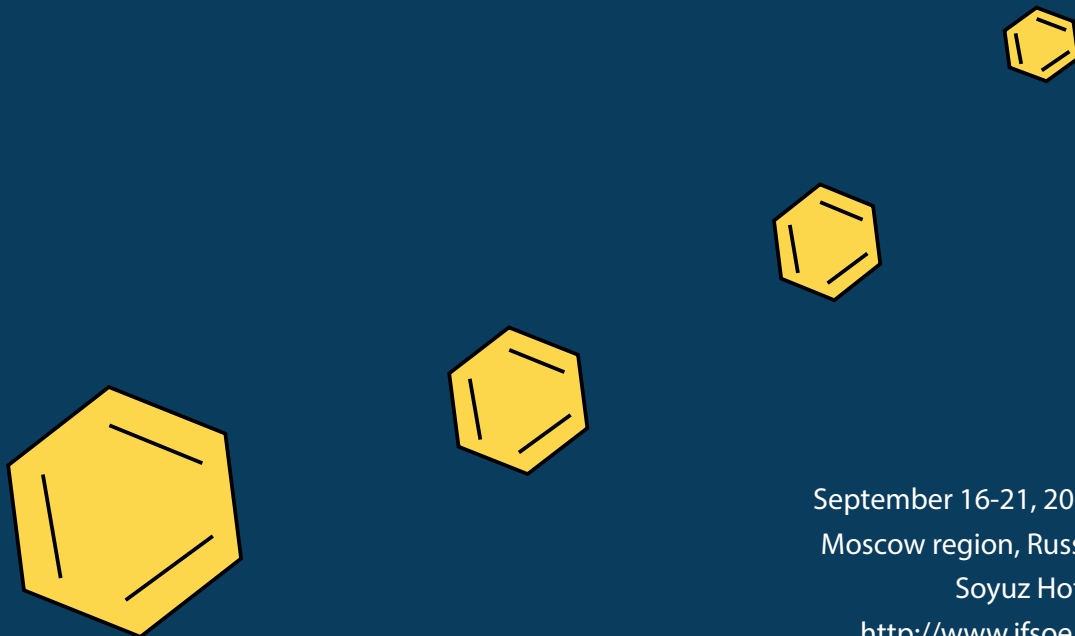




4th International Fall School
on Organic Electronics
and
Satellite event "IFSOE Sensor Day"

Book of Abstracts



September 16-21, 2018
Moscow region, Russia
Soyuz Hotel
<http://www.ifsoe.ru>

4th INTERNATIONAL FALL SCHOOL ON ORGANIC ELECTRONICS – 2018 (IFSOE-2018)

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)

Russian Foundation for Basic Research (RFBR)

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)

Chair of the Sensor Day

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Dr. Alexey Sizov

Askold Trul

Daniil Anisimov

School-conference program

The 4th International Fall School on Organic Electronics – 2018 Time Schedule

	Sunday <i>September 16th</i>	Monday <i>September 17th</i>	Tuesday <i>September 18th</i>	Wednesday <i>September 19th</i>	Thursday <i>September 20th</i>	Friday <i>September 21st</i>		
	<i>School-Conference</i>					<i>Sensor day</i>		
9:00		Sergey Ponomarenko	Harald Ade	Vladimir Dyakonov	Natalie Stingelin	Jürgen Brugger	9:00	
10:00		Michele Muccini	Anna Koehler	Maxim Pshenichnikov	Fabio Biscarini	Corrado Di Natale	10:00	
11:00	Visit to Kolomenskoe Museum (optional)	Coffee-break						11:00
12:00		Pavel Troshin	Andreas Kafizas	Alexandra Freidzon	Annalisa Bonfiglio	Alexey Vasiliev	12:00	
		Aldo Di Carlo	Elena Obraztsova	Andrey Sosorev	<u>Oral talks 5</u>			
13:00		Artem Bakulin	<u>Oral talks 2</u>	Yuriy Luponosov	School-Conference closing	Carlo Bortolotti	13:00	
	Koen Vandewal	<u>Oral talks 3</u>		<u>Oral talks 6</u>				
14:00	Lunch	Lunch						14:00
15:00	Registration at ISPM RAS	<u>Oral talks 1</u>	Evening lecture Stephan Kirchmeyer	<u>Oral talks 4</u>	15:00 Departure to Moscow	Departure to Moscow	15:00	
16:00	16:00 Departure to Conference site		Coffee-break				Coffee-break	16:00
17:00	Hotel arrival.	<u>Poster session 1</u>	Sport activities (swimming pool, wellness, spa)	<u>Poster session 2</u>	Sport activities (swimming pool, wellness, spa)		17:00	
18:00	Registration						18:00	
19:00	Dinner			Conference dinner	Dinner		19:00	
20:00	Opening ceremony Vitaly Podzorov	Evening lecture Maxim Pshenichnikov	Moscow sightseeing tour			Sport activities (swimming pool, wellness, spa)		20:00
21:00	Welcome-party	Leisure time						21:00
22:00-22:30								

Sunday, September 16th

11:00 – 16:00	Visit to Kolomenskoe Museum (optional) Registration at ISPM RAS. Departure to conference site
19:00 – 20:00	Dinner
20:00 – 20:15	School-conference opening
20:15 – 21:15	T-1. Vitaly Podzorov. Avoiding artifacts and errors in characterization of organic field-effect transistors
21:15 – 22:30	Welcome-party

Monday, September 17th

8:00 – 9:00	Breakfast
	Chair: <i>Koen Vandewal</i>
9:00 – 10:00	T-2. Sergey Ponomarenko. Molecular design of highly efficient functional materials for organic electronics and photonics
10:00 – 11:00	T-3. Michele Muccini. Organic field-effect transistors as a truly multifunctional platform: from light-emission to cell stimulation and sensing
11:00 – 11:30	Coffee-break
	Chair: <i>Vitaly Podzorov</i>
11:30 – 12:00	I-1. Pavel Troshin. Perovskite solar cells with long operation lifetimes: myth or reality?
12:00 – 12:30	I-2. Aldo Di Carlo. Dye sensitized and perovskite photovoltaics: from cells to modules
12:30 – 13:00	I-3. Artem Bakulin. Photophysics of organic solar cells with non-fullerene acceptors
13:00 – 13:30	I-4. Koen Vandewal. The influence of charge-transfer state properties on the performance of organic photovoltaic and photo-detecting devices
13:30 – 15:00	Lunch
	Oral talks 1. Chair: <i>Artem Bakulin</i>
15:00 – 15:15	O-1. Andriy Zhugayevych. Polymorphism and charge transport in organic semiconductors
15:15 – 15:30	O-2. Ernest Pastor. Charge transport mechanism in transition metal oxides photoelectrocatalysts and its similarities to molecular crystals
15:30 – 15:45	O-3. Alexey Sizov. Langmuir monolayer OFETs for multiparametric detection of toxic gases
15:45 – 16:00	O-4. Vladimir Bruevich. Large-area single-crystal oligothiophene-based monolayers for field-effect devices

16:00 – 16:15	O-5. <i>Dmitry Maslennikov</i> . Impact of terminal substituents on Raman spectra, crystal structure, and charge mobility in diphenyl-bithiophene single crystals
16:30 – 17:00	Coffee-break
17:00 – 18:30	Poster session 1 (P-1 – P-28)
19:00 – 20:00	Dinner
20:00 – 21:00	Evening lecture. <i>Maxim Pschenichnikov</i> . How to keep up with the scientific literature?

Tuesday, September 18th

8:00 – 9:00	Breakfast
	Chair: <i>Heinz Bäessler</i>
9:00 – 10:00	T-4. <i>Harald Ade</i> . Importance of molecular interactions and the need for vitrification in nonfullerene organic solar cells
10:00 – 11:00	T-5. <i>Anna Koehler</i> . How does delocalization affect exciton dissociation in organic solar cells?
11:00 – 11:30	Coffee-break
	Chair: <i>Maxim Pshenichnikov</i>
11:30 – 12:00	I-5. <i>Andreas Kafizas</i> . Can water fuel our future? Developing upscalable routes to economical devices
12:00 – 12:30	I-6. <i>Elena Obratsova</i> . Films of filled single-wall carbon nanotubes as transparent conductive electrodes
	Oral talks 2.
12:30 – 12:45	O-6. <i>Vasiliy Trukhanov</i> . Cross-contact space-charge effect on performance of organic field-effect transistors
12:45 – 13:00	O-7. <i>Filipp Obrezkov</i> . Photoswitchable organic field-effect transistors with bis(hetaryl)ethene molecules at the semiconductor-dielectric interface: material structure – device performance
13:00 – 13:15	O-8. <i>Galina Yalovega</i> . Regularities of formation Me(Co,Cu)/PAN nanocomposites conducting structure: investigation using X-ray spectroscopy
13:30 – 15:00	Lunch
15:00 – 16:00	Evening lecture. <i>Stephan Kirchmeyer</i> . How to write a patent?
16:00 – 18:00	Sport activities
18:15 – 19:00	Dinner
19:00 – 23:00	Moscow Sightseeing tour

Wednesday, September 19th

8:00 – 9:00	Breakfast
	Chair: <i>Anna Koehler</i>
9:00 – 10:00	T-6. <i>Vladimir Dyakonov.</i> Role of spins in next generation OLEDs
10:00 – 11:00	T-7. <i>Maxim Pshenichnikov.</i> Artificial light harvesters for molecular excitonics
11:00 – 11:30	Coffee-break
	Chair: <i>Vladimir Dyakonov</i>
11:30 – 12:00	I-7. <i>Alexandra Freidzon.</i> Theoretical prediction of operational stability of potential OLED host molecules by multireference quantum chemistry
12:00 – 12:30	I-8. <i>Andrey Sosorev.</i> Impact of low-frequency vibrations on charge transport in high-mobility organic semiconductors from Raman scattering data
12:30 – 13:00	I-9. <i>Yuriy Luponosov.</i> Alkyl-free donor-acceptor oligomers as highly stable electron donor materials for organic photovoltaics
	Oral talks 3.
13:00 – 13:15	O-9. <i>Anastasia Markina.</i> Non-fullerene acceptors with tailored properties for organic solar cells
13:15 – 13:30	O-10. <i>Raaghesh Vijayan.</i> Morphology control of bulk heterojunction solar cells with external electric field assisted annealing
13:30 – 15:00	Lunch
	Oral talks 4. Chair: <i>Stephan Kirchmeyer</i>
15:00 – 15:15	O-11. <i>Rashid Nazmitdinov.</i> On efficiency increase of perovskite photovoltaic elements
15:15 – 15:30	O-12. <i>Jinhan Wu.</i> Investigation of recombination processes in organic light-emitting diodes using Suns-Voc method
15:30 – 15:45	O-13. <i>Valentina Utochnikova.</i> Lanthanide-based OLEDs: the second wave
15:45 – 16:00	O-14. <i>Igor Koskin.</i> Way to highly emissive materials: increase of rigidity by introduction of a furan moiety in co-oligomers
16:00 – 16:15	O-15. <i>Oleg Borshchev.</i> New organic luminophores: only beautiful chemistry or new perspectives in organic photonics and electronics?
16:15 – 16:30	O-16. <i>Aleksandra Boldyreva.</i> Gamma ray induced degradation effects in triple cation perovskite solar cells
16:30 – 17:00	Coffee-break
17:00 – 18:30	Poster session 2 (P-29 – P-65)
19:00 – 22:30	Conference dinner

Thursday, September 20th

8:00 – 9:00	Breakfast
	Chair: <i>Sergey Ponomarenko</i>
9:00 – 10:00	T-8. <i>Natalie Stingelin.</i> Designing solution-processed photonic light- and heat-management structures for optoelectronic devices
10:00 – 11:00	T-9. <i>Fabio Biscarini.</i> Ion-gating in organic transistors: how it affects specific recognition of neurotransmitters
11:00 – 11:30	Coffee-break
	Chair: <i>Dmitry Paraschuk</i>
11:30 – 12:00	I-10. <i>Annalisa Bonfiglio.</i> Field effect organic devices for multimodal sensing platforms
	<u>Oral talks 5.</u>
12:00 – 12:15	O-17. <i>Yingquan Peng.</i> Advances in broadband photodiodes and phototransistors exploiting organic semiconductors
12:15 – 12:30	O-18. <i>Maria Kotova.</i> Charge transfer states and triplet excitons in non-fullerene acceptor based organic solar cells
12:30 – 13:30	Closing ceremony
13:30 – 15:00	Lunch
15:00 – 15:15	Departure to Moscow
15:00 – 19:00	Sensor day registration Sport activities
19:00 – 20:00	Dinner
20:00 – 22:00	Sport activities

Friday, September 21st – *Satellite*: Sensor day

8:00 – 9:00	Breakfast
	Chair: <i>Alexey Vasiliev</i>
9:00 – 10:00	T-10. <i>Jürgen Brugger.</i> Nanosystems fabrication: from rapid prototyping to scalable manufacturing
10:00 – 11:00	T-11. <i>Corrado Di Natale.</i> Porphyrins based chemical sensors
11:00 – 11:30	Coffee-break
	Chair: <i>Corrado Di Natale</i>
11:30 – 12:30	T-12. <i>Alexey Vasiliev.</i> Additive technologies for chemical sensors

12:30 – 13:00	I-11. <i>Carlo Bortolotti</i> . Organic electronic transistors as ultra sensitive and label free biosensors
	Oral talks 6.
13:00 – 13:15	O-19. <i>Daniil Anisimov</i> . Electronic nose based on Langmuir monolayer OFETs with metal-containing porphyrins as a selective layer
13:30 – 15:00	Lunch
15:00 – 15:15	Departure to Moscow

Poster session 1

Monday, September 17th, 17:00

Akkuratov, Alexander V.	P1	Design of novel low molecular weight donor molecules based on pyrrolo[3,4-c]pyrrole-1,4-dione, thiophene and benzothiadiazole for organic solar cells
Aleksandrov, Aleksey E.	P2	Hybrid photovoltaic diodes based on PbS quantum dots
Aslandukov, Andrey N.	P3	Lanthanide aromatic carboxylates as emitters for solution-processed OLEDs: new approach for host selection
Balakirev, Dmitry O.	P4	Novel triphenylamine-based luminophores: synthesis and property studying
Bauer, Marius	P5	Spectroscopic and microscopic characterization of RISC OLED thin films
Beletskaya, Elizaveta A.	P6	Light-induced charge separation at donor/acceptor composite PCDTBT/PC ₇₀ BM
Nevostuev, Danil A.	P7	Bis(dicyanothienoanthraquinoides) – novel promising acceptor materials for organic photovoltaics
Bhattacharyya, Kalishankar	P8	External electric field assisted charge transport in PCBM-SA48 solar cell: a theoretical perspective
Blinova, Lubov I.	P9	Visible and NIR-luminescent lanthanide complexes with perfluorinated 2-mercaptobenzothiazolate ligands
Bodrova, Ekaterina S.	P10	Gamma-ray induced degradation in organic solar cells
Borzdu, Natalia I.	P11	Molecular dynamics simulations of nanoarchitectures based on thiophene-phenylene oligomers
Brotsman, Victor A.	P12	Ternary solar cells based on highly soluble double-caged fullerene derivatives
Chekusova, Victoria P.	P13	Thiophene-based monolayer OFETs with metalloporphyrin receptor layers as a perspective devices for toxic gases detection
Dashitsyrenova, Dolgor D.	P14	Self-assembled monolayers of porphyrin dyads enable light-induced switching in OFET-based optical memory devices

Dashitsyrenova, Dolgor D.	P15	Impact of the semiconductor/dielectric interface modification on the performance of OFETs and memory devices
Fedorenko, Roman S.	P16	Ultrathin solution-processed thiophene-phenylene co-oligomers field-effect transistors with electrical performance exceeding single-crystal ones
Feriancova, Lucia	P17	Design and synthesis of bithiophene derivatives with anchoring groups for organic electronic applications
Frericks, Markus B.	P18	Electronic structure at interfaces of hole transport materials
Gultikov, Nikita V.	P19	Photothermal deflection spectroscopy as a probe of ppm-doping level in organic semiconductor single crystals
Juhasz, Peter	P20	Contact resistance temperature dependence of organic transistor
Kalinichenko, Nadezhda K.	P21	Synthesis and properties of novel conjugated donor-acceptor oligothiophenes with electron-withdrawing methylcyanovinyl groups for organic photovoltaics
Kolesnikov, Efim A.	P22	Optical and luminescent properties of copper and silver cesium iodides
Komissarova, Ekaterina A.	P23	A new series of pyrimidine-containing chromophores naphthalene, anthracene and cyclic imide derivatives: synthesis, investigation of spectral and electrochemical behavior
Konstantinov, Vladislav G.	P24	Highly bendable thiophene-phenylene co-oligomer single crystals
Korovin, Alexey N.	P25	Effect of counter ion on structure of thin polyaniline films on air-water interface
Kotova, Maria S.	P26	In situ impedance spectroscopy of polymer structures by resistive switching
Kuevda, Alexey V.	P27	Photon counting multi-channel scaler for phosphorescence spectroscopy of organic semiconductors
Kumar, Rhea	P28	Vibronic control of organic electronic devices

Poster session 2

Wednesday, September 19th, 17:00

Dubinets, Nikita O.	P29	COPHEE: Condensed phase excitation energies database
Koshelev, Daniil S.	P30	Toward the design of lanthanide heteroaromatic carboxylates
Kushch, Nataliya D.	P31	New bifunctional organic conductor (BETS) ₂ Cu(dca) ₃ and semiconductor (BEDT-TTF) ₂ Cu ¹⁺ Cu ²⁺ (dca) ₄ with the dicyanamidocuprate anions
Kusnetsov, Ilja E.	P32	Novel low molecular weight semiconductor materials based on rhodanine, thiophene and benzothiadiazole for organic electronics
Lukonina, Natalia S.	P33	<i>p</i> -Doping of poly(3-hexylthiophene-2,5-diyl)/carbon nanotubes composites with strong acceptor C ₆₀ F ₄₈

