches 20% it begins to increase rapidly and the reversible dielectric breakdown is observed at RH of 80%. Most probably, such behavior is related to polymer dielectric swelling in humid air and the devices are able to operate again after dehydration in dry air atmosphere during a few days. Substrate temperature increasing leads to decreasing of the response parameter however the irreversible breakdown is observed under the keeping of sensor temperature at 50 °C during a few hours. It can be caused by increasing of the polymer chains mobility at higher temperature. Thus, such sensors are able to work only once, however, low cost of printed devices allows their disposable application in air with moderate humidity.

¹ Andringa, A.-M.; Spijkman, M.-J.; Smits, E. C. P. et al. *Org Electron* 2010, **11** (5), 895-898.

² Trul, A. A.; Chekusova, V.P. et al., *Sens. Actuators B – Chem* 2020, **321**, 128609.

Two-phase composite employing liquid-gas phase transition for large volume expansion

*I.V. Bezsudnov¹, A.A. Kalinina^{1,2}, Yu.I. Bezsudnova¹, A.G.Kazaeva¹,
E.V. Agina^{1,2}, S.A. Ponomarenko^{1,2}*

¹Enikolopov Institute of Synthetic Polymeric Materials of RAS, Moscow, Russia

²Printed Electronics Technologies LLC, Moscow,

*e-mail: bezsudnov_iv@ispm.ru

The purpose of the work was to investigate physical properties of two-phase composite material silicon – ethanol. This and similar composites demonstrate large volume expansion when heated due to liquid-gas transition of low-boiling solvent (ex. ethanol) presented in the composite. The structure of the investigated composite – isolated spherical pores with a drops of ethanol in soft silicone matrix. Raising over solvent boiling temperature converts liquid ethanol to the gas and consequently raising gas volume expands significantly the volume of the whole composite. The composite can be made by mixing silicone rubber with ethanol and then curing at room temperature. The composite was first described in¹.

We use platinum-catalyzed two-component silicone Ecoflex 00-50 (Smooth-On, PA, USA) is used as a matrix material and ethanol $\geq 99.0\%$ as a phase for liquid-gas transition material.

Our measurements show essential dependency of material density and Young's modulus on ethanol content in composite. Higher ethanol content makes them lower; 25% ethanol makes density 13% less and lowers composite stiffness for 30%.

Developed volume expansion measurement device PARUS measures the elongation of the sample in a square cross section cell during heating at constant power.

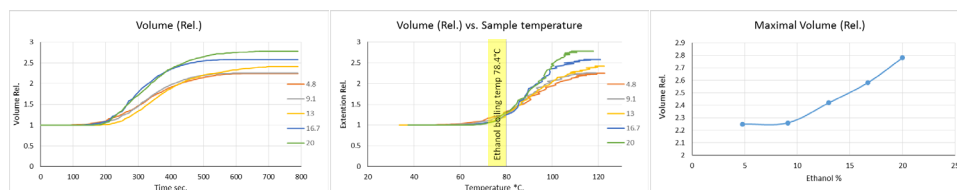


Fig. 1. Relative volume of the composite as a function of heating time (left) and sample temperature (center) at different composite ethanol content (shown on figure). Maximal volume growth for composites with different ethanol contents (right).

Large volume expansion of investigated silicone-ethanol composite makes it promising for mechanical actuator manufacturing. Measured complex of parameters allows us to predict the behavior of investigated composites at different loads and conditions.

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

LS monolayer OFETs with outstanding electrical performing as highly sensitive gas sensors to ethyl mercaptan

V.P. Chekusova^{1*}, *A.A. Trul*¹, *D.S. Anisimov*¹, *A.A. Abramov*¹, *O.V. Borshchev*¹, *E.V. Agina*¹,
*S.A. Ponomarenko*¹

¹Enikolopov Institute of Synthetic Polymeric Materials RAS

*e-mail: chekusova@printeltech.com

Forehanded detection of alkyl mercaptans is a problem of current interest since they are used for natural gas odorization, and highly sensitive sensors could help to detect gas leaks in real-time regime preventing gas explosion. Earlier we developed OFET-based sensors having high sensitivity to the presence of NH_3 and H_2S in the atmosphere.¹

In this work we investigated self-assembly processes for the range of synthesized BTBT-derivatives in Langmuir layers on the water surface, in Langmuir-Schaefer (LS) and Langmuir-Blodgett (LB) layers on silicon substrates as well as in self-organized layers fabricated by spin-coating (SC) technique. Optimal fabrication conditions such as solution concentrations, spreaded solution amount, barriers movement and rotational speed were selected. As far as preliminary processing of the substrate surface also affects to the layer formation and electrical properties of devices we studied the influence of OFET's surface modification by various dielectrics such as poly(methyl metacrylate) (PMMA Sigma-Aldrich 350k), polystyrene (PS Sigma-Aldrich 280k) and octyldimethylchlorosilane (ODMS). Identification of factors affecting electrical characteristics allowed qualitative optimization of the monolayer OFETs fabrication process. As the result we obtained a device with record electrical characteristics for monolayers devices based on BTBT-derivatives (max hole mobility was $0.47 \text{ cm}^2/\text{Vs}$, average hole mobility was $0.20 \text{ cm}^2/\text{Vs}$), high reproducibility, stable operating in air even under relative humidity up to 95%. This device showed outstanding sensory properties in relation to ethyl mercaptan demonstrating linear behavior in the sub-ppm range, fast and reversible response and LOD in the range of 30-40 ppb. Fabricated sensor could be promising device for real-time detection of natural gas leaks.

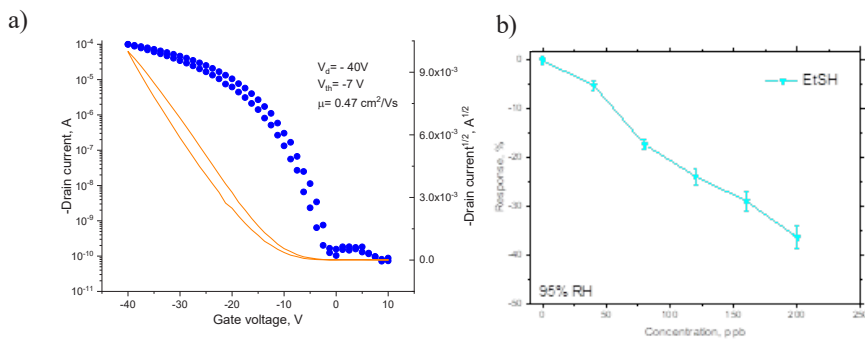


Figure 1. Typical (a) transfer and (b) response to Et-SH humid air at 95% RH curves.