Majhi, Koushik	P34	Photophysical behavior of <i>meta</i> -aminophenol in the hydrophobic environment of β -cyclodextrin nano-cage: An experimental and theoretical approach
Malakhova, Yulia N.	P35	Nonwoven materials in the development of organic memristive element based on polyaniline/polyethylene oxide
Mannanov, Artur L.	P36	Charge generation and recombination in single material organic solar cells based on donor-acceptor star-shaped molecules
Martynov, Ilya V.	P37	Fullerene derivatives as promoters or inhibitors of the photo-oxidation of conjugated polymers used in organic solar cells
Martynova, Natalia A.	P38	Electrochemical formation of ZnO(Al) films for photoanodes in photovoltaic devices
Meier, Tobias	P39	Investigating the influence of morphology on the charge-carrier mobility in organic field-effect transistors
Nuraliev, Muzaffar K.	P40	Assessment of charge transfer reorganization energy for organic semiconductors by Raman spectroscopy
Prudnov, Fedor A.	P41	Photoactive layer / metal electrode interface as one of the origins of the burn-in degradation of organic solar cells
Rohnacher, Valentina	P42	Infrared spectroscopic study on solution-processed metal oxides as efficient charge transport layer in organic photovoltaic cells
Savchenko, Peter	P43	Application of spectral technique for accurate efficiency measurements of organic and perovskite solar cells
Sivanesan, Vipilan	P44	Excited states dynamics in TIPS-Pentacene studied with femtosecond time-resolved second harmonic generation
Sizov, Alexey S.	P45	Langmuir films of organosilicon conjugated oligomers: thermodynamics of their self-assembly on the water surface
Skorotetcky, Maxim S.	P46	New nanostructured luminophores based on 1,3,5-benzene
Skorotetcky, Maxim S.	P47	Novel organosilicon luminophores based on arylenevinylens for organic photonics
Sobolev, Vitaliy S.	P48	Influence of the carboxylic acid anhydride substitution on the electronic properties of the ultra thin naphthalene films
Sobolev, Vitaliy S.	P49	Modification of the work function and of the conduction band density of states profile using end substituents in thiophene/phenylene co-oligomers
Solodukhin, Aleksandr N.	P50	Novel donor-acceptor triphenylamine-based oligomers of different architecture for organic photovoltaics
Susarova, Diana K.	P51	The impact of the molecular structure of conjugation polymers on the indoor operation stability of solar cells
Trainov, Konstantin P.	P52	Novel D- π -A chromophores based on the hydrazono-cyclopentadiene accepting moiety
Travkin, Vladislav V.	P53	Light-induced processes in the multilayer structures incorporating molecular and perovskite-type materials
Trukhanov, Vasiliy A.	P54	Organic single-crystal light-emitting transistors with polycrystalline under-electrode interlayers
Trul, Askold A.	P55	Toxic gas detection with fully printed organic field-effect transistor

Tukachev, Nikita	P56	On theoretical prediction of electronic properties of novel conjugated polymers
Witte, Katharina	P57	Molecular orientation in thin films of conjugated polymers
Doroshkevich, Aleksandr S.	P58	Functional environments for precision humidity sensors based on dielectric nanoparticles in a hydrophilic polymer
Inasaridze, Liana N.	P59	Photoinduced degradation of a series of conjugated polymers under different oxygen level conditions
Shmelin, Pavel S.	P60	Synthesis of unsymmetrical 2-[2-vinyl-chromen-4-ylidene]-malononitrile dyes via Knoevenagel reaction
Umedov, Shodruz T.	P61	New materials in CsI-SnI ₄ -GaI ₃ ternary system
Zelenyak, Tatyana Yu.	P62	Synthesis of perovskite of methylammonium triiodide and study of structural degradation
Dominskiy, Dmitry I.	P63	Thiophene-phenylene co-oligomer single crystals: effect of molecular end-groups on structural and electronic properties
Rehamnia, Rabah	P64	Electrochemical preparation of MoO ₃ buffer layer deposited
Wang, Nianxing	P65	The application of viologen materials in organic electronics
Gallop, Nathaniel	P66	Understanding the photophysics of efficient nonfullerene acceptors

Tutorial lectures

Avoiding artifacts and errors in characterization of organic field-effect transistors

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Organic field-effect transistors (OFETs) are the primary building blocks of organic electronics, necessary for the operation of various applied circuits. In addition, OFETs are used in fundamental studies of charge carrier transport and mobility in organic semiconductors (see, e.g., ^{1,2}). Thus, understanding charge transport properties and the intrinsic mobility of organic semiconductors are very important. However, carrier mobility is frequently extracted from less than optimal devices, when the standard model of transistor operation (the so-called, Shockley model) is not even applicable. In addition, devices are sometimes measured under extreme biasing conditions, such as too high applied voltages or excitation current densities, that bring OFETs out of the linear Ohmic operation regime and beyond the range of model applicability. This results in an abundance of reports with unfeasible, misleading and irreproducible carrier mobility claims in OFETs.

This talk will first briefly overview some of the main reproducible results obtained in high-performance OFETs based on organic single crystals, where the intrinsic properties of organic semiconductors can be addressed without the detrimental influence of disorder (see, e.g., ¹). We will then outline the recommended good practices of charge carrier mobility extraction in OFETs that have been recently formulated³. Among these are the careful attention to the linearity of FETs' characteristics, characterization of contact resistance, as well as Hall effect measurements. In addition, several important parameters need to be estimated in each particular FET study in the context of results' reliability. These include the measurement reliability factor, r , the maximum power density, P_{\max} , dissipated in the transistor's channel, as well as the maximum current density, j_{SD}^{\max} , in the channel of OFETs, as defined in Ref.3.

¹ V. Podzorov, *MRS Bulletin*, 2013, **38**, 15-24.

² Tutorial slides are downloadable at <http://www.physics.rutgers.edu/~podzorov/index.php>

³ H. H. Choi, K. Cho, C. D. Frisbie, H. Sirringhaus and V. Podzorov, *Nature Mater.*, 2018, **17**, 2-7.

Molecular design of efficient functional materials for organic electronics and photonics

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Tremendous progress in organic electronics during the last years originates from the appearance of novel highly efficient functional materials with outstanding semiconducting, optical, self-assembling and other important properties and their combinations. It became possible due to fast development of modern methods of selective organic synthesis, which allow to prepare conjugated organic molecules with atomic precision [1]. Among them are different techniques of C-C bond formation via Suzuki, Kumada, Stille cross-coupling and direct C-H arylation in combination with the other organic and organometallic reactions. Moreover, an important role in electronic and physical properties of conjugated organic molecules plays molecular architecture. For instance, branching often helps to increase solubility of conjugated molecules, change their aggregation in the solution and ordering in the bulk. In this lecture different aspects of molecular design and synthesis of highly efficient functional materials for organic electronics and photonics will be considered.

First, a right choice of the synthetic strategy for preparation of highly pure conjugated molecules and unexpected useful consequences of the presence of some impurities in the organic semiconductors will be discussed [2]. Then different examples of successful synthetic strategy for preparation of various functional materials of different molecular architecture and their application in organic electronics and photonics will be considered. Among them are: (i) conjugated linear organic semiconductors and luminophores [3,4]; (ii) self-assembled organic semiconductors [5,6], (iii) star-shaped donor-acceptor oligomers [7,8] and (iv) branched and dendritic nanostructured organosilicon luminophores [9,10].

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¹ V.P. Ananikov, L.L. Khemchyan, Y.V. Ivanova, et al., *Rus. Chem. Rev.* 2014, **83**, 885.

² O.D. Parashchuk, A.A. Mannanov, V.G. Konstantinov, et al., *Adv. Funct. Mater.* 2018, **28**, 1800116

³ L.G. Kudryashova, M.S. Kazantsev, V.A. Postnikov, et al. *ACS Appl. Mater. Interfaces*, 2016, **8**, 10088

⁴ M.S. Skorotetcky, E.D. Krivtsova, O.V. Borshchev, et al. *Dyes & Pigments*, 2018, **155**, 284

⁵ O.V. Borshchev, A.S. Sizov, E.V. Agina, et al. *Chem. Commun.*, 2017, **53**, 885

⁶ E. Agina, A. Mannanov, A. Sizov, et al. *ACS Appl. Mater. Interfaces*, 2017, **9**, 18078

⁷ S.A. Ponomarenko, Y. N. Luponosov, J. Min, et al. *Faraday Discuss.*, 2014, **174**, 313

⁸ J. Min, Y.N. Luponosov, Ch. Cui, et al., *Adv. Energy Mater.* 2017, **7**, 1700465

⁹ T.Yu. Starikova, N.M. Surin, O.V. Borshchev, et al. *J. Mater. Chem. C*, 2016, **4**, 4699

¹⁰ O.V. Borshchev, E.A. Kleymyuk, N.M. Surin, et al., *Org. Photon. Photovolt.*, 2017, **5**, 1

**Organic field-effect transistor structures as a truly multifunctional platform:
from light-emission to cell interfacing**

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Organic light-emitting diodes (OLEDs) are a well-established class of devices for electroluminescence generation. Alternative driving schemes to generate electroluminescence from organic materials and to combine multiple functionalities, which offer fundamental advantages with respect to OLEDs, might impact a number of organic photonics applications including display technology and bio-sensing.

Here we discuss the concept of Organic Light-Emitting Transistors (OLETs)¹, highlight their specific electrical, optoelectronic and photonic characteristics with respect to OLEDs, and discuss their potential for practical applications.

In addition, we explore the use of organic transistor structures as a tool to stimulate and transduce the bioelectrical activity of neural cells. We demonstrate that transparent silicon-free transistor structures based on organic semiconductors are fully biocompatible and preserve the electrophysiological activity of both primary neural cells and non-excitabile brain cells. On the one hand transparent Organic Cell Stimulating and Sensing Transistor (O-CST)² architecture fabricated with N, N'-ditridecylperylene-3,4,9,10-tetracarboxylic diimide (P13), provides bidirectional stimulation and recording of primary neurons. On the other hand, O-CST is able to elicit and monitor intracellular calcium signalling in primary rat neocortical astrocytes. These studies demonstrate that a properly designed organic transistor structure can be the base to develop bio-organic interfaces with unprecedented capabilities for the study of brain functions and for the therapy of brain pathologies.

¹ (a) M. Muccini, *Nature Mater.*, 2006, **5**, 605-613. (b) R. Capelli, et al., *Nature Mater.*, 2010, **9**, 496-503. (c) M. Muccini, et al., *Laser Photonics Rev.*, 2012, **6**, 258–275. (d) M. Natali et al., *Advanced Functional Materials*, 2017, **27**, 1605164.

² (a) Benfenati, et al., *Nature Mater.*, 2013, **12**, 672. (b) S Toffanin, et al., *Journal of Materials Chemistry B*, 2013, **1**, 3850-3859.

Importance of Molecular Interactions and the Need for Vitrification in Nonfullerene Organic Solar Cells

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Organic solar cells (OSCs) continue to be a promising low-cost and lead-free photovoltaic technology, which can achieve >14% efficiency and be processed from a single, benign solvent with efficiency over 12% along with good stability¹. Of critical importance to continued advances of OSCs is understanding and manipulating the composition of the amorphous mixed phase, which is governed by the thermodynamic molecular interactions^{2,3} of the polymer donor and acceptor molecules and the kinetics of the casting process. Here we highlight the significance of molecular interaction and vitrification in understanding the important aspects of morphology, performance, and stability of OSC. We discuss the temperature dependence of these molecular interactions as encoded by the effective temperature-dependent Flory-Huggins interaction parameter $\chi(T)$ in a model system PCDTBT:PCBM. We relate $\chi(T)$ to the device processing and performance and develop a framework that we successfully apply to 15 pairs of nonfullerene small molecule acceptor (NFA) systems^{4,5}. It is also shown and argued that polymer:NFA systems with a amorphous-amorphous χ and binodal composition near the percolation threshold, during normal device operating conditions, can exhibit a stable morphology only if the crystallization of small molecule acceptor in active layer is suppressed due to a vitrified structure in the host polymer. Consequently, determining χ at processing and operating temperatures can serve as a feasible tool to predict device performance and in turn guide the choice of processing conditions where the binodal composition is close to the percolation threshold. Most significantly, our framework will pave a way to predict the morphology and stability of OSCs at actual processing and operating temperatures.

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¹ S.Li, L. Ye, W. Zhao, H. Yan, B. Yang, D. Liu, W. Li, H. Ade, J. Hou, *JACS*, 2018, **140** (23), 7159–7167.

² L. Ye, Y. Xiong, Q. Zhang, S. Li, C. Wang, Z. Jiang, J. Hou, W. You, H. Ade, *Adv. Mater.*, 2018, **30**, 1705485.

³ M. Ghasemi, L. Ye, Q. Zhang, L. Yan, J. H. Kim, O. Awartani, W. You, A. Gadisa, H. Ade, *Adv. Mater.* 2017, **29**, 1604603.

⁴ L. Ye, B. A. Collins, X. Jiao, J. Zhao, H. Yan, H. Ade, *Adv. Energy Mater.* 2018, 1703058.

⁵ L. Ye, H. Hu, M. Ghasemi, T. Wang, B. A. Collins, J.-H. Kim, K. Jiang, J. Carpenter, H. Li, Z. Li, T. McAfee, J. Zhao, X. k. Chen, J. Y. L. Lai, T. Ma, J.-L. Bredas, H. Yan, H. Ade, *Nat. Mater.*, 2018, **17**, 253–260.

How does delocalization affect exciton dissociation in organic solar cells?

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The process on what controls the photogeneration of free charges in organic donor-acceptor films is still not well understood. In this presentation I shall discuss the role of delocalization in either the donor phase or the acceptor phase for the dissociation process¹. In particular, I will also highlight that the primary step of electron transfer from a photoexcited donor to the acceptor in an organic donor-acceptor type film is independent of the driving force². The subsequent step of dissociating the thus-formed charge-transfer (CT) state strongly depends on energetics, and is assisted by delocalization. I will also discuss the role of disorder versus delocalization in the dissociation process and the energetics of the CT state³.

¹ F. J. Kahle et al. Does Electron Delocalization Influence Charge Separation at Donor-Acceptor Interfaces in Organic Photovoltaic Cells, **submitted**

² T. Unger et al., *J. Phys. Chem. C*, 2017, **121**, 22739-22752.

³ F-J Kahle, A Rudnick, H Bässler, A Köhler, How to interpret absorption and fluorescence spectra of charge transfer states in an organic solar cell? **submitted**.

Role of Spins in Next Generation OLEDs

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We will discuss the photophysics and particularly the role of spin in thermally activated delayed fluorescence (TADF) in films and organic light emitting diodes (OLEDs). In particular, whether the TADF process is spin-dependent and, if yes, what is the exact mechanism and what are the precursor states. We perform direct spin-sensitive measurements on TADF-OLED devices applying multi-frequency electroluminescence and electrically detected magnetic resonance (ELDMR, EDMR). The idea behind these experiments is that the static magnetic field applied to devices modifies only the energy levels of spin-carrying states due to Zeeman splitting, thus changing the emission rates. We observe that the resonant microwave radiation, applied to OLEDs, leads to enhancement of the EL intensity. The effect was found to be very sensitive to experimental conditions, thus modifying the resonance frequency, temperature and microwave power we were able to shed light on the underlying mechanism of the reverse intersystem crossing from triplet to singlet exciplex states and the spin states involved, schematically shown in see Fig. 1.

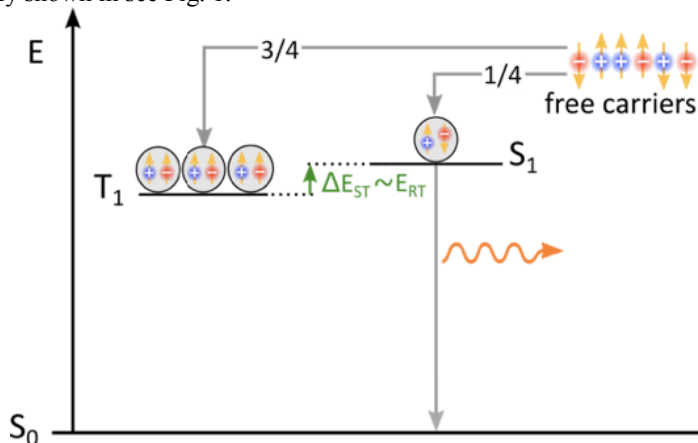


Fig. 1. Principles of Thermally Activated Delayed Fluorescence OLED

With temperature-dependent ELDMR, the singlet-triplet splitting ΔE_{ST} can be determined, as we reported for two model TADF systems¹. Comparing ELDMR, and PLDMR, we revealed differences in TADF processes under optical excitation and electrical injection. The information gained from magnetic resonance experiments can potentially help to design new cost-effective OLED materials as well as to further improve their performance.

This work was supported by the EU H2020 through the grant SEPOMO (No 722651) and by the DFG through the project FOR1809.

¹ S. V  th, K. Tvingstedt, M. Auth, A. Sperlich, A. Dabulienė, J. V. Grazulevicius, P. Stakhira, V. Cherpak, V. Dyakonov, *Adv. Opt. Mater.* 2017, **5**, 1600926.

Artificial light harvesters for molecular excitonics

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The unprecedented quantum efficiencies of natural light-harvesting complexes rely on the strong coupling between thousands of densely packed chromophores giving rise to highly delocalized excitons. However, the structural complexity of these systems leads to spectral congestion thereby blurring individual exciton transfer pathways that are vital to unravel for potential applications. Here we demonstrate a novel spectroscopic/microfluidics approach to deconvolute the supramolecular hierarchy of the model system, multilayered nanotubes. The outer shell is selectively *unwrapped* in a microfluidic cuvette thereby providing a sufficient time window for ultrafast spectroscopy, before the original structure is re-established. We will also discuss the intermediate dynamical states of self-assembly by combining microfluidics, 2D spectroscopy and extensive computer simulations.

Designing solution-processed photonic light- and heat-management structures for optoelectronic devices

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An ever increasing interest in the development and application of innovative optical and optoelectronic devices places greater emphasis for the advancement of new smart and functional materials that are readily processable. Significant progress has already been realised in the fields of organic light-emitting diodes (OLEDs) and photovoltaic cells (OPVs) through development of novel semiconducting materials. Here we discuss developments and advancements in materials design towards photonic structures that aid and improve light management in organic and inorganic/organic hybrid devices. We cover systems targeted for use in light input-/output-coupling structures, anti-reflection coatings, waveguides, and beyond. Extension to architectures for heat management, important e.g. for a broad range of photovoltaic device platforms, will also be presented.