This work was supported by Russian Foundation for Basic Research (grant 20-03-00810).

¹ A.A. Trul, V.P. Chekusova, et.al. *Sensors and Actuators B: Chemical*, 2020, **321**, 128609

Photoluminescence anisotropy in organic 2D semiconductors

A.V. Kuevda^{1,2*}, *R. S. Fedorenko*^{2,3}, *O.V. Borshchev*², *S.A. Ponomarenko*², *D.Yu. Paraschuk*^{2,3}

¹Skoltech Institute of Technology, Department of Materials Science

²Institute of Synthetic Polymeric Materials RAS

³Moscow State University, Faculty of Physics

*e-mail: alexey.kuevda@skoltech.ru

2D organic electronics became in recent years an area of active research and applied development attempting to create superlightweight, ultraflexible, transparent and inexpensive electronic devices based on organic semiconductor films with a thickness of one or few molecular layers. However, 2D optoelectronics is still greatly undeveloped and luminescent properties of 2D organic crystals are unknown¹. Thiophene-phenylene based materials are promising for organic optoelectronics because of lucky combination of decent charge-carrier mobility and high luminescence. These molecules with long alkyl terminal substituents easily form large-area 2D single-crystal monolayers².

In this work, we study anisotropic properties of photoluminescence (PL) of 2D samples based on (Dec-P)₂-BTBT (Fig.1, top) and other thiophene-phenylene molecules. The 2D samples were prepared by drop- or spin-casting and studied with the use of confocal laser scanning, optical interference, and atomic-force microscopies. Fig. 1 shows that PL polarization of different domains of a 2D film is differently oriented, which indicates that the domains are single crystals. We suggest that the PL polarization anisotropy reflects various orientations of 2D single-crystal domains. We compare PL anisotropic properties in monolayer and a-few-layer domains of 2D films.

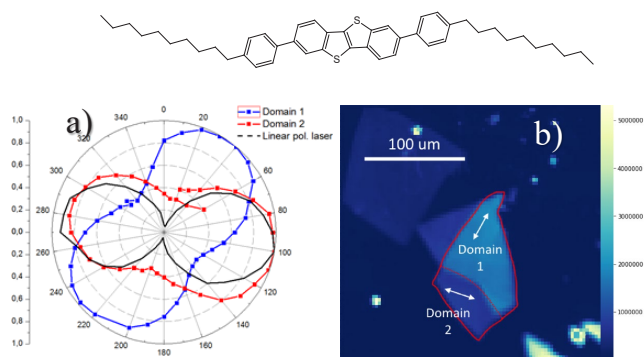


Fig 1. PL data on (Dec-P)₂-BTBT. Top: chemical structure of (Dec-P)₂-BTBT. Bottom: PL anisotropy of different domains (blue and red) of a trilayer film (a), the black line is the reference data for the linearly polarized laser excitation; PL map revealing the domain structure in the trilayer film (white arrows show direction of PL polarization) (b).

This work was supported by Russian Science Foundation, project № 18-12-00499.

¹ E. V. Agina, et al. *ACS Appl. Mater. Interfaces* 2017, **9**(21), 18078–18086.

² V. V. Bruevich, et al. *ACS Appl. Mater. Interfaces* 2019, **11**(6), 6315–6324.

Spectral technique for precise efficiency measurements of various types of advanced solar cells

A.L. Mannanov^{1,3*}, *A. Gavrik*¹, *S. Tsarev*², *V.V. Bruevich*¹, *V.A. Trukhanov*¹,
*Yu.A. Chernikov*¹, *P.S. Savchenko*^{1,3}, *J.D. Gvozdkova*⁴, *A.N. Solodukhin*³,
P.A. Troshin^{2,5}, *S.A. Ponomarenko*³, *D.Yu. Paraschuk*^{1,3}

¹International Laser Center and Faculty of Physics, Lomonosov Moscow State University

²Center for Electrochemical Energy Storage, Skolkovo Institute of Science and Technology

³Enikolopov Institute of Synthetic Polymer Materials, RAS

⁴Moscow Aviation Institute (National Research University)

⁵The Institute for Problems of Chemical Physics of the Russian Academy of Sciences

*e-mail: al.mannanov@physics.msu.ru

Intensive research in photovoltaics has led to the appearance of emerging solar cells such as organic, perovskite, etc. As the solar-cell power conversion efficiency (PCE) is the main driver of the field, its accurate measurement is vitally necessary. However, the accurate PCE evaluation is not easy in a typical research laboratory and, because of enormous pressure of competition, the correctness and validity of the reported PCE values is a recognized issue. The reference-cell PCE measurement method¹ is a workhorse in the community; however, this method is reliable only if the absorption spectra of the reference and test cells are coincident. In practice, this condition is generally not satisfied especially for emerging solar cells based on novel materials. Moreover, the accuracy in the PCE measured — a property crucial for a consistent experiment — is unavailable. Here, we present a laboratory measurement technique — the spectral technique² — and demonstrate its applicability for organic, perovskite, and dye-sensitised solar cells. The spectral technique is based on the control of the solar simulator spectrum (Fig.1) and allows reliable evaluation of the PCE values and their inaccuracies. We anticipate that the spectral technique will facilitate easier comparison of the results across the community and between various solar cell technologies contributing to credibility of photovoltaic research and development.

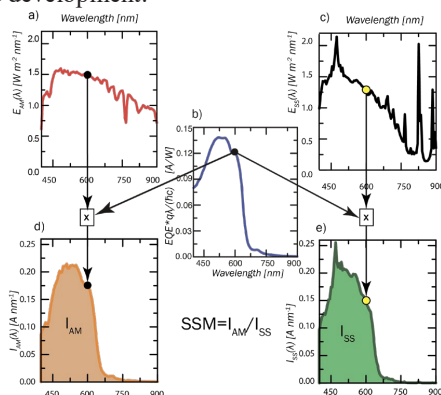


Fig. 1. The spectra required for the spectral technique and calculation of sun-simulator mismatch (SSM) correction factor: a) AM1.5G spectrum, b) spectral responsivity of cell under test (CUT), c) simulator spectrum, d) CUT photocurrent density spectrum under AM1.5 illumination, e) CUT photocurrent density spectrum under simulator illumination.