Ion-gating in organic transistors: how it affects specific recognition of neurotransmitters

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Organic electronics devices are emerging as ultra-sensitive and specific biosensors. Electrolyte gated organic field effect transistors (EGOFET) and organic electrochemical transistors (OECT) are the most used architectures. According to the current understanding two different doping mechanisms intervene in these devices: EGOFET operate in accumulation due to electrostatic doping of ions at the electrical double layer at the interface between the organic semiconductor and the electrolyte; OECT operate in depletion by electrochemical doping upon gate-modulated cation exchange. I will discuss here a unified view of ion-gating mechanism in the two architectures by means of a common mechanism that is based on ion- π conjugated molecule interaction, a strong non-covalent interaction that is widely studied in protein chemistry and ion batteries, but still largely ignored in organic bioelectronics. The shift of HOMO-LUMO levels in the π -materials indicate that the ions can modulate the hopping rate of the charge carriers, and specifically for p-type materials, cations will slow down producing a lower conductivity, while anions will accelerate it, thus increasing the current. This scenario also hints to the fact that the "bulk" of an organic semiconductor thin film is involved in the modulation of the charge transport in EGOFET, similarly to the mechanism invoked in OECT.

These concepts have inspired us to design a new sensor for dopamine (DA), which can be ultra-sensitive and specific at the same time. The selectivity of the sensor was also tested in operational conditions nearer to the *in vivo* ones in co-presence of physiological concentration of ascorbic acid and uric acid: DA levels in the brain of healthy people are in the nanomolar range of concentration and decrease to picomolar range in patients with Parkinson's disease (PD). Once properly engineered, the proposed sensor could be coupled with actuating devices, leading to the implementation of implantable architectures for the Central Nervous System, that may perform loco-regional delivery of L-Dopa in response to [DA] lowering in animal models, and later in patients, affected by Parkinson's disease.

This work is supported by UNIMORE Project FAR 2015 PRODE, EuroNanoMed III Project AMI, and IIT.

Nanosystems fabrication: from rapid prototyping to scalable manufacturing

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In this paper I will present our work in the field of process (nano)engineering. Besides relying on established techniques using charged particle lithography and thin film processing, we (and many others) constantly explore new emerging nanopatterning methods that are not harmful to sensitive functional material required for nanosystems. I will focus here on our progress we made in three methods: i) nanostenciling, ii) thermal scanning probe lithography and iii) nanoparticle capillary assembly. After a short review of nanostenciling as ultra-clean, vacuum-based material adding method¹ I will show our recent results for fabricating ultra-flat nanophotonic system for cell membrane bioimaging² and in the field of organic electronics³. In the latter case we show for instance that the growth of crystals can be tuned by controlling the flux through nanoapertures. A second emerging technique for fabricating functional nanosystems is thermal scanning probe lithography (t-SPL). Our current research focuses on one hand side to allow for improved 3D capabilities using the t-SPL. On the other hand side, we explore the spatial and temporal control of localised heat generation to induce changes in functional materials, such as supramolecular glasses⁴ and silk⁵. The third class of emerging techniques that presumably has the potential to be scaled up to large areas is capillary assembly of nanoparticles by using surface templates. Following the pioneering work done earlier that shows the potential of this combination of top-down template making and bottom-up particle assembly, we have taken up the challenge to further explore the limits of the precision, orientation and yield⁶. By carefully designing the templates, interparticle gap of Au nanorods can be controlled down to the 1-nm scale. In future, we may devise combinations of those emerging methods into a comprehensive nano-toolbox allowing for hybrid mix-and-match fabrication also combined with conventional lithography.

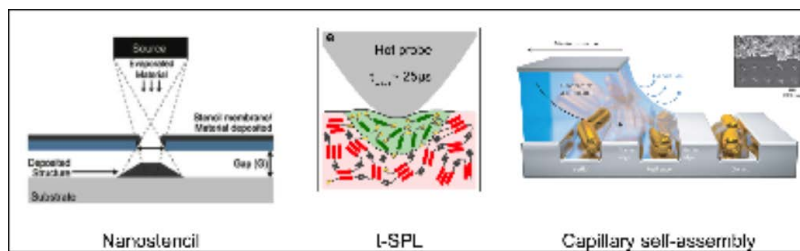


Figure showing schematics of the three emerging nanoprocessing methods.

This work was supported by grants from ERC and Swiss National Science Foundation.

¹ O. Vazquez-Mena, et al, *Microelectronic Engineering*, 2015, **132**, 236-254.

² V. Flauraud, et al, *Nano Letters*, 2015, **15**(6), 4176-4182.

³ P. Fesenko, et al, *ACS Appl. Mater. Interfaces*, 2017, **9**(28), 23314-23318.

⁴ S. Zimmermann, et al. (submitted)

⁵ S. Zimmermann et al. *MNE 2017, Braga, Portugal*

⁶ V. Flauraud, et al, *Nature Nanotechnology*, 2017, **12**, 73-80.

Porphyrins based Chemical Sensors

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The role of porphyrins in life processes is well known. Iron complexes for instance are prosthetic groups of important proteins such as hemoglobine and cytochromes. On the other hand, reduced porphyrins, as magnesium chlorin complexes, are fundamental in the photosynthetic processes. Such richness of properties is particularly attractive for chemical sensing. The molecular framework of porphyrins is a unique site for a wide range of interaction mechanisms useful for analyte binding. the interactions span from Van der Waals forces to hydrogen bond, to π interactions and to the coordination to the central metal ion.

The concurrence of all these mechanisms makes difficult the development of selective sensors, even if selectivity can in some cases found or improved by a suitable design of the sensor. On the other hand, the sensitivity of porphyrins can be oriented, through a proper molecular design, towards different classes of analytes. This control is of great value for the design of sensor arrays where several sensors non-selective but different among them are considered together.

We have been interested since about two decades to the use porphyrins to develop sensors for volatile compounds and gases. The physical properties of porphyrins restrict the transduction mechanisms that can be exploited to create an electric signal from the porphyrin-analyte interaction. It is important to recall that a chemical sensor actually measures a physical quantity of the sensing material that is affected by the interaction with the analyte.

We developed sensors measuring the mass, the optical absorbance, the surface potential and the charge transferred either to or from inorganic semiconductors¹.

The sensing properties in all these devices can be related to the properties of the individual porphyrins, for instance the Hard and Soft Acids and Bases (HSAB) Pearson's rule can be invoked to elucidate the sensitivity of porphyrins coated quartz microbalance sensors with regards to amines and alcohols.

In this paper, we will provide a rationale for the development of porphyrins based gas sensors discussing the pros and the cons of each transduction principle. A review of the applications will also be illustrated with a special emphasis on medical diagnosis through the analysis of volatile compounds.

¹ Paolesse, R., Nardis, S., Monti, D., Stefanelli, M., Di Natale, C. *Chemical Reviews*, 2017, **117**, 2517-2583.

Additive technologies for chemical sensors

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The application of MEMS technology for the fabrication of MOX sensors with low power consumption becomes now a very important trend in gas sensor design. However, traditional silicon technology has some evident disadvantages, when applied in high-temperature devices produced in limited batch. We present our attempt to combine the advantages of ceramic MEMS technology (high working (600°C) and technological treatment (1000°C) temperature, chemical stability at high temperature) with the advantages of additive technologies for the fabrication of functional elements of gas sensor (heaters, sensing, and catalytic layers). We prepared conductive silver, gold and platinum nanoparticle (10–30 nm) inks usable in ink and aerosol jet printers and demonstrated the possibility to fabricate narrow conductive lines of microheaters and electrodes of sensor (line width ~ 35 μm). The combination of jet printing onto thin ceramic substrate with laser cutting enables the fabrication of advanced cantilever type sensors operating in pulsing heating mode.

We developed the technology of thin ceramic membranes usable in high-efficiency ceramic MEMS devices operating at temperature up to 450 – 500°C. The material of these ceramic membranes could be LTCC, Al₂O₃, or yttria stabilized zirconia YSZ (10 – 20 μm thick).

Membrane is stretched on rigid frame. This is necessary to make the overall device suitable for machining. The heater is fabricated using ink or aerosol jet printing with Pt nanoparticle. Typical particle size of these inks is of 3 – 8 nm. After sintering, this print gives a microheater stable at temperature up to 500°C. The sensor chip based on these Pt printed microheaters after lasering giving cantilever shaped device is packaged in TO8 holder.

Power consumption of the sensor based on thin alumina membrane is ~70 mW at 450°C, this is comparable with Si-based MEMS. Power consumption of LTCC based MEMS device is higher, it is of about 150 mW at 450°C.

The difference in power consumption of microheater with ~1 and ~ 3 micron platinum is almost the same, therefore higher power consumption of LTCC-based MEMS compared to alumina based one is due to higher heat conductivity of ceramics.

The deposition of metal oxide nanoparticle semiconductor or catalytic sensing layer of chemoresistive of thermochemical gas sensors is possible using the same printing technique.

Cantilever shaped microhotplate improves the stability of the microheater at temperature cycling. Temperature cycling enables an improvement of sensor selectivity, the selectivity factor for CO and H₂ is of ~10, and a decrease in power consumption down to < 1 mW. The sensors demonstrate usual response to gases in this operation mode, it is equal, for example, to factor of 7 – 10 at methane concentration of 1 vol. %. Detection limit of selective measurement of CO and H₂ is of about 1 ppm.

Another application of ceramic MEMS devices is the monitoring of the composition of natural gas composition. There is common opinion that the gas companies dilute natural gas, especially in EC countries, with nitrogen and CO₂. This is done, first, to increase pressure in pipelines and, second, to increase income of gas company, The application of ceramic MEMS thermoconductometric sensor permits online monitoring of N₂ admixture with precision of about 1 vol. %.

Smart module fabricated for controlling ceramic MEMS sensors are developed to assure plug-and-play operation mode of sensor units.

Low Conformational Disorder Semiconducting Polymers

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Synthesis of conjugated aromatic polymers typically involves carbon coupling polymerisations utilising transition metal catalysts and metal containing monomers. This polymerisation chemistry creates polymers where the aromatic repeat units are linked by single carbon-carbon bonds along the backbone. In order to reduce potential conformational, and subsequently energetic, disorder due to rotation around these single bonds, an aldol condensation reaction was explored, in which a bisatin monomer reacts with a bisoxindole monomer to create an isoindigo repeat unit that is fully fused along the polymer backbone. This aldol polymerization requires neither metal containing monomers or transition-metal catalysts, opening up new synthetic possibilities for conjugated aromatic polymer design, particularly where both monomers are electron deficient. The condensation reaction locks the repeat units together with a carbon-carbon double bond link, eliminating free rotation of the repeat units and thus rigidifying the polymer conformation. Polymers with very large electron affinities can be synthesised by this method, resulting in air stable electron transport, demonstrated in solution processed organic thin film transistors. The rigid, planar nature of the backbone also facilitates extended delocalisation of both frontier molecular orbitals and a subsequently low bandgap. We present an electrical, optical and morphology characterisation of polymer thin films, illustrating structure-property relationships for this new class of polymers.

Invited lectures

Perovskite solar cells with long operation lifetimes: myth or reality?

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The emerging perovskite solar cells have demonstrated impressive power conversion efficiencies exceeding 22%, while their practical application is restricted mainly by poor operation stability. We have reported recently that hybrid MAPbX₃ (X=I, Br, I+Br, I+Cl) perovskites undergo facile thermal and photochemical degradation even under anoxic conditions without exposure to oxygen and moisture, while their all-inorganic counterparts CsPbX₃ proved to be significantly more stable¹.

Here we will discuss our the most recent results coming from a systematic study of the intrinsic stability of a broad range of materials represented by various lead-based perovskites as well as lead-free complex halides of tin, germanium, bismuth and antimony. The revealed pathways of thermal, photochemical and electrochemical degradation processes will be presented and a conclusion on the potential of different groups of materials for practical application in PV technology will be drawn.

We will also analyze the interface degradation effects occurring between the electrodes, charge transport layer materials and the photoactive layer induced by electric field, elevated temperatures, solar light or a combination of these stress factors^{2,3}. Finally, it will be shown that reaching any commercially interesting operation lifetimes for perovskite solar cells requires a considerable shift from the currently used device design paradigms as well as a comprehensive multiparametric optimization of all used materials and functional components.

¹ A. F. Akbulatov, K. J. Stevenson, P. A. Troshin et al., *J. Phys. Chem. Lett.*, 2017, **8**, 1211

² S.Yu. Luchkin, P. A. Troshin, K. J. Stevenson et al., *ACS App. Mater. Interfaces*, 2017, **9**, 33478

³ A. F. Akbulatov, K. J. Stevenson, P. A. Troshin et al., *Adv. Energ. Mater.*, 2017, **7**, 1700476

Dye Sensitized and Perovskite Photovoltaics: from cells to modules

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This lecture is devoted to hybrid organic/inorganic solar cells focusing on Dye Sensitized Solar Cells (DSSCs) and Perovskite Solar Cells (PSCs).

DSSCs have revealed important features in terms of cost, lightning conditions and lifetime, with respect to other photovoltaic (PV) technologies. Processing of DSSCs enables a full customization of the photo-active area of the devices that allows for achieving aesthetical requirements partially disabled by traditional photovoltaic technologies. In the first part of this lecture, I will focus on this technology, its application in Building Integrated PV (BIPV) and as light harvester for sensor and IoT devices. Finally the possible routes to scale up DSSCs, in a pilot line production system, up to module size will be presented.

The second part of this contribution is devoted to Organometal Lead Halide Perovskites, such as $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPI), which have opened up new directions to fabricate cost effective and high efficient PV devices. After a general introduction on perovskite solar cells (PSCs), the lecture will focus on the use of Graphene and related 2D materials in conjunction with PSCs. Many factors can influence the efficiency and stability characteristics of PSCs. In this perspective, 2D nanomaterials, such as graphene and related materials can play a primary role owing to their 2D nature and the large variety of 2D crystals, whose complementary opto/electronic properties, can be on-demand tuned by chemical functionalization and edge modification. Here, we show the use of graphene and 2D materials as an effective way to control the morphology¹ and to stabilize the device's interfaces. Several strategies have been used to master interface properties both at the anode and cathode parts of the cell. By dispersing graphene flakes into the mesoporous TiO_2 layer and by inserting graphene oxide (GO)² or MoS_2 as interlayer between perovskite and Spiro-OMeTAD layers, we show that PCE exceeding 20% with a two-step MAPI deposition can be achieved also for process in air. This approach can be exploited for the fabrication of state-of-the-art large area perovskite modules with a PCE of 13.4% on an active area exceeding 100 cm^2 . The use of 2D materials permitted to increase the PCE by more than 10% with respect to “conventional” modules³. A discussion on the relation between 2D interface engineering and stability of the PSC will be presented.

¹ F. Biccari et al. *Adv. Energy Mat.* 2017, **7**, 1701349.

² A. Agresti et al. *ChemSusChem* 2016, **9**, 2609.

³ A. Agresti et al. *ACS Energy Lett.* 2017, **2**, 279–287.

⁴ A. Palma et al. *IEEE J. Photovoltaics* 2017, **7**, 1674.

Photophysics of Organic Solar Cells with Non-Fullerene Acceptors

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The major disadvantage of organic solar cells (OSCs) compared to inorganic and perovskite solar cells is a large open-circuit voltage (VOC) loss with respect to the optical bandgap. The main phenomena responsible for low VOC are energetic losses during exciton dissociation and charge separation at donor (D) acceptor (A) interfaces, and non-radiative recombination.

We combine spectroscopic and quantum chemistry approaches to formulate the key rules for minimizing VOC losses: (i) low energy offset between D and A molecular states, and (ii) high photoluminescence yield of the low-gap material in the blend. Following these rules, we present a range of D:A systems (figure 1) which combine efficient photocurrent generation with a record electroluminescence yield of up to 0.03%, leading to non-radiative VOC losses as small as 0.21 V.

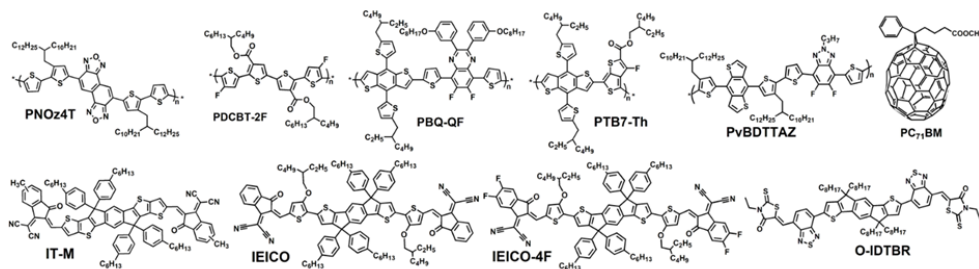


Figure 1. Materials under study.

We show that the unusual photophysics of these materials emerges from the non-trivial combination of (i) and (ii).¹ Specifically - CT excitons formed after initial charge transfer become hybridized with emissive local excitonic states. This leads to slow charge separation as observed in ultrafast PL and transient absorption measurements, as well as to the minimization of non-radiative relaxation to the ground state. As a result, the new OSC systems show non-radiative recombination and VOC similar to that of the devices based on pristine D or A, and achieve PCE up to 11.4%.

This work was supported by Royal Society and ERC Starting Grant (VIBCONTROL).

¹ D.Qian et al, *Nature Materials*. 2018, **accepted**.

The influence of charge-transfer state properties on the performance of organic photovoltaic and photo-detecting devices

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Intermolecular charge transfer (CT) states at the interface between electron-donating and electron-accepting (A) materials in organic thin films are characterized by absorption and emission bands within the optical gap of the interfacing materials. Depending on the used donor and acceptor materials, CT states can be very emissive, or generate free carriers at high yield. The former can result in rather efficient organic light emitting diodes, via thermally activated delayed fluorescence, while the latter property is exploited in organic photovoltaic devices and photodetectors. In this contribution, we will discuss the fundamental properties of CT states and link them to organic opto-electronic device performance. We will discuss the influence of intra- and inter-molecular properties, such as the energy of the CT state, the electronic coupling between electron donor and acceptor, the molecular reorganization energy as well as non-radiative triplet states on radiative and non-radiative free carrier recombination. Furthermore, we introduce a new device concept, using an optical cavity resonance effect to boost CT absorption at photon energies below the optical gap of both donor and acceptor, enabling narrow-band, near infrared (NIR) photo-detection. Our findings imply that the power conversion efficiency of organic photovoltaics and maximum achievable detectivities for organic NIR detectors are limited by the presence of high energy vibrational modes and electron-phonon coupling, intrinsic to organic semiconductors.

Can water fuel our future?
Developing upscalable routes to economical devices

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CO₂ emissions from the use of fossil fuels are the primary cause of global warming, damaging the earth's climate and ecosystems. Aviation and shipping account for 7.5% of our CO₂ emissions, and currently, there are no electrical means of feasibly powering ships and planes. To realise a carbon-neutral economy, we need to develop renewable fuels on a scale that can meet large-scale demand.

One of the most promising approaches to solving this problem is solar water splitting, where solar energy, our most abundant renewable source of energy, drives the conversion of water to produce hydrogen fuel¹. To date, inorganic devices show the highest light conversion efficiencies; however, recent studies have shown that organic materials can also split water and show similar durability to their inorganic counterparts^{2,3}.

Given the need to synthesise water splitting devices at scale, we use chemical vapour deposition to grow our materials (the go-to industrial method for growing large area coatings for a wide range of applications)⁴. Currently, the prevailing strategy to improve the light conversion efficiency in water splitting devices is to grow tailored inorganic: inorganic heterojunctions⁵. These junctions need to be grown with precise control of their composition, size and structure on the nanoscale, where our synthetic method is arguably the only scalable process that can afford this level of control. In this talk I will discuss our recent work on growing the inorganic: inorganic heterojunction – WO₃/ BiVO₄ – using our upscalable method. I will also present our recent work on organic materials – F8BT: aza[6]helicene blends – and how chirality affects the water splitting reaction.

Imperial College London is thanked for a Junior Research Fellowship and the Royal Society for a Research Grant (RSG\R1\180434).

¹ Lewis N.S. *et al.*, *Chem. Rev.*, 2010, **110** (11), 6446–6473

² Bojdys M.J. *et al.* *Nature Rev. Mater.* 2017, **2**, 17030

³ Cooper A.I. *et al.* *J. Am. Chem. Soc.*, 2015, **137** (9), 3265–3270

⁴ Choy K.L. *Prog. Mater. Sci.*, 2003, **48**, 57-170

⁵ Cowan A.J. and Durrant J.R., *Chem. Soc. Rev.*, 2013, **42**, 2281-2293

Films of filled single-wall carbon nanotubes as transparent conductive electrodes

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Thin films of single-wall carbon nanotubes (SWNTs) filled with electron-accepting molecules organized in one-dimensional crystals in the nanotube inner space (Fig. 1)^{1,2,3} have a transparency of about 90% and a surface resistance of 50 Ω /square. These parameters make them a real candidate for replacing the most popular today material for transparent electrodes - ITO (indium tin oxide). Non-covalent doping is a promising way to reach a high doping level keeping the material crystalline structure. We doped thin films of SWNTs with iodine or CuCl from gas phase. The doping level increased with the treatment time and finally saturated (after 12 hours). The maximal Fermi level shift reached 1 eV. The form of optical absorption spectra and a high-frequency shift of Raman tangential mode proved the doping. Electrophysical measurements demonstrated a decrease of surface resistance up to one order of magnitude. Due to their higher optical transparency in UV spectral range (comparing with ITO) such films are promising for transparent conductive electrodes in solar cells and light-emitting GaN diodes (Fig.2). The test experiments have been performed.

The work was supported by RFBR project 16-02-00979.

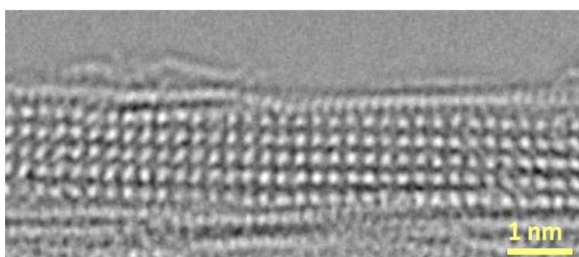


Figure 1. HRTEM image of SWNT filled with iodine.

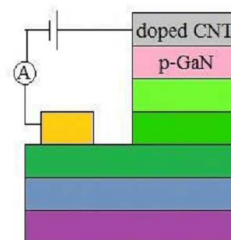


Fig.2. Scheme of GaN diode

¹ Tonkikh A.A., et al., *Physica Status Solidi B*, 2012, **249**, 2454–2459.

² Tonkikh A.A., et al., *Carbon*, 2015, **94**, 768-774.

³ Tsebro V.I., et al., *Phys. Rev. B*, 2016, **94**, 245438 (1-10).

Theoretical Prediction of Operational Stability of Potential OLED Host Molecules by Multireference Quantum Chemistry

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Low operational stability is the main limiting factor for commercialization of the blue phosphorescent organic light emitting diodes (PhOLEDs). The high energy and long lifetime of triplet excitons in blue PhOLEDs makes them more prone to degradation. Degradation of the host molecules in the emitting layer of PhOLEDs is one of the possible mechanisms leading to the luminosity loss in the course of device operation. Although possible degradation mechanisms are proposed in the literature, predicting the degradation kinetics is not straightforward because the evolution of excited states should be accurately described.

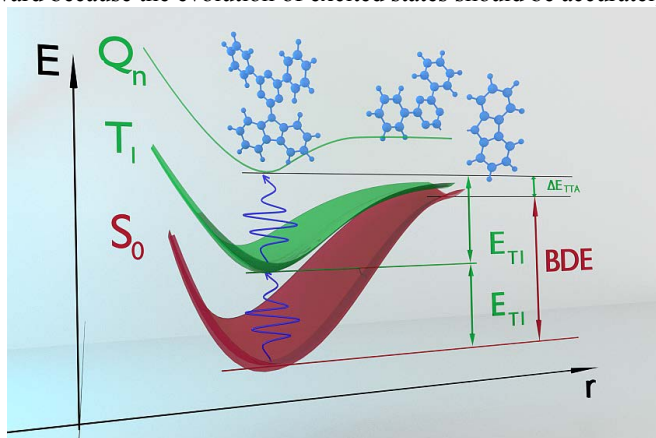


Fig. 1. Studied compounds and stability series with respect to excited-state dissociation.

We propose a computational scheme to assess the operational stability of PhOLED host materials.¹ Our protocol relies on the usage of the multireference CASSCF/XMCQDPT2 method. In the present work we consider the degradation of four prototypical blue PhOLED host molecules in the charged and excited states as well as the degradation induced by exciton–polaron and exciton–exciton annihilation processes with the focus on breaking of exocyclic C–C or C–N bonds and triazine ring fission. By analyzing the calculated activation energies for different mechanisms we found the least stable states and the most probable dissociation pathways. On the basis of our computations, we derived a stability series for the studied molecules and determine the structural features that provide higher stability with respect to the unimolecular dissociation.

This work was supported by RSF (project № 14-43-00052).

¹ Freidzon A., Safonov A., Bagaturyants A., Krasikov D., Potapkin B., Osipov A., Yakubovich A., Ohyun Kwon. *J. Phys. Chem. C* 2017, **121**, 22422–22433.

Impact of low-frequency vibrations on charge transport in high-mobility organic semiconductors from Raman scattering data

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High charge mobility is a prerequisite for efficient operation and commercial viability of organic electronic devices, but only several organic semiconductors (OSCs) have demonstrated reproducible charge mobilities above $1 \text{ cm}^2/(\text{V}\cdot\text{s})$, and a few of them have shown coherent band-like charge transport. Charge transport in high-mobility OSCs is controlled by the interplay of intermolecular charge delocalization, which is favorable for charge mobility, and charge localization at one molecule, which is detrimental for it¹. Recently, it was suggested that low-frequency vibrations limit coherent charge transport in high-mobility OSCs because they introduce strong dynamical disorder inducing charge localization^{2,3}. Nevertheless, experimental data on the impact of low-frequency vibrations on charge mobility are scarce.

In this study, we suggest a novel spectroscopic method for experimental investigation of the impact of various low-frequency vibrations on charge transport and fast estimation of charge mobility. This method is based on the proposed relationship between the Raman intensity of the vibrational mode and its contribution to the electron-phonon coupling. As a result, we formulate a figure-of-merit (FOM) for the search of OSCs with weak non-local electron-phonon coupling and hence potentially high charge mobility. Test of the method on a set of high-mobility OSCs demonstrated that the FOM clearly correlates with the charge mobility (Fig. 1). Moreover, the temperature dependence of FOM correlates with that of charge mobility as well. We anticipate that the proposed approach enables an easy and practical way for fast screening of high-mobility OSCs prior their studies in electronic devices.

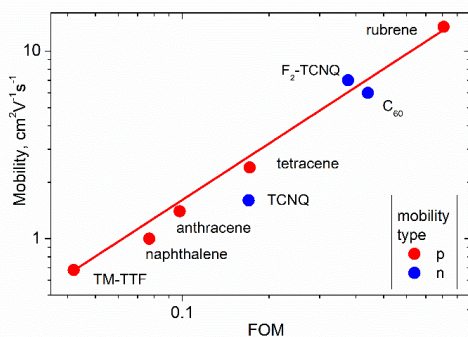


Fig. 1. Correlation between charge mobility and FOM for high-mobility p- and n-type OSs. This work was supported by Russian Foundation for Basic Research (projects #16-32-60204 mol_a_dk, #17-02-00841).

¹ Y. Li, V. Coropceanu, J.-L. Brédas, in *The WSPC Reference on Organic Electronics: Organic Semiconductors* (Eds. J.-L. Brédas, S. R. Marder), World Scientific: Singapore, 2016; pp. 193–230.

² Fratini, S.; Mayou, D.; Ciuchi, S. *Adv. Funct. Mater.* 2016, **26**, 2292-2315.

³ A. Troisi. *J. Chem. Phys.* 2011, **134**, 034702

Alkyl-free donor-acceptor oligomers as highly stable electron donor materials for organic photovoltaics

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In this work, we report on the design, synthesis and complex study of new family of triphenylamine-based star-shaped and unsymmetrical molecules having phenyl substituent at dicyanovinyl (DCV) group^{1,2,3} well as on the comparison of their properties and photovoltaic performance to those of full analogs with pristine DCV or alkyl-modified DCV groups.^{3,4,5,6,7,8,9} The modification of DCV unit by the phenyl substituent brings many positive changes to the physical properties of the molecules, including significant increase of thermal stability (up to 100 °C), electrochemical stability, solubility in organic solvents and better photovoltaic properties as compared to the analogs.

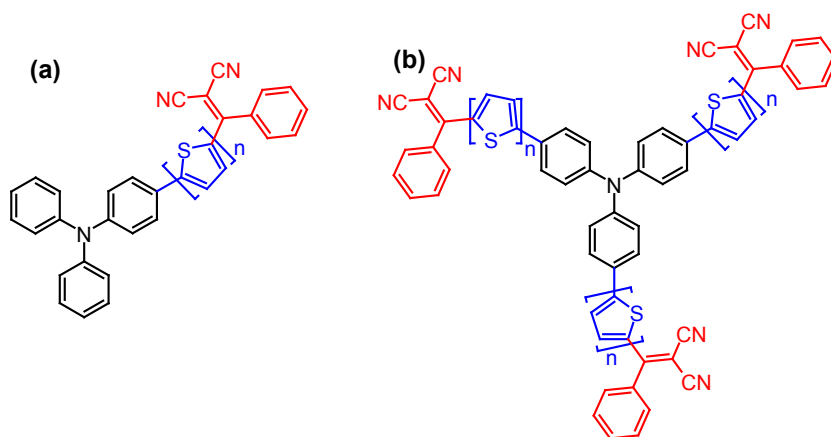


Fig. 1. Schematic representation of (a) unsymmetrical and (b) star-shaped D-A oligomers

This work in the part of star-shaped oligomers was supported by Russian Science Foundation (RSF) (14-13-01380), whereas in the part of linear molecules by RSF (17-73-10485). YNL acknowledges also the Program of President of Russian Federation (MK-933.2017.3). The work was performed in the framework of leading science school NSh-5698.2018.3

¹ O.V. Kozlov, Y.N. Luponosov, et al., *Organic Electronics*, 2018, **53**, 185.

² Y.N. Luponosov, et al., *Organic Electronics*, 2017, **51**, 180.

³ A.N. Solodukhin, et al., *Mendeleev Communications*, 2018, in print.

⁴ Y.N. Luponosov et al. *J. Mater. Chem. C* 2016, **4**, 7061.

⁵ Y.N. Luponosov, et al. *Organic Electronics* 2016, **32**, 157.

⁶ J. Min et. al., *Adv. Funct. Mater.*, 2016, **26**, 4543.

⁷ O.V. Kozlov, Y.N. Luponosov, et. al., *Adv. Energy Mater.*, 2015, **5**, 1401657.

⁸ J. Min, Y.N. Luponosov et al., *Adv. Energy Mater.* 2017, 1700465.

⁹ O.V. Kozlov, Y.N. Luponosov, et al., *Adv. Optical Mater.* 2017, 1700024.

Field effect organic devices for multimodal sensing platforms

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The introduction in the early 70s of the Ion Sensitive Field Effect Transistor (ISFET) represented a real turning point in several fields since it allowed the realization of compact, label-free, and versatile sensors and biosensors based on the concept of transistor meant as a charge sensor. Despite their great potentiality, ISFET-like devices generally suffer from an intrinsic limitation in sensitivity, the so-called Nernst limit. Moreover, the high costs, the restricted range of employable materials associated to the silicon technology, and the need for a reference electrode, have reduced the applicability of such devices in the bio-sensing field, in particular in in vivo applications. We have developed a reference-less sensor based on an organic semiconductor device, called Organic Charge-Modulated Field-Effect Transistor (OCMFET), that thanks to its peculiar transduction principle and structure, offer the possibility to modulate its sensitivity by acting on geometry-related parameters of the device itself. The proposed approach has been applied to several sensing tasks as, for instance, pH, DNA detection, monitoring of cell electrical activity, etc., thus giving rise to a new family of highly sensitive, reference-less, and low-cost devices for a wide range of bio-sensing applications.

This extreme versatility allows designing multimodal sensing platform having the ability to measure, at the same time, several physico-chemical parameters by means of devices realized with the same technology, on a variety of different substrates, in a variety of applications.

Organic Electronic Transistors as ultra sensitive and label free biosensors

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Electrolyte-gated OFETs (EGOFETs) and Organic Electrochemical transistors (OECTs) are emerging as an important class of chemo- and biosensors to meet the main requirements of healthcare diagnostics: portability, manufacturing with low cost, miniaturization, low-temperature processing.^{1,2} We operate both kinds of devices as biosensors, typically by immobilizing sensing elements (antibodies, aptamers) at the gate electrode, or by confining a recognition element (typically, a protein) through the use of hydrogels. The working principle is that biorecognition events at the gate electrode between the surface-immobilized biomolecule and the corresponding partner in solution result in concentration dependent changes in the device performances due to the capacitive coupling between the organic semiconductor channel and the gate. We typically follow changes in the current flowing between source and drain, but the multiparametric nature of these devices allows for other observables, such as threshold voltage or transconductance, to be used as monitoring tools for the binding events at the functionalized surface. I will present some examples of EGOFET- and OECT-based biosensors developed in our group for the label-free detection of different analytes, ranging from small molecules to proteins and even viruses, and discuss opportunities and limitations of these organic electronics architectures for biosensing.

This work was supported by FAR2015 "PRODE" and by EuronanomedIII Project "AMI"

Evening lectures

How to keep up with the scientific literature?

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Groningen, The Netherlands

Searching the vast scientific literature is a vital skill for anyone engaged in scientific research. Likewise, reading the scientific papers must be done efficiently to extract the critical information without having to read hundreds of pages of text slowly. This lecture discusses coherent strategies for searching the scientific literature and reading scientific papers. The following issues will be addressed:

1. How to translate a specific question or topic into a targeted literature search, and execute it using modern search engines;
2. How to read scientific papers effectively and quickly by understanding how papers are structured;
3. What the differences are between different types of publications and their purposes and how they are evaluated by the peer review and editorial processes.

How to write a patent?

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Scientists, specifically coming from academia, are trained (and have experience) to write scientific publications. Frequently, patents are believed to be just another way to publish scientific results. This is correct and incorrect as well. Patents are legal documents made with one or several government agencies to disclose proprietary information called intellectual property (typically an invention) and in return receive the right to exclusively use this information for commercial uses. As a consequence, patents are both, a publication and a legal document.

In order to have an invention patented, the invention has to fulfill a number of criteria: novelty, inventiveness, and commercial usability. Typical for the chemistry business are patents claiming new compounds or compositions, new manufacturing processes, and new (commercial) uses. Novelty is defined with respect to “state of the art”, meaning publicly available information. Simply, new compounds never mentioned in any publication (scientific, patent, internet) are new. If covered by any generic formula in any publication, compounds considered to be not new anymore, even if a specific compound has never been synthesized previously. Inventiveness is less easy to define. It is best explained as an invention which is not obvious to a person “skilled in the art”. This opens space for interpretation (and discussions with the examiner). Commercial usability is usually not a big issue but should be carefully considered before applying for a patent (and generating cost).

The process of getting a patent granted may vary from country to country. In general, it consists of the following steps: reporting the invention to the employer (in case not being self-employed), writing and submitting the patent application to the patent office, negotiating with the examiner, having the patent published, and having the patent granted. This has to be done for every country seeking patent protection.

Writing an optimal patent the following considerations needs to be taken into account:

- Optimization of the patent scope (in general broad claims are more valuable),
- Optimization of the probability of having the patent granted (in general selective claims are more likely to be granted),
- Optimization of the area protection (in general more countries mean a better protection)
- Optimization of cost (cost for a patent will dramatically increase with the number of countries)
- Optimization of the enforceability (there is no use for a patent without a chance to enforce it)

As a general rule, enterprises do well having a clear patent strategy before starting claiming patents. In the long run patents may cost hundreds of thousands of USD during their life time and need to be matched with the business strategy. Valid patent strategies that will be discussed are the protective strategy to defend existing products, the explorative strategy to claim new fields, and the destructive strategy to keep competitors from claiming certain fields.