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

¹ V. Shrotriya et al. *Adv. Funct. Mater.* 2006, **16**, 2016–2023

² A. Gavrik et al. *Solar Energy* 2020, **206**, 770–777.

Anisotropic low-frequency Raman scattering in organic semiconductors for probing non-local electron-phonon interaction

O.D. Parashchuk^{1,2}, *M.V. Vener*¹, *D.R. Maslennikov*¹, *D.I. Dominsky*^{1,2}, *I.Yu. Chernyshov*¹, *D.Yu. Parashchuk*^{1,2}, *A.Yu. Sosorev*^{1,2}

¹Institute of Spectroscopy of the Russian Academy of Sciences

²Faculty of Physics, Lomonosov Moscow State University

Organic semiconductor crystals (OSCs) show the highest charge-carrier mobility, which is a key for high performance organic electronic devices. Non-local electron-phonon interaction in OSCs is suggested to limit the charge transport.¹ However, non-local electron-phonon interaction in OSCs is far from being well studied, and one of promising methods for probing it can be Raman spectroscopy.^{2,3}

In this study, we establish a relationship between the non-local electron-phonon interaction in various charge-transport directions and anisotropic low-frequency (LF) Raman scattering in two organic semiconductors with relatively high electron mobility, naphthalene diimides (Fig. 1): N,N'-Dicyclo-hexyl-naphthalene-1,8;4:5-dicarboximid (NDI_CHex) and N,N'-bis(hexyl)naphthalene diimide (NDI-Hex). We determine the contributions of various LF vibrational modes to the non-local electron-phonon interaction and show that they correlate with the corresponding Raman intensities, divided by frequency. We reveal computationally the LF vibrational modes that strongly modulate charge transfer integrals in different directions and show that this modulation can be assessed experimentally using low-frequency Raman spectroscopy (Fig.2). Importantly, the anisotropy of the Raman scattering correlates with the anisotropy of the non-local electron-phonon interaction, indicating that Raman spectroscopy can probe the latter in various charge transport directions. Our findings will be used to study the effect of the non-local electron-phonon coupling on the electron mobility in the crystals.

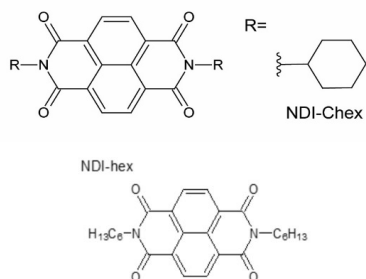


Figure 1. Chemical formula of studied OSCs

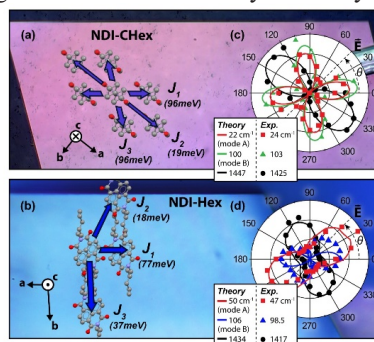


Figure 2. Raman anisotropy of the selected Raman modes for NDI-Chex (a, c) and NDI-Hex (b, d) single crystals.

This work was supported by Russian Science Foundation, project #18-72-10165.

¹ A. Yu. Sosorev, D. R. Maslennikov, O. G. Kharlanov, I. Yu. Chernyshov, V. V. Bruevich, D. Yu. Parashchuk, *Phys. Status Solidi RRL* 2018, **13**, 1800485.

² A. Yu. Sosorev, D. R. Maslennikov, I. Yu. Chernyshov, D. I. Dominsky, V. V. Bruevich, M. V. Vener and D. Yu. Parashchuk, *Phys. Chem. Chem. Phys.*, 2018, **20**, 18912-18918

³ I.Yu. Chernyshov, M.V. Vener, E.V. Feldman, D.Yu. Parashchuk, A.Yu. Sosorev. *J Phys Chem Lett.* 2017, **8**(13), 2875-2880.

Water-gated organic field-effect transistor based on the blend of 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene and polystyrene

P.A. Shaposhnik^{1,2}, D.A. Anisimov², A.A. Trul², E.V. Agina², S.A. Ponomarenko^{1,2}*

¹Lomonosov Moscow State University, Department of Chemistry

²Enikolopov Institute of Synthetic Polymer Materials RAS

*e-mail: polinashaposhnik@ispm.ru

Electrolyte-gated field-effect transistors (EGOFET) are proven to be a remarkable platform for ultra-sensitive and specific biosensors that could be utilized for point-of-care diagnostics. In EGOFET-based biosensors water act both as electrolyte and sample-carrying media¹. However, operation in aqueous environment could negatively affect device performance due to an electrochemical doping and degradation of semiconducting materials². One of the ways to overcome this issue is to use semiconducting materials with high crystallinity. It could be provided by small molecule semiconductors such as 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C8-BTBT). C8-BTBT is well investigated semiconductor that is often exploited as high-performance material for OFETs. Yet there are very few examples of C8-BTBT application in aqueous environment. The main reason is the tendency of C8-BTBT to 3D crystal growth while smooth semiconducting film is required for use in water-gated FET. According to recent studies, using a semiconductor blend with dielectric polymer is able to suppress molecule aggregation and to induce the formation of flat crystals³.

In this work we used C8-BTBT:polystyrene blends combined with Doctor Blade deposition technique. To improve a charge injection we modified source/drain (S/D) electrodes with 2,3,4,5,6-pentafluorothiophenol (PFBT). In order to optimize deposition parameters, we tried different solvents and different semiconductor concentrations with fixed polystyrene concentration, various temperatures and blade-shearing directions. We have found that devices fabricated from 15 mg/ml C8-BTBT solution in toluene blended with polystyrene in ratio 4:1 showed the best electrical performance. Parameters measured in OFET configuration in saturation regime were $I_{on/off}$ up to 10^7 , μ_{sat} up to 10^{-2} $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. Devices were tested in EGOFET configuration with distilled water as electrolyte. Parameters obtained in saturation regime were $I_{on/off}$ up to 10^4 , $g_m = \partial I_{DS} / \partial V_{GS}$ up to 7 mS with applied voltage no more than -0,5 V and low hysteresis which is among the best EGOFET devices prepared with C8-BTBT. Average V_{th} measured in OFET configuration was 2V, in EGOFET configuration 0,1 V. These results evidence that the described water-gated FET could be further modified with receptor molecules for specific detection and then utilized for biosensor application.