Oral talks

Polymorphism and charge transport in organic semiconductors

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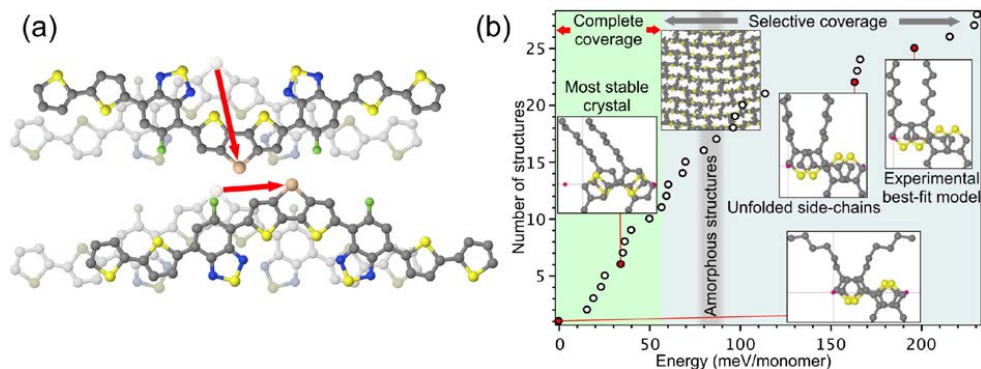


Fig. 1. Illustration of polymorphism in (a) organic molecular crystals¹ and (b) conjugated polymers². In panel (a), two types of intermolecular packings, antiparallel and parallel, show order of magnitude difference in hole mobility³. In panel (b), pronounced polymorphism of P3HT polymer results in coexistence of different phases in bulk material⁴.

Structural polymorphism is ubiquitous for molecular solids. While many macroscopic parameters are not very sensitive to changes in intermolecular packing, charge carrier transport strongly depends on intermolecular geometry. In this report we discuss several scenarios of polymorphism in molecular crystals and crystalline polymers with emphasis on charge carrier transport. In particular, a class of molecules shown in Fig.1a prefer either parallel or antiparallel π -stacking. The delicate balance between the two alternative packings can be controlled by tiny modifications of the chemical formula. In the parallel orientation molecules in the π -stack are largely shifted with respect to each other resulting in the so called slip-stack geometry. This immediately increase intermolecular hopping distance leading to large increase of charge carrier mobility. For the P3HT polymer illustrated in Fig.1b, multiple competing intra- and intermolecular interactions make this system statistically frustrated. As a result, many different nearly isoenergetic structures exist leading to intrinsic disorder at elevated temperatures. Other scenarios of polymorphism include oligothiophenes, indigo crystal, biopolymers.

This work is supported by Volkswagen Foundation (A115678).

¹ A. Zhugayevych, O. Mazaleva, A. Naumov, S. Tretiak, Lowest-energy crystalline polymorphs of P3HT, *J. Phys. Chem. C* 2018.

² Q. Cui, Y. Hu, C. Zhou, F. Teng, J. Huang, A. Zhugayevych, S. Tretiak, T.-Q. Nguyen, G. C. Bazan, *Adv. Func. Mater.* 2018, **28**, 1702073.

³ T. S. van der Poll, A. Zhugayevych, E. Chertkov, R. C. Bakus II, J. E. Coughlin, G. C. Bazan, S. Tretiak, *J. Phys. Chem. Lett.* 2014, **5**, 2700.

⁴ F. Panzer, M. Sommer, H. Bassler, M. Thelakkat, A. Koehler, *Macromolecules* 2015, **48**, 1543.

Charge transport mechanism in Transition Metal Oxides photoelectrocatalysts and its similarities to molecular crystals

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Developing energy storage mechanisms is a crucial step to secure a sustainable energy economy. This is particularly important for solar power because there is a mismatch between the periods of peak energy harvesting and peak consumption. Similar to the natural photosynthetic process, we can transform solar energy directly into chemical energy (fuels) using photocatalysts. Despite some recent work employing organic semiconductors for solar fuel generation, the field of photo(electro)catalysis has traditionally been dominated by inorganic system due to their stability in liquid electrolytes and the remarkable catalytic properties of metallic surfaces. However, inorganic systems often underperform and only poor quantum yields are achieved. One reason behind this poor activity is the coexistence of inefficient excited transport mechanisms with very slow surface kinetics. Currently, large efforts are devoted to understand the dynamics of photoexcited charge carriers in metal oxides and identify clear synthetic strategies to control their properties. In this talk, I will draw parallels between the photophysics of organic semiconductors with those of inorganic systems. These similarities are biggest in transition metal oxides, such as Fe_2O_3 or WO_3 , in which the electronic properties are dominated by coulomb interactions between the highly anisotropic d orbitals. I will present ultrafast optical studies based on pump-probe and pump-push measurements of photoelectrochemical devices (**Figure 1A**). Similar to molecular crystals, I will show data that demonstrates how the formation of localised self-trapped (polaron) electron states in TMO is critical for device performance. *Small polaron* formation results in incoherent hopping mechanisms (**Figure 1B**) which favour recombination paths however, as in organic systems, carrier mobility is facilitated by specific lattice motions which opens to possibility to synthetic control hopping rates in oxides. I will also show how in the most efficient inorganic systems, crossover between molecular-type localised transport and band-type transport co-exist and is critical for activity. Our results show that it might be possible to (re)apply some of the models developed for organic systems to guide the design of new inorganic oxides.

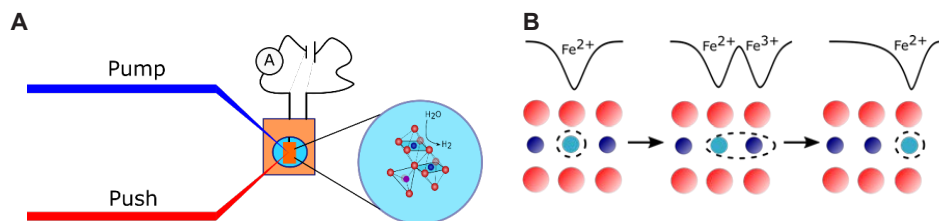


Figure 1: **A**: Schematic representation of optical measurements of Photoelectrochemical devices for solar fuel generation. **B** Small electron polaron motion in Fe_2O_3 involving a phonon-assisted reorganisation of the lattice.

Langmuir monolayer OFETs for multiparametric detection of toxic gases

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Organic field-effect transistors (OFETs) have attracted considerable attention because of their application in large-area, low cost and low power electronics.¹ The reliability of organic electronics devices still remains a crucial issue due to a strong sensitivity of organic semiconductors (OSCs) to chemical, optical and mechanical impacts, thus limiting the OFET technology commercialization as a competitor to traditional silicon electronics.² While such sensitivity is traditionally considered as a drawback, it simultaneously enables utilization of OFETs in various sensing applications, including chemical sensing. The number of OFET-based gas sensors reported up to date typically lack of air operation capability, selectivity to water and easy scalable fabrication technique.³

In this work we have investigated gas sensing properties of Langmuir-Schaefer monolayer organic field-effect transistors (LS OFETs) prepared from organosilicon derivative of [1]benzothieno[3,2-b][1]-benzothiophene (Fig. 1a). We showed that the instantaneous sensor response can be splitted into the variations of two OFET parameters, namely, the charge carrier mobility and the threshold voltage. The response to ammonia originates from the gate-bias controlled charge trapping, which results in threshold voltage shift (Fig. 1b). At the same time, the sensitivity to hydrogen sulfide is based on the modulation of grain boundaries resistance of the LS film and therefore causes the alteration of charge carrier mobility (Fig. 1c). The fabricated LS OFET sensor is reusable, has long life-time and demonstrates good reproducibility of results. The reported data open new perspectives for the OFET-based gas-sensing technology and pave the way to development of complex air analysis systems based on a single sensor.

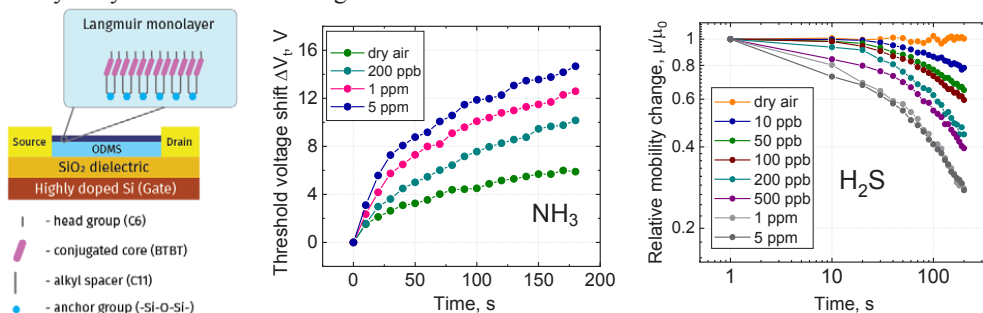


Fig. 1. OFET device architecture (a), OFET threshold voltage shift as a function of time upon exposure to different concentrations of ammonia (b) LS OFET relative mobility change as a function of time upon exposure to different concentrations of hydrogen sulphide (c)

This work was performed in the framework of leading science school NSh-5698.2018.3. Authors are also grateful to RFBR (grants 17-03-00222) for financial support.

¹ H. Sirringhaus, *Adv Mater* 2014, **26**, 1319.

² P. A. Bobbert, A. Sharma, S. G. J. Mathijssen, et al. *Adv Mater* 2012, **24**, 1146.

³ C. Zhang, P. Chen, W. Hu, *Chem Soc Rev* 2015, **44**, 2087.

Large-Area Single-Crystal Oligothiophene-Based Monolayers for Field-Effect Devices

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*Y.N. Luponosov*³, *A.V. Bakirov*^{3,5}, *M.A. Shcherbina*^{4,5}, *S.N. Chvalun*^{3,5},
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Recent progress in organic field-effect devices based on ultrathin (mono- of a few layer) single crystals highlights their high potential for transparent highly-flexible electronic, sensing, and light-emitting devices. Very high charge mobility was recently demonstrated in such ultrathin films based mainly on condensed aromatics. On the other hand, ultrathin light emitting devices are still to be demonstrated, for which oligothiophene-based materials are among the most promising ones.

In this contribution, we present a thorough study of ultra-thin highly crystalline films of thiophene-based oligomers for organic field-effect transistors. We chose 4 alkyl-terminated oligomers for comparative study of their chemical composition on the structure of ultra-thin (2D) crystals and their charge transport properties: the conjugated core was quinquethiophene (5T) or phenylene-bis-bithiophene (TTPTT) with dihexyl (DH) or didecyl (DD) terminal substituents. The ultrathin crystals were grown from solution by drop or spin casting with subsequent slow drying on substrates with various surface energies and roughness, their structure was studied by differential interference contrast and atomic force microscopies as well as grazing incidence X-ray diffraction and reflectivity. The single-crystal monolayers showed exceptionally high structural order and provided a charge mobility of up to $0.2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which is the highest among the oligothiophene monolayers and approaches that of the bulk films of the similar oligomers. Figure 1 shows typical device characteristics (a and b) and the summary of charge mobilities of 4 materials studied (c).

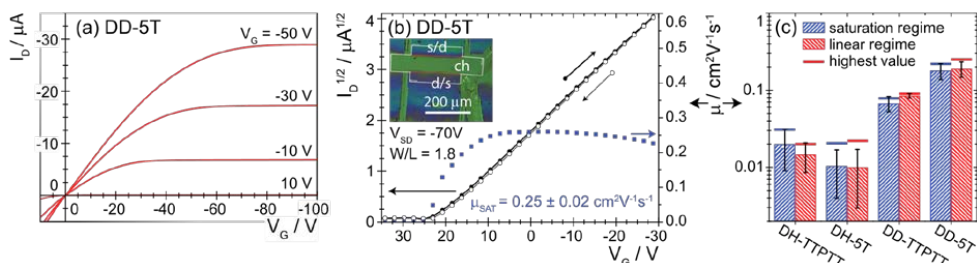


Figure 1. Electrical characteristics of DD-5T single molecular layer based FET (a,b) and charge mobilities data for the studied materials (c). Inset shows the device image.

We suggest that solution processed oligothiophene-based monolayer single crystals open the way to ultrathin electroluminescent devices.

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

Impact of terminal substituents on Raman spectra, crystal structure, and charge mobility in diphenyl-bithiophene single crystals

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Organic thiophene phenylene co-oligomer (TPCO) single crystals are promising material for organic electronics. They combine efficient charge transport with high photoluminescence quantum yield¹ (above 40%), which makes them suitable for using in optoelectronic devices. The best TPCO devices are based on 4/5-ring TPCOs. However, such long conjugation length leads to the lack of solubility, which is undesirable for practical application. Adding terminal functional groups is a standard technique to overcome this shortcoming and also for tuning properties required by a particular device². However, the use of different terminal groups is often expressed not only in changing the chemical properties of the molecule, but also affects strongly on crystal packing. This structure-property coupling in TPCO crystals have not been properly understood.

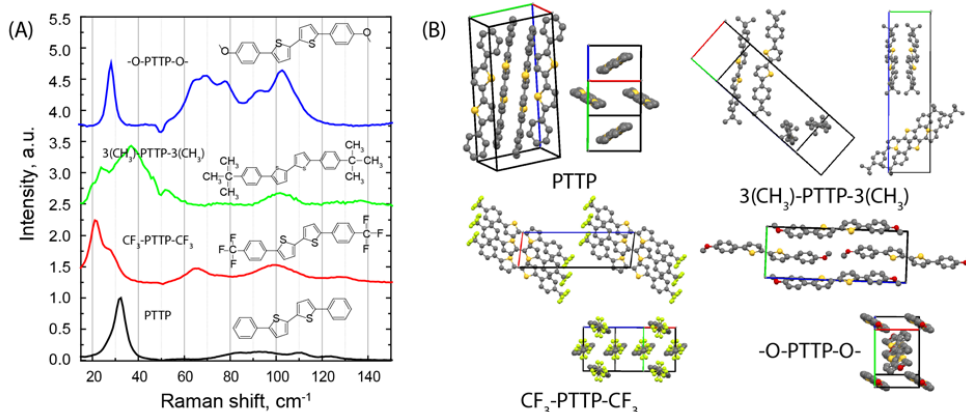


Fig. 1. (A) Low frequency Raman spectra of several studied PTPP derivatives. (B) Their crystal structure derived from X-Ray analysis.

Here we perform a combined study of structural and electronic properties of several diphenyl-bithiophene (PTPP) derivatives with different terminal functional groups (Fig 1., B). Crystalline packaging were derived from X-Ray data, while electronic properties were considered from the FET point of view. To understand coupling between them we apply Raman spectroscopy as it exhibits strong sensitivity for both electronic and crystalline material structure (Fig 1., A). We discuss the FET performance in relation with structural features studied by X-Ray and Raman of the crystalline PTPP derivatives.

This work was supported by RFBR (project № 17-02-00841A).

¹ L. Kudryashova, M. Kazantsev, *ACS Applied Materials & Interfaces*, 2016, **8**(16), 10088-10092.

² A. Glushkova, *ICOE-2017 Book of abstracts*, 2017, 62.

Cross-contact space-charge effect on performance of organic field-effect transistors

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Organic field-effect transistors (OFET) are key basic elements for low-cost, light-weight and large-area electronics. The most important parameter that characterizes the OFET performance is the charge carrier mobility in the OFET active layer. The common method of mobility measurement in OFET consists in approximation of the OFET transfer characteristics by the Shockley equations in the linear and saturation regimes. However, this method can lead to incorrect estimation of charge mobility in organic semiconductor. In the common staggered device architecture, e.g. top-contacts and bottom-gate OFET geometry, the current needs to pass through the thickness of organic semiconductor layer under the source and drain contacts, and the voltage can drop across the layer due to space charge limited current (SCLC). This can significantly decrease the source-drain current¹ and consequently the apparent (effective) OFET mobility μ_{app} .

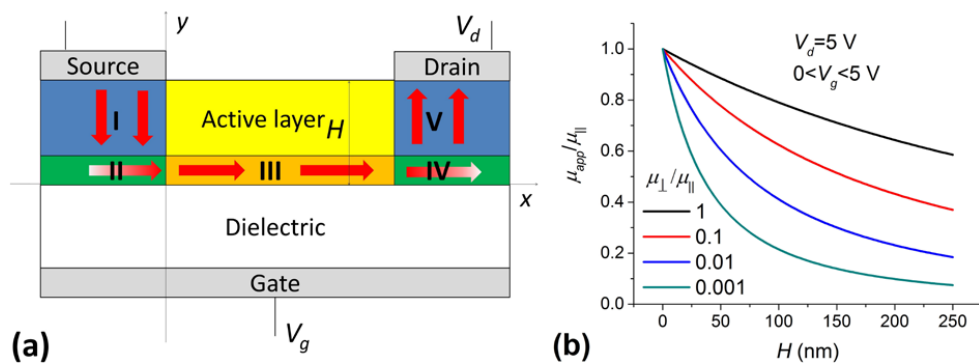


Fig. 1. (a) OFET scheme with areas of current flow. (b) Apparent mobility in the saturation regime vs the active layer thickness H for different mobility ratios $\mu_{\perp}/\mu_{||}$.

In this work, we study how the SCLC under the source and drain electrodes (cross-contact SCLC) affects the apparent mobility, μ_{app} , extracted from the OFET transfer characteristics. We developed analytical OFET model with cross-contact SCLC and found how μ_{app} changes with the active layer thickness. In this model, the current flow is divided into five areas (Fig. 1a): areas I and V with vertical SCLC, areas II and IV with horizontal increasing/decreasing current and OFET channel III. The modeling showed that μ_{app} drops with increasing the active layer thickness H and decreasing the intrinsic transverse charge mobility μ_{\perp} (across the active layer) relatively to intrinsic “longitudinal” mobility $\mu_{||}$ (along the channel length). On the other hand, modeling shows that cross-contact SCLC does not lead to appearance of threshold voltage. These findings allow more accurate evaluation of the intrinsic OFET mobility and provide guidelines for further improvement of OFET performance.

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

¹ Sohn C.W., Rim T.U., Choi G.-B., Jeong Y.-H. *IEEE Trans. Electron Dev.* 2010, **57**(5), 986-994.

Photoswitchable organic field-effect transistors with bis(hetaryl)ethene molecules at the semiconductor-dielectric interface: material structure – device performance

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Research interest to the optical memory devices based on light-switchable photochromic organic molecules has been steadily growing during the last several years. However, considering the recent review¹, one can notice that the electrical performance of such materials remains inferior as compared to other types of the state-of-the-art organic memories. In particular, light-induced current modulation (switching coefficient) is generally very low (below 10), while the time required for programming of such devices is too long (ranging from 10 seconds to several minutes). Therefore, there is an obvious need for further exploration of this research field in order to boost the electrical performance of the devices.

Bis(hetaryl)ethenes represent one of the most important types of photochromic materials due to a favorable combination of chemical stability, versatility of the molecular design and exciting optical characteristics². Recently, we have applied a bis(hetaryl)ethene-based photochromic material as a light-sensitive component for designing photoswitchable organic field-effect transistors (OFETs) and optical memory elements³.

In this report we will discuss results of our systematic study of a series of differently substituted photochromic bis(hetaryl)ethenes in OFET-based optical memory elements. The synthesis of eight compounds of 2-oxazolyl-3-thienyl-cyclopentenone will be presented. We will show that electron-rich and electron-withdrawing substituents in photochromic molecules strongly affect ON/OFF switching coefficients, programming speeds, write-read-erase cycling stability, width of memory windows and retention characteristics of the devices.

The obtained results allowed us to find some fundamental correlations between the chemical structure of the photochromic materials and their electrical performance in photoswitchable OFETs. Eventually, further development of this project might result in a significant progress in the design of OFET-based optical memory elements with the characteristics meeting the pragmatic commercialization benchmarks. There is also a promise to apply the same concept and materials for construction of ultrasensitive photodetectors with high (>1000) signal amplification ratios.

¹ Orgiu, E.; Samori, P. *Adv. Mater.* **2014**, *26*, 1827.

² Zhang, J.; Zou, Q.; Tian, H. *Adv. Mater.* **2013**, *25*, 378.

³ Frolova, L.; Rezvanova, A.; Shirinian, V.; Lvov, A.; Kulikov, A.; Krayushkin, M.; Troshin, P. *Adv. Elec. Mater.*, **2016**, *2(3)*, 1500219.

**Regularities of formation Me(Co,Cu)/PAN nanocomposites conducting structure:
investigation using X-ray spectroscopy**

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Hybrid materials based on conducting polymers and inorganic semiconductors undoubtedly constitute one of the most promising classes of new materials due to their controllable electrical conductivity and large variety of applications. The structural ordering PAN (polyacrylonitril) determines the intensity of intermolecular interactions, the number of electron transfer in them and, therefore, their electrical properties. Incorporation of Co and Cu salts in the organic matrix affects the conductivity obtained composite material, due to the manner in which the metal is incorporated into the polymer. Hence the question occurred: which the atoms of the organic matrix are involved in formation of composites, which way the conductivity of charge carriers generated in this case.

The nanocomposite materials Me(Co,Cu)/PAN was prepared by mixing the modifying agents (CoCl₂,CuCl₂) and PAN using IR-pyrolysis under low vacuum conditions. The weight concentration of the modifying agent in the film-forming solutions was 0.25, 0.4, 0.5, 0.75, 1.0 %. The C and N K-edges, as well as Co,Cu L_{2,3}-edge NEXAFS spectra with photon energy resolution of 0.26 and 0.40 eV, respectively, were recorded in the partial KVV Auger electron yield detection mode at the Materials Science Beamline at Elettra-Sincrotrone Trieste, Italy. The samples were located at the different angle geometry to the incident photon beam. The XPS spectra were recorded at various incident energy in the region of the C1s, N1s, Me3p and Me2p.

Using XPS and polarized C and N K-edge as well as Me L_{2,3}-edge NEXAFS spectra the changes in structural ordering of both pristine PAN and Me/PAN nanocomposite with different Me concentration was investigated and analysed. Investigation of changes in the π resonance region of the NEXAFS spectra in PAN/Me allowed identifying the difference in the charge transfer Co- π conjugated polymer chain system. In addition, changes in the intensity ratio of the spectral features allowed one to observe changes in the ratio of the conjugate (= C = C =, = C = N =) and non-conjugated bonds in various PAN/Me composites. The clear relationship between changes the local atomic structure and the concentration of cobalt was observed. XPS and XANES investigations showed existence of coordinated by oxygen and nitrogen Co²⁺, Co³⁺ ions. Besides, as a result of interaction between PAN matrix and Co ions unsaturation in the polymer backbone is observed as well as transformation of the C \equiv N triple bond to a C=N double bond while formation of Co-N bond.

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Non-fullerene acceptors with tailored properties for organic solar cells

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To date, most of the electron acceptors used in organic solar cells are fullerenes or their derivatives. As fullerenes exhibit only weak light absorption in the Vis spectral region, practically half of the active material does not contribute to exciton and charge generation, limiting the maximum efficiency of these devices to ca. 12%. The way forward to reach higher solar cell efficiencies is to replace fullerenes with strongly-absorbing dye molecules, namely, nonfullerene acceptors (NFAs).

However, the systematic design of acceptor molecules with tailored properties has yet to be demonstrated. The difficulty here is that, while fullerene is an electrostatically “inert” molecule, new acceptors typically have strong static quadrupole moments. This complicates the interplay of electrostatic forces at the donor-acceptor interface, making it difficult to predict and design appropriate donor-acceptor combinations. As a result, in order to optimize solar cell efficiency, one has to appropriately balance the individual electrostatic contributions to energy profiles.

Exploring the long-range electrostatic interaction at the interface^{1,2,3}, we demonstrate for a set of recently developed NFAs that the electrostatic bias potential can be directly related to the stabilization (or destabilization) of CT states as well as changes of the photovoltaic gap. Therefore, it is an important quantity to account for when designing non-fullerene acceptors. Furthermore, we compare theoretically-predicted properties of the NFAs with experimental data to assess the quality of our approach.

We find that the correlation between quadrupole moments, charge separation efficiency, and CT-state energy predicted by our model, is experimentally reproduced for several different small molecule and polymer donor / non-fullerene acceptor combinations. This allows us to predict new NFA structures using combinations of readily available molecular building blocks that can potentially reach to even higher performances than currently achieved in state-of-the-art NFA devices.

¹ C. Poelking, M. Tietze, C. Elschner, S. Olthof, D. Hertel, B. Baumeier, F. Wurthner, K. Meerholz, K. Leo, D. Andrienko, *Nat. Mater.* 2014, **14**, 434.

² C. Poelking, D. Andrienko, *J. Am. Chem. Soc.* 2015, **137**, 6320.

³ G. D’Avino, L. Muccioli, F. Castet, C. Poelking, D. Andrienko, Z. G. Soos, Jerome Cornil, and D. Beljonne, *J. Phys.: Condens. Matter* 2016, **28**, 433002.

Morphology control of bulk heterojunction solar cells with external electric field assisted annealing

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Organic solar cells based on the concept of bulk heterojunctions (BHJ) are gradually reaching promising performance levels and may become commercially viable in the near future. Besides the molecular features of the materials involved, processing factors play a crucial role in arriving at a morphology suited to extract the highest level of performance from the devices. In our approach, application of external electric field (EF) on the spin-coated BHJ films during the thermal annealing stage has shown to make a difference to the microstructure. A judicious choice of additives, EF, and thermal annealing parameters can further optimize devices to access higher efficiencies. Our earlier studies focussed on EF treatment on macromolecular donor BHJ systems¹. It is expected that the EF treatment may be more suited for characteristic small-molecule donors in a more direct manner. We probe the effect of EF treatment on triphenyl amine derivatives (donor molecules) based BHJs. We observe a trend where applied EF treatment has a strong correlation with device performance with efficiencies increasing at lower field strengths and reducing at higher field strengths when compared to control devices. EF treatment appears to make a difference even for apparently symmetric systems, indicative of higher order moments at play. The secondary factor of organization in the acceptor component via diffusive processes also play a critical role in the resulting morphology. Increase in the device efficiency has been correlated with results from various characterization techniques including light-intensity dependent open-circuit voltage and short-circuit current measurements, GIWAXS and AFM. Simulations have been carried out to understand how the EF treatment affects the donor-acceptor interactions at a molecular level.

This work was supported by DST Indo-Russia Project.

¹ Raaghesh Vijayan, K. Swathi, and K. S. Narayan, *ACS Appl. Mater. Interfaces*, 2017, **9**(23), 19436-19445.

On efficiency increase of perovskite photovoltaic elements

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Rapid progress in efficiency of photovoltaic elements, based on hybrid organic-inorganic perovskites, attracts a tremendous experimental as well as theoretical attention. In particular, it was reported recently on the power conversion efficiency (PCE) around 22%¹. Evidently, there is a desire to use promising perovskite photovoltaic elements (PPEs) in variety of optoelectronic devices. Our theoretical estimates predict that for standard PPEs the PCE limit is expected to be about 30-33%². A question remains whether an experimental figure of the PCE for existing PPEs can be improved without complex refining of a standard cell structure, in order to come close to the theoretical limit.

In this contribution, we discuss a few mechanisms that might reduce the energy losses in PPEs and, therefore, result in the increase of the efficiency. In order to elucidate these losses in PPEs we investigate by means of our model² the connection between the current-voltage characteristics of an illuminated PPE with: i) the purity of perovskite absorbing material, determined by the non-radiative recombination time; ii) parasitic resistances of contacts and feeding conductors. We estimate as well the influence of current leakage, related to local short circuiting of electrons/holes transport material layers; and the losses, stipulated by the reflection from the front surface. Applying the aforementioned approach, we have analyzed the available data for PCEs of different groups, assuming that only intrinsic undoped perovskite was used as an absorber. According to our studies of these data, the main efficiency increase is related to: i) the absorber purification; ii) amount of a trapped light, owing to the increase of the absorber thickness and the use of anti-reflecting coatings. In general, ohmic losses in contacts were roughly the same for all examined samples. We found that the amount of trapped light is close to its maximum value for best test models.

From our analysis it follows that the uniformity of a sample increase and contact layer resistances decrease can add about 2% to the PCE. Evidently, the increase of an absorber purity and structural quality would increase a diffusion length of a sample, which results in the increase of the efficiency. However, without further absorber purification, there is another source of the PCE improvement. It could be stipulated by the absorber doping value. We found that for the diffusion lengths $>30 \mu\text{m}$ the influence of doping is small. However, for diffusion lengths $<30 \mu\text{m}$ the increase of the doping value of the absorber leads to the increase of the open-circuit voltage without the decrease of the short circuit current. It results in to $\sim 5.6\%$ PCE increase. Thus, only the uniformity of a sample, a decrease of contact layer resistances, and the absorber doping may increase the PCE by additional $\sim 7\%$.

¹ Yang W.S., Park B.-W., Jung E. H., Jeon N. J., Kim Y.C., Lee D.U., Shin S.S., Seo J., Kim E.K., Noh J.H., Seok S. I., *Science* 2017, **356**, 1376-1379.

² Martynov Y.B., Nazmitdinov R.G., Moia-Pol A., Gladyshev P.P., Tameev A.R., Vannikov A.V., Pudlak M., *Phys.Chem.Chem.Phys.* 2017, **19**, 19916-19921

Investigation of Recombination Processes in organic light-emitting diodes using Suns-Voc method

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Although organic light-emitting diodes (OLEDs) are now commercially used in displays, there is still a lack of profound knowledge about recombination processes of free charge carriers. In this work, we demonstrate that the Suns-Voc method, which is often applied to solar cells, can also be used for state-of-the-art OLEDs. This technique measures the open-circuit voltage (V_{oc}) is measured for varying illumination intensities. In contrast to conventional current-voltage characteristics, the Suns-Voc method is free from undesired voltage drops related to charge carrier injection and transport¹. The fact that OLEDs are able to split a sufficient amount of charge carriers can be utilized to investigate their subsequent recombination at V_{oc} (Fig. 1, right).

By measuring red-emitting OLEDs at various temperatures, we are able to reveal a comprehensive picture of the recombination processes taking place in the device. We find two distinct ideality factors (n_{id}) which imply in comparison with luminance-voltage measurements a radiative and a non-radiative recombination². In order to model this behavior, two simplified homogeneous diode equations are introduced which perfectly agrees with the experimental data. As a result, the energy where free charge carriers recombine is determined, giving us access to the energy landscape of the OLED (Fig.1, right). Moreover, the maximum hypothetical recombination current is extracted via the model and used to estimate the recombination coefficient³.

Based on our results, a new access to OLEDs is established which yields numerous information about the recombination processes and pathways. Especially, the extraction of the energy where free charge carriers recombine is a powerful tool in order to optimize the layer and material properties as well as to quantify the voltage losses due to charge transport and charge injection.

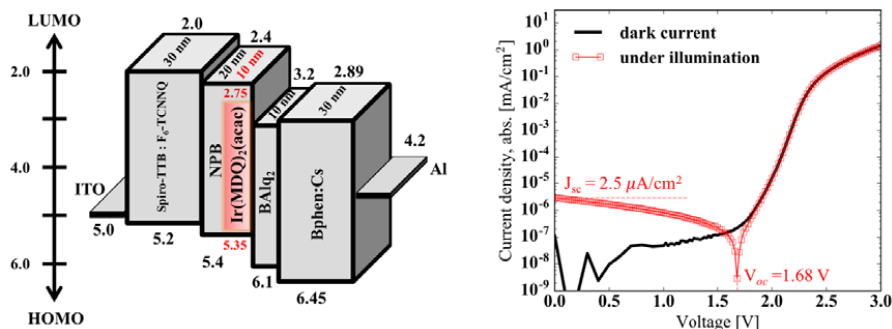


Fig. 1: Left: The energy diagram and the materials of the investigated red-emitting OLED. Right: The corresponding current-voltage curves under dark and illumination condition

¹ K. Tvingstedt et al., *Adv. Energy Mater.* 2016, **6**, 1502230

² G. A. H. Wetzelaer et al., *Phys. Rev. Lett.* 2011, **107**, 066605

³ J. Wu et al., in preparation

Lanthanide-based OLEDs: the second wave

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The triplet excited state involvement in luminescence process makes lanthanide coordination compounds (Ln CCs) promising materials for emission layers in organic light-emitting diodes (OLEDs). They are of particular interest due to such a unique feature as narrow emission bands, resulting in higher color purity. Aromatic carboxylates possess the highest luminescence intensity and stability among Ln CCs, however, these advantages are nullified by their low solubility and extremely low intrinsic charge carrier mobility¹.

To solve this problem we considered two novel approaches². The first one was the introduction of a luminescent material into such a transport material host, which is able to coordinate the lanthanide ion directly and to sensitize its luminescence. The second approach was the increase of the anionic ligand transport properties due to modification of its structure.

To check the prospects of the first approach, materials known for their electron transport have been chosen, and among these materials the effective sensitizers have been selected, where the sensitization efficiency reached 100%.

To implement the second approach, highly conjugated aromatic carboxylate ligands were used, including electron-deficient heteroaromatic carboxylates, due to they were expected to provide electron transport properties (Fig. 2). Quantum yields of new lanthanide complexes with these ligands reached 100% in the visible range and 2.5% in the NIR range; the latter value is the highest for solid state ytterbium complexes and was reached thanks to concentration quenching elimination.

OLED tests revealed the effectiveness of both approaches and allowed obtaining the diodes with pure ionic lanthanide luminescence. OLED brightness in the visible range reached 350 Cd/m² and was comparable with the brightness of nowadays solution-processable OLEDs. While in NIR range the efficiency up to 400 μW/W was obtained, which is the highest-to-date value for >1000 nm emitting OLEDs³.

Combination of the approaches of ligand design, resulting in high complex mobility, with the use of gadolinium to provoke phosphorescence resulted in the obtaining of the series of blue-emitting phosphorescent materials with encouraging performance in OLEDs. This may be considered as another promising approach to substitute blue-emitting iridium-based materials.

This work was supported by RFBR (project № 16-29-10755, 16-53-76018 and 17-32-80050) and President's grant MK-2810.2017.3.

¹ V. Utochnikova et al. *Organic Electronics*, 2016, **28**, 319-329.

² V. Utochnikova et al. *Organic Electronics*, 2017, **44**, 85-93.

³ V. Utochnikova et al. *J. Mater. Chem. C*, 2016, **4**, 9848-9855.

Way to Highly Emissive Materials: Increase of Rigidity by Introduction of a Furan Moiety in Co-Oligomers

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Linear conjugated thiophene/ and furan/phenylene co-oligomers combining high luminescence efficiency and semiconducting properties are of great interest for organic optoelectronics¹ as an active layers for light-emitting diodes and transistors. We have recently reported² a semiconducting and highly emissive furan/phenylene co-oligomer BPFB which surpasses its thiophene analogue in terms of photoluminescence quantum yield in both solution and single crystal. However, intramolecular factors governing difference in optoelectronic properties between these systems still remain poorly understood.

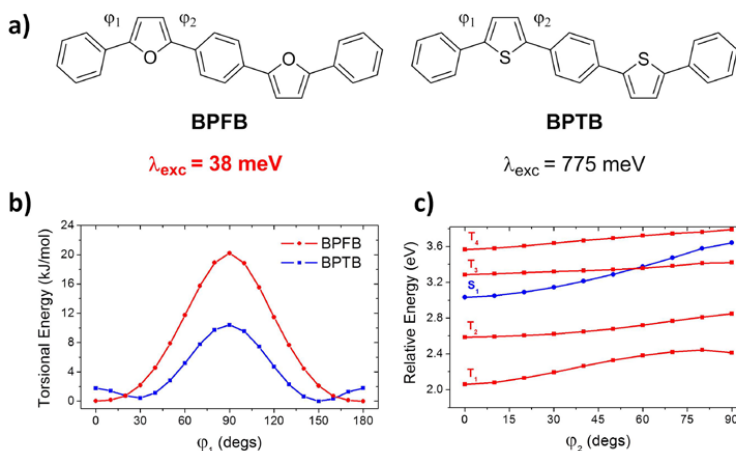


Fig. 1. (a) Structures of investigated compounds and their exciton reorganization energy (λ_{exc}); (b) S_0 state potential energy surfaces upon rotation of ϕ_1 dihedral angle; (c) Conical intersection of S_1 and T_3 excited states upon rotation of ϕ_2 dihedral angle of BPTB compound.

In this study³ we explored intramolecular factors affecting the optoelectronic properties of furan/ and thiophene/phenylene co-oligomers. We demonstrated that BPFB shows almost twice higher torsional rigidity than BPTB solely due to more efficient conjugation. The higher rigidity was also suggested to hinder one of the possible luminescence quenching pathways. Finally, we demonstrated that the higher the torsional rigidity, the lower the reorganization energy for a charge as well as for an exciton transfer. The obtained data significantly supplement the previously reported experimental findings serving also as a basis for the molecular design of rigid high performance emissive organic semiconductors.