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

¹ Wang D., V. Noël, B. Piro. *Electronics*. 2016, **5**(9)

² Picca R.A., K. Manoli, E. Macchia, A. Tricase, C. Di Franco, G. Scamarcio, N. Cioffi, L. Torsi. *Front. Chem.* 2019, **7**(667)

³ Wang W., B. Lu, W. Deng, X. Zhang, Z. Lu, D. Wu, J. Jie, X. Zhang. *Nano Res.* 2020, **13**(9), 2478–2484

Ink-jet printing of PEDOT:PSS for organic electronic devices

Y.O. Titova¹, A.A. Tru¹, E.V. Agina¹, S.A. Ponomarenko¹*

¹Enikolopov Institute of Synthetic Polymeric Materials RAS

*e-mail: yaroslava.gorbunova@ispm.ru

Currently there is broad interest to electronic devices, which are lightweight, flexible, cheap and can be easily manufactured. Such an opportunity is provided by organic electronics, the devices of which include conductive or semiconductor layers consisting of polymers with different conductivity. The fabrication of structures and devices from conductive polymers mainly relies on traditional manufacturing technologies such as spin-coating, Dr. Blade, screen printing, inkjet printing or roll-to-roll coating. Advantages of inkjet printing include low cost, usage of automatic design, reasonably high production speed, capability of printing fine and smooth details.

One of the promising conductive materials for practical use is poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS). Printing of conductive contacts based on commercially available highly conductive PEDOT:PSS (Clevios PH 1000) is a good alternative to sputtering of metal contacts, as it can be applied on various flexible substrates at normal conditions and allows one to change the contact architecture if necessary.¹ Low conductive version of PEDOT: PSS (Clevios P VP AL 4083) can be used to create electrolyte-gated organic transistors (EGOT)² and hole transport layers in organic photovoltaics (OPV).³

For efficient inkjet printing of various components of electronic devices, it is especially important to obtain one single spherical droplet per a trigger pulse, because any imperfection, such as satellite droplets or tails, can easily lead to complete failure of the entire device. The quality of droplet formation depends on the properties of both: (i) the inks, such as density, viscosity and surface tension, and (ii) the print head used itself. It is achieved only if characteristics of the print head and carefully selected pulse shape exactly match to the properties of the ink.⁴

The properties declared by manufacturers of widely used PEDOT: PSS solutions are usually not intended for inkjet printing. In this work they were optimized for Spectra S class SE 128 AA and Konica-Minolta KM512 MN printheads with different characteristics. For this purpose, an optimal viscosity was selected, which was measured using an Ubbelohde capillary viscometer. Addition of water to the conductive ink allowed to reduce the viscosity. For changing the surface tension of the inks based on highly conductive PEDOT: PSS, mono n-butyl ether of propylene glycol was added for printing with the Konica-Minolta KM512 MN head, while non-ionic surfactant Triton X-100 was added to the inks for Spectra S class SE 128 AA head. To achieve high conductivity declared by the manufacturer, 5% DMSO was added to PEDOT: PSS Clevios PH 1000. As a result, it was possible to print conductive structures with a conductivity exceeding those declared by the manufacturer.

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

¹ Nan Liu et al., *Advanced Electronic Materials* 2017, **3** (9),

² Emre Kayali et al., *ACS Appl Mater Interfaces* 2018, **10** (31), 25834-40

³ Jie Min et al., *Organic Electronics* 2018, **55**, 42–49

⁴ P. Maisch, Obtaining the PhD degree DR.-Ing, 25.02.2019.

Electroluminescent 2D Organic Semiconductor Single Crystals with High Charge-carrier Mobility

V.A. Trukhanov^{1,2*}, *R.S. Fedorenko*^{1,2}, *V.G. Konstantinov*^{1,2}, *O.V. Borshchev*²,
*S.A. Ponomarenko*², *D.Yu. Paraschuk*^{1,2}

¹ Faculty of Physics and International Laser Center, M.V. Lomonosov Moscow State University

² N.S. Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Science

*email: trukhanov@physics.msu.ru

Organic light-emitting transistors (OLETs) can have several advantages over the more traditional organic light-emitting diodes (OLEDs) such as higher brightness and efficient light outcoupling.¹ However, the main difficulty in creation of high-performing OLET is the combination of efficient luminescence and high charge mobility in one material. Also, optical waveguiding effect in OLET active layer strongly decreases light emission from its top surface degrading the OLET performance. To avoid this, 2D films thinner than 100 nm would be beneficial. In this work, we report on OLETs based on solution-processed 2D films of BTBT-based molecules, 2,7-bis(4-decylphenyl)[1]benzothieno[3,2-b][1]benzothiophene (DPBTBT), which uniquely combine high charge mobility reaching 7.5 cm²/Vs and pronounced electroluminescence (Fig. 1). DPBTBT molecules are self-organized in large-area ultrathin films consisting of one or a few molecular layers, which are single crystal according to optical, atomic-force and photoluminescence microscopy. The 2D DPBTBT OLETs demonstrated particularly good shelf-life stability in the ambient air under normal laboratory conditions. The charge-carrier mobility changes by about 15% after 3 months of storage. High charge mobility, good shelf-life stability and good luminescence properties suggest that 2D BTBT-based materials are a promising platform for OLETs.