The work was supported by RFBR (project №16-33-60011 mol_a_dk) and by the Ministry of Education and Science of the Russian Federation (grant number 4.7154.2017/8.9).

¹ Zhang, L. et al, *ACS Appl. Mater. Interfaces* 2014, **6**, 5327–5343.

² Kazantsev, M. S. et al, *RSC Adv.* 2016, **6**, 92325–92329.

³ Koskin, I.P. et al, *J. Phys. Chem. C* 2017, **121**, 23359 – 23369.

New organic luminophores: only beautiful chemistry or new perspectives in organic photonics and electronics?

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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 at 1-2 nm distance necessary for efficient Förster energy transfer.^{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 spectral shifters in new highly effective plastic scintillators (radiation detectors). Since two different luminophores are fixed properly on the nanoscale distance at the same branching molecule, both the light output and the attenuation length of the plastic scintillators significantly increase. This lead to a new type of scintillating devices with nanostructured luminophores¹. Heat treatment of the NOLs and organosilicon oligomers having reactive vinyl and the hydride groups in solution, allowed to obtain transparent fluorescent organosiloxane composites stable over a wide temperature range⁹. The new NOLs used in various devices of organic photonics and electronics, such as spectral shifting fibers, 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 performed in the framework of leading science school NSh-5698.2018.3. Synthesis of model linear benzothiadiazole-based oligomers supported by Foundation of President of the Russian Federation (project MK 364.2017.3).

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

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

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

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

⁵ Yu.N. Luponosov, S.A. Ponomarenko, N.M. Surin, et. al., *Chem. Mater.* 2009, **21**, 447.

⁶ O.V. Borshchev, Y.N. Luponosov, E.A. Kleymyuk, et. al., *Russ. Chem. Bull.*, 2010, **4**, 781.

⁷ M.S. Skorotetcky, E.D. Krivtsova et. al., *Dyes and Pigments* 2018, **155**, 284–291.

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

⁹ M.S. Skorotetcky, O.V. Borshchev, N.M. Surin, et. al., *Silicon*, 2015, **7**, 191-200.

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

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

Gamma ray induced degradation effects in triple cation perovskite solar cells

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Solar cells based on complex lead halides with the perovskite structure have attracted particular attention of material scientists and engineers all over the world. Rapid improvement in terms of power conversion efficiencies, which exceeded 22% in combination with potentially low fabrication costs of perovskite solar cells might accomplish a revolution on the PV market. Perovskite solar cells can also be fabricated on ultrathin and lightweight substrates, which makes them particularly attractive for both terrestrial and space applications. Conventional solar cells based on silicon, gallium arsenide or A3B5 type absorbers are usually installed on the satellites. However, these materials rapidly degrade under severe radiation exposure in space. While high-energy particles can be blocked efficiently by the solar cell encapsulation layers, the degradation induced by gamma irradiation from random Sun flares can hardly be avoided. Therefore, development of novel PV materials and solar cell architectures capable of sustaining significant gamma irradiation represents a highly relevant task. In this paper, we will report an experimental evaluation of the gamma radiation tolerance of perovskite solar cells. The effects of the light absorber (MAPbI₃ vs. triple cation MA_(x)FA_(y)CS_(z)PbBr_nI_{3-n}) formulation and the electron transport materials on the device stability will be discussed in detail. The proposed pathways of the radiation-induced degradation will be presented with a particular focus on the self-healing effects revealed in these experiments. Finally, we will conclude on the potential of the perovskite photovoltaics with respect to the space applications.

Advances in broadband photodiodes and phototransistors exploiting organic semiconductors

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Broadband photodetectors that can detect light from ultraviolet (UV) to Vis and NIR are critical for imaging, optical communication and environmental monitoring. We fabricated photodiodes (PDs) based on two- and three component organic bulk-heterojunction (BHJ)/Si heterostructure that demonstrated broadband photoresponse. The three-component one achieved high photosensitivity of 30~50 A/W¹. Using organic planar heterojunction (PHJ) of C₆₀/chloroaluminum phthalocyanine (AlClPc) as the active structure, broad spectral response photosensitive organic field-effect transistors (PhOFETs) with high photoresponsivity were realized². By adopting hybrid planar-bulk heterojunction (HPBHJ) as the active structure that containing three molecules with complementary optical absorption, we realized broad spectral response PhOFETs. PhOFETs based on the HPBHJ composed of 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA), AlClPc and C₆₀, exhibited photoresponse in the broadband wavelength range of 300~850 nm. At an incident optical intensity of 0.07 mW/cm², the mean photoresponsivity and uniformity factor were 0.40 A/W and 0.79, respectively³. By adding a third component, lead phthalocyanine (PbPc) in the HPBHJ and replacing SiO₂ gate dielectric with polyvinyl alcohol (PVA), the device performance was further improved. The photoresponsivity, external quantum efficiency and specific detectivity reached up to 108 A/W, 25300% and ~2.7×10¹² Jones, respectively, which are comparable or even superior to those of commercially silicon and indium gallium arsenide photodetectors or other reported organic photodetectors⁴.

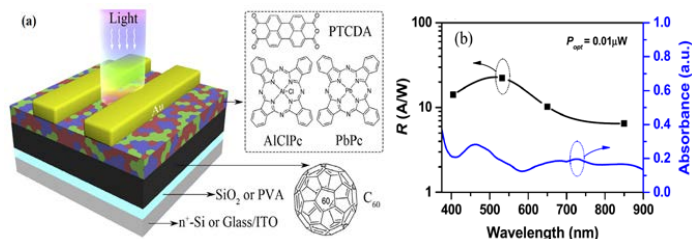


Fig.1 Photosensitive field-effect transistors based on three components HPBHJ. (a) Device structure; (b) Wavelength dependent photoresponsivity and absorption.

¹ Feiyu Zhao, et al, *J. Mater. Chem. C*, 2016, **4**, 815-822.

² Lili Du, et al, *Carbon*, 2016, **96**, 685-694.

³ Yingquan Peng, et al, *Organic Electronics*, 2017, **43**, 27-32.

⁴ Fobao Huang, et al, *Carbon*, 2017, **118**, 666-674.

Charge transfer states and triplet excitons in non-fullerene acceptor based organic solar cells

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Organic solar cells (OSC) attract significant attention as promising energy technology already for several decades with an impressive power conversion efficiency (PCE) record of over 17% very recently published for tandem devices¹. In the past, most of the OSCs employed soluble fullerene derivatives as the electron acceptors due to their superior electron affinity and transport properties. Nevertheless, these acceptors have limited absorption of the solar spectrum, air- and light-induced degradation issues and it is difficult to modify their energy levels. Development of novel non-fullerene acceptors (NFA) that overcome some of these issues, lead to a rapid progress and PCE of over 12% has been achieved in single junction devices².

The fundamentals of NFA based bulk-heterojunctions and solar cells are not yet fully investigated compared to fullerene-based devices and particularly the fate of photogenerated charge carriers and excited states is of importance in view of exploring the full potential of this young technology. In this work we studied optical, electrical and spin properties of ITIC:PBDB-T blends and solar cells based on them. This material combination including the indacenodithiophene based acceptor (ITIC) was shown to be very efficient in solar cells with PCE values between 8 and 11% upon morphology and electrode interlayer optimization³. We fabricated ITIC:PBDB-T solar cells with PCE of 9.8% and an external quantum yield EQEPV of up to 70 %. To address photoexcited neutral and charged excited states in these state-of-the-art blends, we performed optical measurements showing efficient singlet exciton dissociation and the formation of charge-transfer (CT) states. CT states were then further examined by spin-sensitive photoluminescence (PL) technique, where the PL intensity was monitored during scanning of the static magnetic field and flipping the spin of electron or hole by resonant microwaves similar to electron spin resonance (ESR). Indeed, a strong signal from CT states was found, but it was superimposed by a much broader, step-like background signal due to highly localized triplet excitons (TE). The latter are not expected in highly performing donor-acceptor blends, such as ITIC:PBDB-T, since singlet excitons are efficiently dissociated and the intersystem crossing to TE is therefore negligible. TE can however be created via electron back transfer from CT states, as we previously observed in the fullerene-based OSC⁴, opening an additional recombination pathway for photogenerated charge carriers prior their extraction.

This work was supported by H2020-MSCA-ITN-2016 "SEPOMO".

¹ Meng L., Zhang Y., et al. *Science* 2018, doi:10.1126/science.aat2612.

² Baran D., Gasparini N., et al. *Nat. Communications* 2018, **9**, 2059.

³ Zhao W., Zhang S., et al. *J. Sci. China Chem.* 2016, **59**, 1574.

⁴ Liedtke M., Sperlich A., et al. *JACS* 2011, **133**, 9088.

Electronic nose based on Langmuir monolayer OFETs with metal-containing porphyrins as a selective layer

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Monolayer organic field effect transistors (OFETs) are known to be very sensitive to different molecular species present in the environment due to direct contact between target analyte and current-carrying layer¹. Wherein a shift of threshold voltage or charge carrier mobility can be significant after analyte exposure, it usually slightly depends on the kind of species present. Introduction of metalloporphyrins (MPs) thin films as a receptor layers can provide analyte selectivity to sensor response keeping relatively high sensitivity. Previously we have demonstrated monolayer Langmuir-Schaefer (LS) OFETs on the base of tetramethyldisiloxane derivative of dialkyl-(1)-benzothieno(3,2-b)(1)-benzothiophene (BTBT) with field effect mobility up to 0.02 cm²/Vs, threshold voltage close to 0 V and On/Off ratio up to 10,000². Such semiconducting monolayers itself are sensitive to polar analytes exposure with sub ppm concentrations, while suffer from indifference to its kind. Additional layer of metal-containing porphyrins induces selective response to different analytes due to different kinetics of their sorption. In this work we have studied sensor properties of LS OFETs modified by different metal-porphyrin receptor layers and combined some of them into arrays for differential detection of various toxic gases. Electrical responses of monolayer LS OFET-based sensor with TiO-TPP layer are presented at the Fig.1a. Linear discriminant analysis (LDA) was used to calculate response map of four sensor array to ammonia, hydrogen sulfide and nitride dioxide, as it is shown at the Fig.1b, and allowed to recognize these gases at concentrations down to 200 ppb.

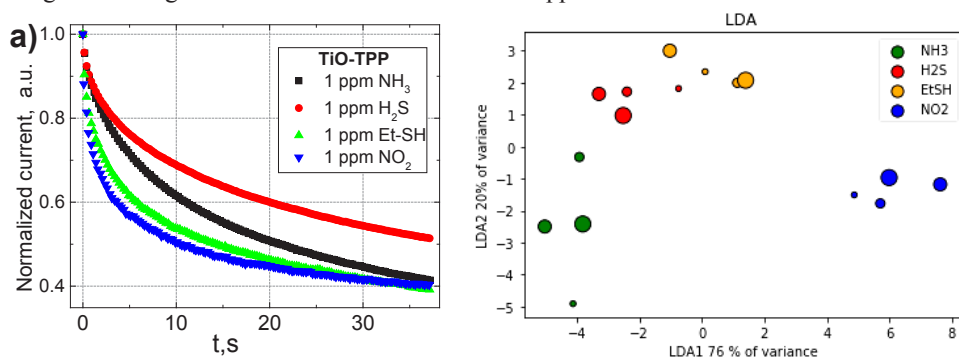


Fig. 1. (a) Time dependence of normalized current for TiO-TPP-containing LS OFET sensor under exposure of different analytes presented at 1 ppm concentration; (b) LDA response map of four LS OFETs modified by different metal-porphyrins to NH₃, H₂S, EtSH, NO₂

This work was supported by RFBR (grant 17-03-00222) and performed in the framework of leading science school NSh-5698.2018.3.

¹ Andringa, A.-M., et al., *Organic Electronics*, 2010, **11**(5): p. 895-898.

² Agina E.V., et al., *Proc. SPIE*, 2017, **10365**, 1036500

Poster presentations

Design of novel low molecular weight donor molecules based on pyrrolo[3,4-c]pyrrole-1,4-dione, thiophene and benzothiadiazole for organic solar cells

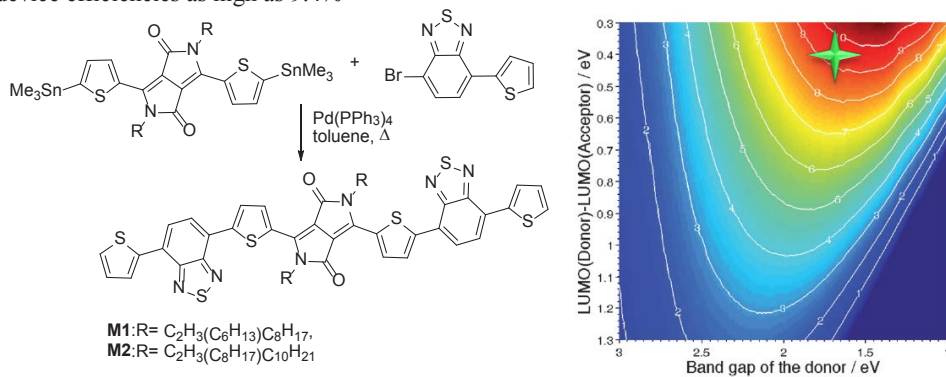
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Conjugated small molecules have attracted a lot of attention with respect to their application in organic electronics because of their well-defined composition and structure, minimal batch-to-batch variation of their properties, easier energy level control. Small molecules were successfully used as both donor¹ and acceptor materials² in organic solar cells (OSC). Here we report the synthesis and investigation of novel small molecules **M1** and **M2**, containing pyrrolo[3,4-c]pyrrole-1,4-dione (DPP), thiophene and benzothiadiazole units (Fig. 1a). DPP is a promising building block that has been widely applied for design of the high performance organic semiconductors. In the field of organic photovoltaics, DPP-based electron donor materials have demonstrated a remarkable device efficiencies as high as 9.4%³



a)

b)

Fig. 1. Molecular structures of **M1** and **M2** (a) and their theoretical potential in OSCs (b)

M1 and **M2** were synthesized *via* standard Stille cross-coupling reaction. Space charge limited current method (SCLC) was used to estimate the charge carrier mobilities of **M1** and **M2**. Small molecules possess high hole mobilities of $1.05 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **M1** and $2.95 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **M2**. The low energy offsets of the absorption bands give estimated band gaps (E_g) of 1.6 eV for both materials. Using cyclic voltammetry measurements the reduction potentials were determined as -1.30 V for **M1** and -1.20 V for **M2** (vs. Fc/Fc⁺), which is translated to estimated LUMO energies of -3.80 eV and -3.90 eV, respectively.

According to the theoretical model of Scharber, the optoelectronic properties of the obtained materials allow achieving efficiencies of 9-10% in bulk heterojunction organic solar cells (Fig. 1b, green label).⁴ Preliminary experimental data on the application of these molecules in organic solar cells and field-effect transistors will be presented and discussed.

The reported study was funded by RFBR according to the research project № 18-33-00667.

A.A.V. acknowledges personal financial support from the Russian President Science Foundation (Fellowship No. SP-835.2016.1)

1. B. Kan et al., *J. Am. Chem. Soc.*, **2015**, 137, 3886

2. W. Zhao et al., *J. Am. Chem. Soc.*, **2017**, 139, 7148

3. H. Choi et al., *Adv. Mater.*, **2015**, 27, 3318

4. M. C. Scharber, *Adv. Mater.* **2016**, 28, 1994; M. C. Scharber et al., *Adv. Mater.*, **2006**, 18, 789

Hybrid photovoltaic diodes based on PbS quantum dots

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An influence of surface ligands of lead sulfide quantum dots (QDs) on the optical properties and photoconductivity of the QD condensate layers was studied. The ligands of various organic molecules with different length were used. On QDs, long length molecules were replaced successfully by short length ones and the result of the procedure was confirmed by IR spectroscopy.

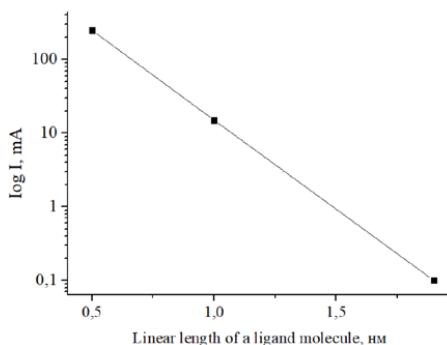


Figure 1. The dependence of the conductivity of PbS QD layers on the ligand length.

Based on the studied QD layers, photovoltaic diodes of the ITO/PEDOT:PSS/QDs PbS/ZnO/Al structure were fabricated. The diodes showed the short-circuit current of 2-4 mA/cm² for QDs layers with either 1,6-hexanedithiol (HDT) or hydrazine ligands. On the contrary, the diodes with QDs layers with an oleic acid (OA) ligand showed negligibly low photocurrents. The conductivity measured by the four probe technique increases exponentially with decreasing ligand molecule length on QDs (Figure 1). Measured by CELIV method in samples of ITO/SiO₂/QD PbS/Al structure, the charge carrier mobility values for QDs with HDT and hydrazine ligands are equal to 7,1·10⁻⁶ and 13,6·10⁻⁶ cm²/(V·s), respectively. The mobility agrees well the conductivity, which confirms the key role of ligand molecules in the transport of excitons and charge carriers in the QD layers. The obtained data for PbS QDs correlate with those for PbSe QDs in Ref.¹

Thus, the replacement of the original long OA molecules by relatively short HDT and hydrazine molecules, which can chemically bind QDs to each other, leads to the improved hopping transport of charge carriers between QDs. The study also reveals that it is the length of the ligand molecules rather than their chemical structure defines the conductivity and hopping transport of charge carriers between QDs in the QD layers.

This work was supported by RFBR (project № 16-29-09623).

¹ Y. Liu, M. Gibbs, J. Puthussery, S. Gaik, R. Ihly, H. W. Hillhouse, and M. Law, *Nano Lett.*, **10**(5), 1960–1969, 2010.

Lanthanide aromatic carboxylates as emitters for solution-processed OLEDs: new approach for host selection

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Over the past few decades lanthanide coordination compounds (Ln CCs) have found their applications in many areas of research, one of which is the fabrication of emission layers in organic light-emitting diodes (OLED). Among other classes of Ln CCs, aromatic carboxylates are interesting as luminescent materials due to the effective luminescence, as well as high chemical, thermal and optical stability. However, their broad implementation as emission layers is difficult, since they do not possess the intrinsic charge carrier mobility.