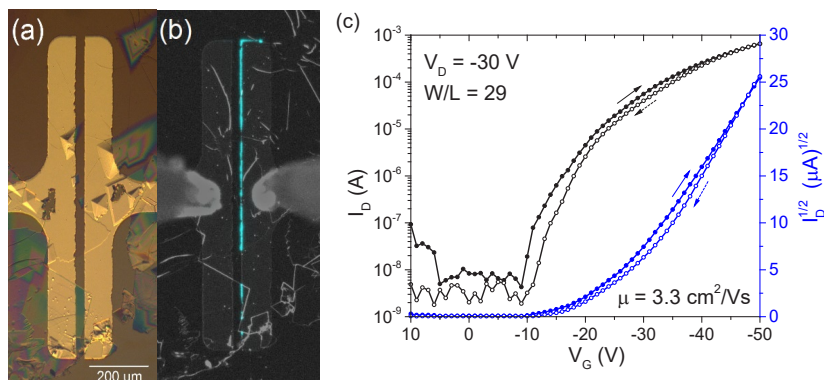


Fig. 1. Optical image of typical 2D OLET sample in C-DIC microscope (a) and during its operation (b) (the electroluminescence image is colored in light-blue and superimposed to the OLET image) and its transfer characteristic in the saturated regime (c). Electroluminescence occurs only where the crystals present in the channel and overlap both the source and drain electrodes. The channel width (W) was calculated as sum of the W values for these crystals.

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

¹ R. Capelli, *et al. Nat. Mater.* 2010, **9**, 496-503.

Photochemical synthesis of 4*H*-thieno[3,2-*c*]chromene derivatives

E.B. Ulyankin^{1,2*}, *A.S. Kostyuchenko*², *Yu.P. Bogza*², *S.A. Chernenko*^{1,2}, *A.S. Fisyuk*^{1,2}

¹Omsk State Technical University, Laboratory of New Organic Materials

²Omsk State University, Department of Chemistry

*e-mail: e.b.ulyankin@gmail.com

The photophysical properties of 4*H*-thieno[3,2-*c*]chromenes make it possible to use these compounds for the preparation of long-wavelength dyes and semiconducting materials¹. It is known that 4*H*-thieno[3,2-*c*]chromene carbaldehydes exhibit a large Stokes shift² due to intramolecular charge transfer and a significant change in the geometry (Fig. 1).

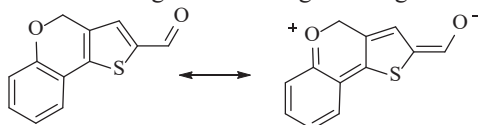


Fig. 1. Intramolecular charge transfer in 4*H*-thieno[3,2-*c*]chromene carbaldehydes

Previously, similar structures were obtained using palladium-catalyzed cross-coupling³. In this work, we studied the possibility of intramolecular photosynthesis of thienochromenes **4** from iodine derivatives of 4-(phenoxymethyl)thiophene-2-carbaldehydes **3** obtained by alkylation of the corresponding phenols with various 4-(chloromethyl)thiophenecarbaldehydes **2** (Fig. 2).

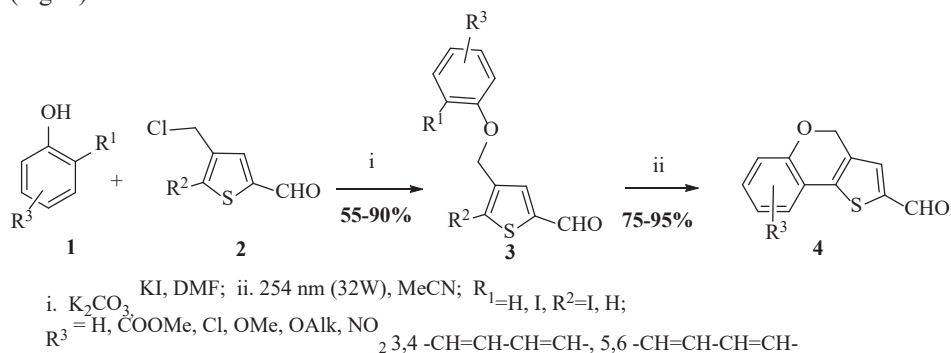


Fig. 2. Synthesis of 4*H*-thieno[3,2-*c*]chromenecarbaldehydes

The influence of the position of the iodine atom (in the benzene or thiophene rings) on the rate and yield of photochemical cyclization was studied. In most cases, the photophysical approach made it possible to achieve an increase in the products yield in comparison with cross-coupling reactions.

This work was supported by the Russian Science Foundation (grant № 20-73-10043).

¹ Li X., Huang H., Peng Z., Sun C., Yang D., Zhou J., Liebman-Pelaez A., Zhu C., Zhang Z.-G., Zhang Z., Xie Z., Ade H., Li Y. *J. Mater. Chem. A*. 2018, **6**, 15933-15941.

² Bogza Yu.P., Rastrepin A.A., Nider V.V., Zheleznova T.Yu., Stasyuk A.J., Kurowska A., Laba K., Ulyankin E.B., Domagala W., Fisyuk A.S. *Dyes and Pigments*. 2018, **159**, 419-428.

³ Fisyuk A.S., Bogza Yu. P., Belyaeva L.V., Belyaev V.B. *Chemistry of Heterocyclic Compounds*. 2012, **48**(7), 1078-1084.

Impact of lead substitution on stability and photovoltaic performance of lead halide perovskites

M.I. Ustinova^{1,2}, N.N. Dremova², S.Yu. Luchkin¹, P.A. Troshin^{1,2}*

¹ Skolkovo Institute of Science and Technology

² Institute for Problems of Chemical Physics of RAS

*e-mail: ustinova1712@gmail.com

Over the past few years, the performance of perovskite solar cells was gradually improved up to >25%, which is close to the characteristics of crystalline silicon photovoltaics. However, high toxicity and low stability of complex lead halides used as absorber materials hamper commercialization of this technology. Compositional engineering of lead halide perovskites was actively pursued in order to improve their stability and/or performance. In particular, a partial or full replacement of Pb^{2+} in APbX_3 is highly desirable in terms of developing more environmentally friendly materials.

Herein, we present a systematic study of lead substitution in MAPbI_3 , CsFAPbI_3 and CsPbI_3 with >20 different cations introduced in atomic concentrations ranging from 10^{-4} to 20-30%. It was shown that replacing even minor fraction of lead could change significantly the perovskite film crystallinity and morphology. Importantly, the efficiency and stability of p-i-n and n-i-p solar cells were improved considerably by appropriate modification of perovskite active layer. Moreover, important relationships were established between the nature of the substituting ions (e.g. ionic radius or charge) and their effects on electronic properties and photovoltaic performance of the resulting perovskites. The obtained results should facilitate rational design of more stable and less toxic absorber materials for advanced perovskite solar cells.

Liquid Metal Melt Electrodes for Low-cost Perovskite Solar Cells

E.E. Vaneeva^{1,2}, S.A. Tsarev², P.A. Troshin^{2,3}*

¹D. Mendeleev University of Chemical Technology of Russia

²Centre of Energy Science and Technology, Skolkovo Institute of Science and Technology

³Institute for Problems of Chemical Physics of the Russian Academy of Sciences

*e-mail: liza.vaneeva@gmail.com

Perovskite photovoltaics is an emerging technology for deployment of renewable energies.¹ The main advantages of the perovskite solar cells (PSCs) are represented by their solution processibility, excellent scalability using roll-to-roll printing and coating technologies and hence potential for ultralow cost. Currently, most of efficient PSC architectures use thermally evaporated top metal contacts. However, the thermal evaporation method is power and time consuming and technologically low promising. In this regard, the development of vacuum-free and low-cost techniques for the top electrode deposition is essential for the future commercialization of the perovskite PV technology.

Herein, we present a simple method of electrode deposition in p-i-n PSCs using low melting point alloys. We proposed to use top electrodes based on Wood's metal, which is an alloy with the melting point of 72°C. Using contact angle measurements of the liquid metal droplets deposited on standard charge-transport layers, we found that phenyl-C₆₁-butyric acid methyl ester (PCBM) has the best adhesion to metal. This finding suggested that p-i-n device architecture such as ITO/PTAA/Cs_{0.12}FA_{0.88}PbI₃/PCBM/Metal electrode can be used for testing our hypothesis.

As a proof of concept, we used a simple lamination of Wood's metal foils on top of the ITO/PTAA/Cs_{0.12}FA_{0.88}PbI₃/PCBM stack. After some optimization of the processing parameters, the champion devices with laminated metal electrodes delivered power conversion efficiencies up to 15%, which is comparable with the characteristics of the conventional device architecture using evaporated Mg/Ag top electrodes (Figure 1). Our facile lamination process enables a simple and technologically relevant SC fabrication process without using vacuum-based or high temperature material deposition stages. Furthermore, it is compatible with modern printing techniques and, therefore, is promising for large-area applications leading to significantly reduced cost of the final product.

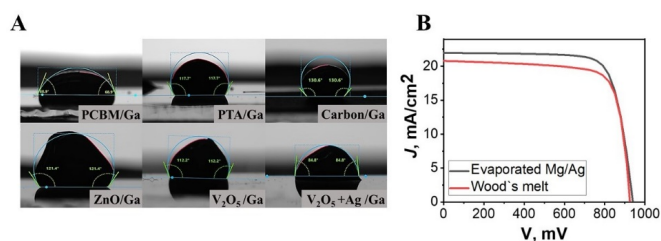


Figure 1. A. Contact angles of a Ga droplet on various coatings. B. Current-voltage curves for champion devices with the conventionally evaporated and laminated top electrodes in ITO/PTAA/Cs_{0.12}FA_{0.88}PbI₃/PCBM/Metal configuration.

¹ Asif, A. A., Singh, R., & Alapatt, G. F.. *Journal of Renewable and Sustainable Energy*, 2015, 7(4), 043120.

The Influence of Electron-transport Layer on the Stability of Perovskite Solar Cells

V. Regina^{1,2*}, *O.R. Yamilova*^{2,3}, *P.A. Troshin*^{2,3}

¹D. Mendeleev University of Chemical Technology of Russia

²Skolkovo Institute of Science and Technology

³Institute for Problems of Chemical Physics of the Russian Academy of Science

*e-mail: dementorrrrr@gmail.com

In the recent years solar cells based on complex lead halides perovskite structure demonstrate an extraordinary growth in power conversion efficiency (PCE) which exceeds 25% for the best laboratory samples.¹ However, their practical use still labored due to low operational stability. In addition to the widely studied effects go photochemical and thermal degradation^{2,3,4} particular/special attention should also be paid to electrochemical stability of absorbing compounds and directly the solar cells themselves.⁵

In this work, electrochemical stability of perovskite solar cells, assembled with various charge-transport materials, were systematically compared. Devices with oxide electron-transport materials such as ZnO and SnO₂ were exposed to the constant influence of electric field with inert atmosphere in the dark and at room temperature to exclude influence of other degradation pathways.

The relation/dependence of the efficiency of solar cells were analyzed on the impact of exposure time of applied voltage. The results showed that electrochemical stability of perovskite solar cells is highly depends on used electron-transport layer materials. Also, it was shown that short biasing of PSC with ZnO can enhance their efficiency. The identified dependencies emphasize the importance of multi-parameter optimization of the structure of solar cells and, most importantly, the composition of the electron-transport layer, to achieve their long-term operational stability.

¹ NREL efficiency chart [Online] - <https://www.nrel.gov/pv/cell-efficiency.html>

² T. T. Ava, A. Al Mamun, S. Marsillac and G. Namkoong, *Appl. Sci.*, 2019, **9**(1), 188-1-188-25.

³ Q. Hong, R. Xu, T. Jin, J. Tang and Y. Li, *Organic Electronics*, **67**, 19-25.

⁴ A. F. Akbulatov, S. Yu. Luchkin, L. A. Frolova, N. N. Dremova, K. L. Gerasimov, I. S. Zhidkov, D. V. Anokhin, E. Z. Kurmaev, K. J. Stevenson and P. A. Troshin, *J. Phys. Chem. Lett.*, 2017, **8**, 1211-1218.

⁵ S. Bae, S. Kim, S.-W. Lee, K.-J. Cho, S. Park, S. Lee, Y. Kang, H.-S. Lee and D. Kim, *J. Phys. Chem. Lett.*, 2016, **7**, 3091-3096.

Influence of the hole-transport layer on the electrochemical stability of perovskite solar cells

O.R. Yamilova^{1,2}, Yu.S. Fedotov³, S.I. Bredikhin³, L.A. Frolova^{1,2}, K.J. Stevenson¹, P.A. Troshin^{1,2}

¹ Skolkovo Institute of Science and Technology

² Institute for Problems of Chemical Physics of RAS

³ Institute of Solid State Physics of RAS

*e-mail: jamilova.olga.r@gmail.com

Recently lead halide perovskite solar cells demonstrated remarkable improvement of power conversion efficiency going beyond 25%. However, operational stability problems have long stood in the way of their practical implementation. In particular, perovskite materials might undergo electrochemical degradation when electric bias is applied to the films. Therefore, the active layer of the operating solar cells has to sustain the electric fields induced by the built-in and light-induced potentials. Otherwise, the electrochemical degradation of the active layer material under the solar cell operation conditions would ruin the device performance.

Here we report a systematic comparative study of the electrochemical stability of lead halide based perovskite solar cells assembled with different hole-transport materials such as PEDOT:PSS, NiOx, PTAA and their combinations. Devices were exposed to a different bias under anoxic conditions in the dark, and the evolution of the solar cell performance induced by different bias voltages was analyzed. We also used ToF-SIMS profiling to unravel ion migration and parasitic redox processes occurring at the cathode and anode. The obtained results showed that the electrochemical stability of perovskite solar cells is largely affected by the used transport materials. The revealed degradation pathways featured a crucial importance of controlling interfacial electrochemistry while designing highly efficient and stable perovskite solar cells.

Studies of the influence of water molecules on the perovskite structure $\text{CH}_3\text{NH}_3\text{PbI}_3$

T.Yu. Zelenyak^{1}, V.A. Turchenko, A.S. Doroshkevich^{1,2}, P.P. Gladyshev³, A.V. Shylo², A. Stanculescu⁴, M. Balasoiu^{1,5}, A.I. Madadzada^{1,6}, E.B. Asgerov^{1,6}*

¹ Joint Institute for Nuclear Research.

² Donetsk Institute for Physics and Engineering named after O O Galkin NAS of Ukraine

³ Dubna International University

⁴ National Institute for Materials Physics (NIMP)

⁵ Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering (IFIN-HH)

⁶ National Nuclear Research Center,

*e-mail: tatyana.zelenyak@bk.ru

The key problem of perovskite solar cells remains their instability in the environment.

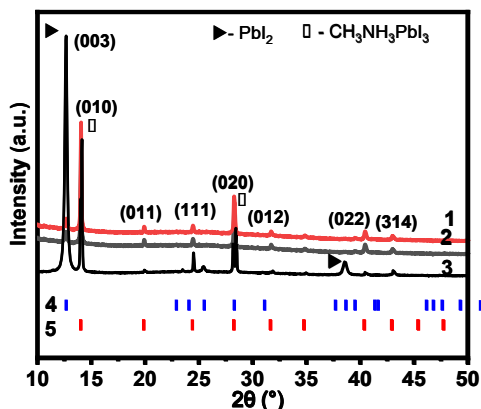


Fig. 1. X-ray diffraction patterns of experimental thin-film perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$: 1 - 0 min on air; 2 - 24 hours in the air; 3 - after 72 hours in the air; 4, 5 are the intense peaks of the phases PbI_2 , $\text{CH}_3\text{NH}_3\text{PbI}_3$.

In this work, X-ray diffraction methods were used to study the change in the crystal structure of perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ films storing in air under normal physical conditions (Fig. 1). The established redistribution of the intensities of the (010) and (003) peaks indicates the monotonic degradation of the tetragonal phase and the corresponding perovskite structure of $\text{CH}_3\text{NH}_3\text{PbI}_3$ storing.

The study was performed in the scope of the Project of JINR – Romania at 2020, order № 269, p 62. and order 268 n.59.

Self-assembly of Lanthanide Double-Decker Crown-substituted Phthalocyaninates into 1D-Supramolecular Semiconductors

*A.I. Zvyagina*¹, *A.G. Martynov*¹, *A.R. Tameev*¹, *A.E. Baranchikov*², *A.A. Ezhov*³, *Y.G. Gorbunova*^{1,2}, *Kalinina M.A*¹

¹Frumkin Institute of Physical Chemistry and Electrochemistry RAS

²Kurnakov Institute of Inorganic Chemistry RAS

³Moscow State University, Department of Physics

*e-mail: zvyagina.ai@gmail.com

Fabrication of organic semiconductors by self-assembly of supramolecular building blocks is an intensely developing field of modern material science. Herein we report a new strategy for fabricating conductive nanowires through self-assembly of lanthanide double-decker crown-substituted phthalocyaninate complexes (ML₂, where M = Lu, Ce, Tb) and potassium tetraphenylborate. The growth of supramolecular structure proceeds through a coordination of crown-ether groups of adjacent ML₂ complexes with potassium ions after the mixing of the ligand and salt in solution (Fig. 1a).

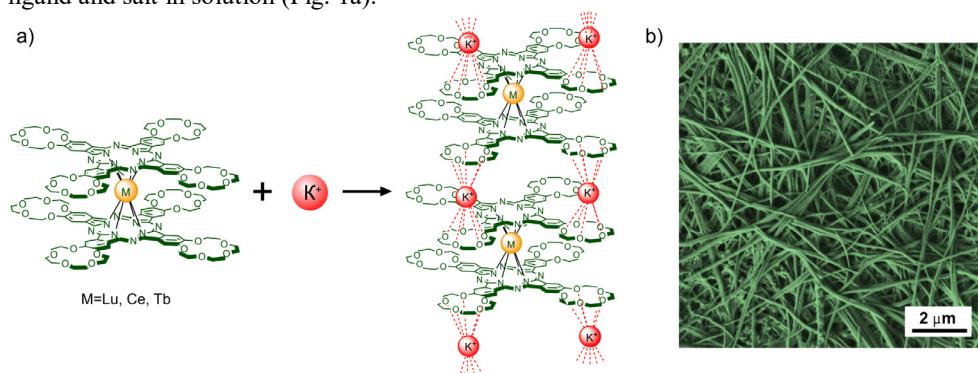


Fig. 1. a) Scheme of formation and b) SEM photo of supramolecular nanowires based on lanthanide bis(tetra-15-crown-5)phthalocyaninate complexes.

The incorporation of large central metal ions such as Ce(III) or Tb(III) in ML₂ can increase the probability of intramolecular binding of K⁺ ions instead of intermolecular coordination of complexes with smaller metal centers such as Lu(III). Spectrophotometric titration showed that the K⁺-induced intermolecular binding dominates irrespective of the chemistry of central metal ion at high concentration of the potassium salt. The SEM investigation of the as-formed supramolecular structures deposited onto the solid supports via dip coating confirmed the formation of nanowires with an extraordinary high aspect ratio and length up to 50 microns (Fig. 1b). The electrical properties of these nanowires depend on the chemistry of central metal ion and dramatically decrease in the order Lu>Ce>Tb. The LuL₂-based nanowires exhibited better electrical properties than those of known conjugated polymer semiconductors. The TbL₂-based 1D structures possessed insulator characteristics, whereas CeL₂-based wires showed semiconductor behaviour.

Our results is important for understanding how the composition of building blocks may affect the properties of resulting 1D supramolecular structures to optimize them for their integration with organic electronic devices.

This work was supported by Russian Science Foundation (project № 19-73-00025).

Photocurrent vibrationally promoted electronic resonance spectroscopy for probing electron-phonon couplings in perovskite solar cells

D.R. Maslennikov^{1}, N. P. Gallop¹, A.A. Bakulin¹*

¹Imperial College London, Department of Chemistry
*d.maslennikov19@imperial.ac.uk

Recently, interactions between vibrational and electronic processes have drawn considerable attention of specialists in a wide range of disciplines ranging from molecular biology to physics and chemistry. These interactions, often referred as electron-phonon or vibronic couplings, have been suggested to play a key role in defining electrical and optical properties in a wide range of functional materials.ⁱ Namely, it was already shown that coupling between thermally populated low frequency vibrations and mobile charges plays the key role in limiting charge transfer properties of crystalline organic semiconductors.ⁱⁱ Yet, because of the current limitations of experimental and computational techniques, the exact role of vibronic couplings in performance of real functional devices remains unclear.

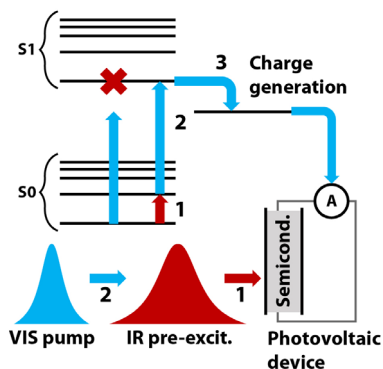


Fig. 1. Main stages of the Photocurrent VIPER spectroscopy. (1) Vibrations of the studied semiconductor (SC) are pre-excited with an infrared (IR) pulse. (2) S1 states are excited with visible (VIS) pulse. Both (IR and VIS) pulses are required to make the electronic excitation within the SC and only preliminary IR pre-excited states contribute to the S0-S1 transition. (3) The electronic excitation is followed by charge generation and photocurrent detection within the device.

In this work we develop a new experimental technique for studying vibronic couplings in functional materials — photocurrent vibrationally promoted electronic resonance (photocurrent VIPER, Fig. 1), which is intrinsically sensitive to vibronic couplings. Because of the state-of-art combination of ultrafast spectroscopy (VIPERⁱⁱⁱ) and photocurrent detection technique, this method allows one to directly track how particular molecular vibrations affect time-resolved performance of real functional devices. We apply this method to study strongly debated in the literature problem of ion-framework vibronic interactions in perovskite (FaPbBr₃) materials and discuss possible applications of photocurrent VIPER for studying vibronic couplings in other types of semiconductors.

This work was funded by the Imperial College President's PhD Scholarships.

ⁱ A.A. Bakulin et al. *Nat. Commun.* 2015, **6**, 7880.

ⁱⁱ A. Y. Sosorev et al. *Phys. Status Solidi RRL*. 2019, **13**(3), 1800485.

ⁱⁱⁱ J. von Cosel et al. *J. Chem. Phys.* 2017, **147**(16), 164116.



Research

Thin-Film Deposition
Device Fabrication
Microscopy
Electrical Characterization
Gas Sensing Properties

Materials

Organic Semiconductors
Porphyrins
Adhesion Promoters
Silicon Substrates

Equipment

Probe Station
Portable Gas Analyzer
Gas Sensor Test Stand
Metal Evaporation Stacks

Software

Conference
Management Tool



Materials and devices for the flexible
electronics technology

Contacts

Printed Electronics Technologies LLC

📍 117393, Moscow, Russian Federation
Profsoyuznaya st. 70, bld. 1, office 410

☎ +7 (495) 332-58-40

🌐 www.printeltech.com

✉ sales@printeltech.com

About Us

Printeltech was founded in 2015 by organic electronics research scientists with an aim to perform R&D activities in the organic thin-film transistor technology. As the company grows, its portfolio now includes organic materials synthesis, hardware and software development.

Our mission is to develop the technology and end-user products for the next generation electronics.

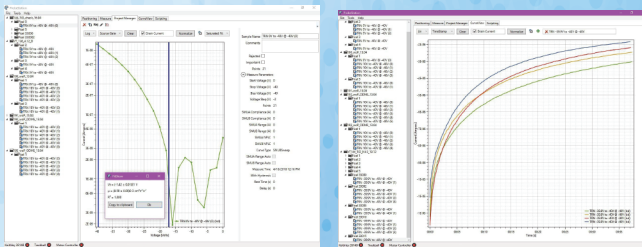
ProbeStation 100

Designed for lab or small-scale production electrical testing



Key features

- Compact design for glove-box installation
- Fully automated sample holder for fast characterization
- High accuracy current measurements with fully triaxial connections
- Multiple-sample testing in continuous mode
- Up to 4 semi-automated probes
- Digital microscope with LED lighting
- External LCD for probes positioning
- Keithley compatible software
- 2D sample positioning with trackball
- Software for measurement automatization
- Automatic FET parameter extraction (mobility, threshold voltage, etc.)



ProbeStation software

Additional options

- Extra probes (4-wire sense)
- Custom sample holders
- Glove-box installation
- Keithley semiconductor analyzer
- Software extensions for other semiconductor analyzers

PRINTELTECH

PRINTED ELECTRONICS TECHNOLOGIES



+7 (495) 332-58-88

<http://www.printeltech.com>

sales@printeltech.com

Profsoyuznaya st. 70,

bld.1, office 410

117393 Moscow, Russia

RSF

Russian
Science
Foundation



PRINTELTech
PRINTED ELECTRONICS TECHNOLOGIES



Printed Electronics Technologies LLC
117393 Moscow, Russia
Profsoyuznaya st. 70, bld.1, office 410

☎ Phone: +7 (495) 332-58-47
🌐 <http://www.printeltech.com>
✉ sales@printeltech.com