In order to improve the transport properties of the Ln-based emission layers, we proposed the new approach: the use of a transport host material for luminescent Ln CC, which is able to coordinate the lanthanide ion directly and to sensitize its luminescence¹.

In order to implement this approach, the o-phenanthroline (**Phen**) and its derivative (**BPhen**) have been chosen as host materials for Eu CC (Fig. 1a) and triphenylphosphine oxide derivatives (**PO1-PO4**) have been chosen as host materials for Tb CC (Fig. 1b) due to their electron transport properties and ability to coordinate the lanthanide ion.

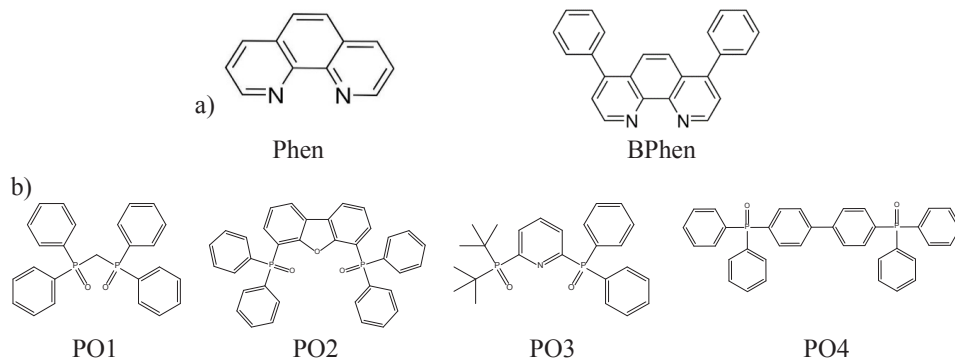


Fig. 1 Host materials for a) europium and b) terbium complexes

The ternary complexes of the composition **Eu(tfb)₃(Q)₂** (tfb⁻ – 2,3,5,6-tetrafluorobenzoate; Q = Phen, BPhen) and **TbL₃(PO)·Solv** (L = Cl⁻, pobz⁻ – 2-phenoxybenzoate; PO = PO1-PO4; Solv = H₂O, (CH₃)₂CO) were obtained, and their photophysical characteristics, including photoluminescence quantum yields, were measured, which allowed selecting among these materials the effective sensitizers of lanthanide ions, which sensitization efficiency Host→Ln³⁺ reached 100%.

The composite films Ln(L)₃(Host):nHost were tested in OLEDs, and it was shown that the use of this approach resulted in the obtaining of diodes with pure ionic terbium or europium electroluminescence. The luminance reached 75 Cd/m² for OLED with a heterostructure ITO/PEDOT:PSS/PVK/Tb(**pobz**)₃(**PO4**)/TPBi/LiF/Al, which is a record value for solution-processed OLED based on lanthanide aromatic carboxylates.

This work was supported by RFBR (project № 16-53-76018).

¹ V.V. Utochnikova, N.N. Solodukhin, A.N. Aslandukov, et al. *Org. Electron.* 2017, **44**, 85-93

Novel Triphenylamine-based luminophores: synthesis and property studying

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π -Conjugated organic light-emitting materials have recently attracted much attention because of their potential applications in biological imaging systems¹, sensors² and light-emitting diodes³. Progress in this field involves first of all the development of new organic semiconducting materials, which combine a high mobility of charge carriers and a high luminescence quantum yield, as well as good stability. It is often difficult to find a material that satisfies all those requirements, since strong intermolecular interactions, which make charge transport possible, are basically accompanied by considerable luminescence quenching effects. Here we report on an efficient synthesis and optical properties studies of novel luminophores based on triphenylamine with different architecture. The molecules have a good solubility in organic solvents and demonstrate interesting optical properties, including high quantum luminescent yields and luminesce spectrum in red and near-IR regions. These compounds may be used as organic semiconducting luminescent materials in devices of the organic photonics and electronics.

This work was supported by the Program of President of Russian Federation (MK-933.2017.3). The work was performed in the framework of leading science school NSh-5698.2018.3.

¹ Picot A., D'Aleo A., Grichine A., Andraud C., et al. *J. Am. Chem. Soc.* 2008, **130**, 1532–3.

² Lochner, C. M., Khan, Y., Pierre, A., & Arias, A. C. *Nature communications* 2014, **5**, 5745.

³ Chen Yi, et al. *ACS applied materials & interfaces* 2017, **9** (16), 14112–14119.

Spectroscopic and Microscopic Characterization of RISC OLED Thin Films

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The development of highly efficient organic light emitting diodes (OLEDs) is desired to realize sustainable and environmentally friendly light sources for various lighting applications. Hereby, the device efficiency is not only determined by the OLEDs chemical composition, but also by its nanostructure and characteristic photophysical processes. To further enhance device efficiencies, it is crucial to gain detailed insights into the physics of device emission and degradation. Therefore, the investigation on a molecular length scale is desired to probe emissive species and their alignment in the three dimensional space. Moreover, measurements on a micrometer scale can be used to obtain local information on film thickness and homogeneity.

Here, we report the investigation of spatially resolved photoluminescence from exciplex forming OLED thin films, composed of 2,4,6-tris[*m*-diphenylphosphinoyl]phenyl]-1,3,5-triazine (PO-T2T) doped with low concentrations of *N,N'*-di(1-naphyl)-*N,N'*-diphenylbenzidine (NPB).¹ The efficiency enhancement in NPB:PO-T2T exciplex based OLEDs mainly results from reverse intersystem crossing (RISC), which is possible due to the small energy gap between the first excited singlet state S_1 and triplet states T_1 of the exciplex. This energy gap is close to thermal energy at room temperature ($E(T_1) - E(S_1) \approx kT$) and enables the conversion of non-radiative triplet exciplexes to radiative singlet exciplexes, known as thermally activated delayed fluorescence (TADF).²

Spatially resolved photoluminescence emission spectra as well as photoluminescence decay curves of NPB:PO-T2T films were obtained by laser scanning confocal microscopy (LS-CM). The information gained by this combined measurement was used to identify and characterize emissive species in the complex system, comprising monomers, excimers and exciplexes. From spatially resolved intensity variations, the film structure could be determined down to a diffraction limited length scale. The observed inhomogeneities provide indications for the growth processes involved in the film deposition. Moreover, the temporal evolution of the emission intensity under constant excitation shows local photoactivation, which is attributed to thermal annealing of the film due to an increase of local temperature, induced by the high excitation powers used.

Our study shows that additional information on processes determining the efficiency of OLED devices is available through spatially resolved optical measurements in comparison to commonly used bulk characterization. This holds particularly true for amorphous organic structures, where properties intrinsically vary as a function of spatial position.

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¹ Lee, J.-H. et al. *ACS Appl. Mater. Interfaces* 2017, **9**(4), 3277-3281.

² Adachi, C. *Jpn. J. Appl. Phys.* 2014, **53**, 060101.

Light-induced charge separation at donor/acceptor composite PCDTBT/PC₇₀BM

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Of all the known ways of using solar energy, the most effective is photoelectric. Nowadays inorganic substances such as silicon are mainly used in solar photocells. These photocells are expensive, therefore today attention is paid to organic photovoltaics.

The active layer of organic solar cells usually comprises a semiconducting polymer and a fullerene derivative (C₆₀). In this mixture the polymer acts as the donor from which the photoexcited electron is transferred to the acceptor (fullerene). Thus, the charge transfer (CT) state is formed. Charges of different sign then move to the electrodes: electrons through acceptor molecules, and holes through polymer chains. Time-resolved EPR experiments have shown that the CT state is a spin-correlated radical pair.¹

A powerful tool for investigating spin-correlated radical pairs is out-of-phase electron spin echo spectroscopy.² Using this method, one can determine distance between charges at a certain time after CT state generation by laser pulse. It is possible to make conclusions about the degree of separation of charges from these data.

In this work, light-induced out-of-phase ESE signal is registered for the composite PCDTBT/PC₇₀BM. Dependence of the out-of-phase echo intensity on the delay between the microwave pulses is studied. The average initial distance between electron and hole in CT state 5 nm (T=80K) is determined.

Recombination of CT state PCDTBT⁺/PC₇₀BM⁻ via singlet channel has characteristic rate constant 3*10⁴ s⁻¹. Recombination via triplet channel is much slower.

¹ Kraffert, F., & Behrends, *J. Molecular Physics*, 2017, **115**(19); 2373-2386.

² Lukina E. A., Popov A. A., Uvarov M. N., Kulik L. V., *J. Phys. Chem.*, 2015, **119**; 13543–13548.

Bis(dicyanothienoanthraquinoides) – novel promising acceptor materials for organic photovoltaics

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In recent years, researchers widely use different π -conjugated small molecule acceptors modified by dicyanomethylene groups as acceptors in fullerene OPV devices. Such blends with benzodithiophene-based polymers demonstrate PCE of 11%¹. However, synthesis of such compounds is often laborious. We propose simple three-step synthesis of **bis(dicyanothienoanthraquinoides) (1)** with different π -linkers (para- and meta-), which affects the optical, electrochemical and morphological properties.

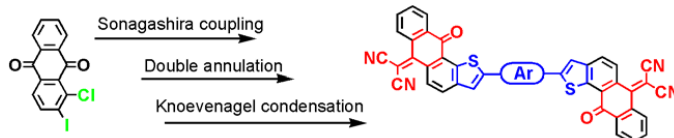


Fig. 1. Three-step synthesis of **1**

As CVA measurements show, introduction of cyano-groups decreases LUMO energy by ~ 0.35 eV. This indicates greater acceptor properties for cyano-substituted species². Optical absorption peaks of **1** in solution are red-shifted by 30-40 nm according to **bis(thienoanthraquinoides) (2)**, and in thin films this effect becomes stronger, because of better intra- and intermolecular π - π interaction. It was proved by atomic-force and optical microscopy that P3HT/**2** is less resistant to thermal annealing than P3HT/**1**, giving very strong phase separation. In blend materials exciton dissociation and charge separation were investigated by luminescence quenching and light-induced EPR (LEPR) spectroscopy. Exciton generation was found to take place in both donor and acceptor phases, but mostly in acceptor phase. LEPR integral value of P3HT/**1** composite signal 10 times larger than of P3HT/**2**, that indicates better charge separation in the former blend. Thus we conclude that dicyanomethylene groups improve acceptor properties of **thienoanthraquinoides**-based molecules, morphological stability under thermal annealing, and charge separation processes.

This work was supported by Russian Science Foundation (project № 17-73-10144).

¹ Zhao W., Qian D et al. *Adv. Mater.* 2016, **28**, 4734–4739.

² Chen W., Zhang Q. *J. Mater. Chem. C* 2017, **5**, 1275-1302.

External Electric Field Assisted Charge Transport in PCBM-SA48 solar Cell: A Theoretical Perspective

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Recently, it was demonstrated that the oriented external electric field can act as a smart technical tool to modulate the electronic and structural properties of a chemical reaction^{1,2}. Here in, we have investigated how charge transport properties of the PCBM-SA48 solar cell are controlled by the application of the external electric field. We have performed time-dependent density functional theory with tuned long-range corrected functional to investigate the nature of the electronic transition. Based on the charge density difference, we have identified the characteristics of excited state properties during photo-induced charge transfer. We find a trend of the rate of exciton separation and charge recombination in PCBM-SA48 complex, resulting from the alignment of electric field along the dipole moment so as to favor electrons flow from a donor (SA48) to acceptor (PCBM) eventually affects the overall efficiency of these bulk heterojunction materials.

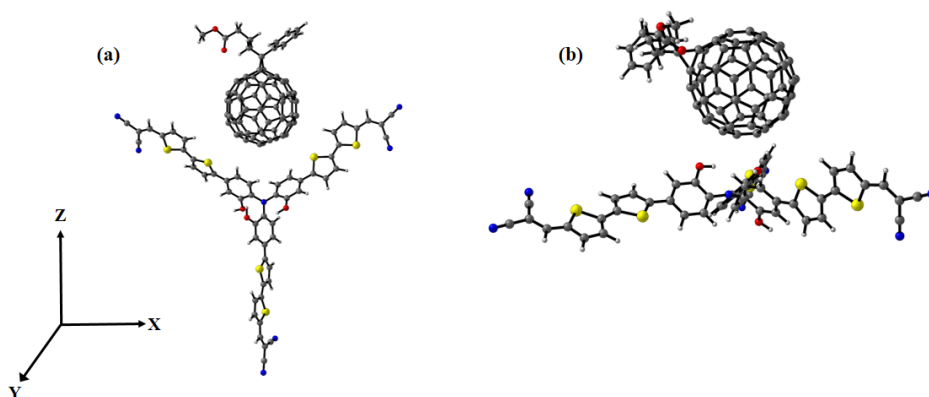


Figure 1. Selected Binding Orientation of PCBM-SA48 complex. The electric field is oriented along the coordinate.

This work was supported by DST Indo-Russia Project.

¹ Shaik, S.; Mandal D.; Ramanan, R. *Nat.Chem.* 2016, **8**, 1091-1098.

² Bhattacharyya, K.; Karmakar, S.; Datta, A. *Phys. Chem. Chem. Phys.* 2017, **19**, 22482-22486.

Visible and NIR-luminescent lanthanide complexes with perfluorinated 2-mercaptobenzothiazolate ligands

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NIR-emitting materials are wide used in many modern technologies such as bioimaging, lasers, organic light-emitting diodes (OLEDs) and others. Lanthanide(III) ions are excellent luminescent centers emitting in different ranges from mild UV to near IR. As it is known lanthanide luminescence requires sensitization because of poor absorption properties of free Ln^{3+} ions. Complexation of lanthanides with highly harvesting organic ligands which can transfer the excitation energy to the metal ion is a widely used way to form intensively luminescent compounds (antenna effect). In the case of NIR-emitting lanthanides it is necessary to take into account the quenching process facilitated by C-H groups of organic ligands. The fluorination of organic ligands is the best solution of the problem of designing the NIR-emitting lanthanide complexes. In present work we used perfluorinated heterocyclic ligand – 4,5,6,7-tetrafluorobenzothiazole-2-thionate (mbt^{F}) to obtain lanthanide containing emitters for the NIR OLEDs. Previous studies showed that mbt^{F} ligands exhibit good sensitization properties because of high triplet level energy.¹ However, complexes of NIR-emitting ions with mbt^{F} showed insufficient luminescent characteristics due to the presence of solvent molecules in first coordination sphere. Also these complexes provide insufficient thermal stability for preparation of OLEDs by vacuum evaporation method. In order to design thermally stable emitters for OLEDs we modified mbt^{F} complexes by addition of 1,10-phenanthroline ligand (Fig. 1). The OLEDs based on these complexes showed red electroplex emission which is caused by deep HOMO energy of the compounds. With the aim to enhance NIR emission the mbt^{F} ionic *ate*-complexes were synthesized (Fig. 1). It has been found that the ionic *ate*-complexes demonstrate an intensive and prolonged luminescence in NIR region. These data allow to consider the obtained ionic compounds as promising emitters for design of electro- and radioluminescent devices emitting in visible and NIR regions.

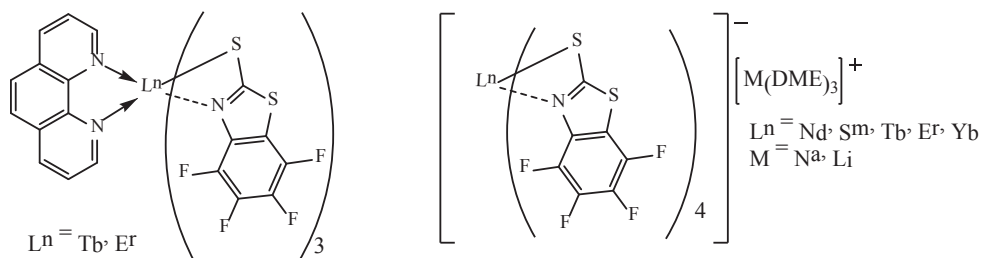


Fig. 1. Lanthanide complexes with perfluorinated 2-mercaptobenzothiazolate and 1,10-phenanthroline ligands

This work was supported by RSF (project № 18-13-00066).

¹ Ilichev V. A., Blinova L. I., Rozhkov A. V., Balashova T. V., Rumyantsev R. V., Fukin G. K., Bochkarev M. N. *J. Mol. Structure*, 2017, **1148**, 201-205.

Gamma-ray induced degradation in organic solar cells

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At present, inorganic solar batteries are used to provide spacecraft with energy. However, to create efficient energy sources for space applications, the following parameters must be taken into account: the power / mass ratio and the volume of the device.^{1,2} Organic solar cells (OSCs) has an advantage such as small weight compared to traditional inorganic solar panels. This makes it possible to install them on flexible substrates. Flexible substrates allow positioning of the solar cells on curved surfaces which allows to generate electric power out of larger area.³ Which makes the OSCs extremely attractive for some space mission, for example small satellites at low orbit of Earth.

Here we report the investigation of the effect of gamma irradiation on the organic semiconductor materials (conjugated polymers P1, P2 and fullerene derivative [60]PCBM) and their photovoltaic performances in OSCs. Photoactive materials were studied by GPC and EPR methods before and after gamma irradiation. The EPR results indicate that gamma radiation does not cause the formation of free radicals in materials. The GPC data indicate that conjugated polymers did not form a low molecular weight compounds as well as cross-linkages under gamma-radiation conditions.

It was studied the changing in photovoltaic properties of devices after gamma—irradiation of the initial semiconductor materials. We found that Gamma-ray irradiation of the [60]PCBM resulted in significant decrease in V_{OC} and FF of OSCs. Irradiation of conjugated polymers P1 and P2 affects J_{SC} in different ways depending on the structure of the polymer. The losses of the photocurrent can be explained by the formation of deep trap states that facilitate the charge recombination. This assumption was confirmed EQE spectra

This work was supported by RFBR (project № 18-33-01086_mol_a).

¹ K. Otte, L. Makhova, A. Braun and I. Konovalov, *Thin Solid Films*, 2006, 511–512.

² A. Kumar, R. Devine, C. Mayberry, B. Lei, G. Li and Y. Yang, *Adv. Funct. Mater.*, 2010, **20**, 2729–2736.

³ S. Guo, C. Brandt, T. Andreev, E. Metwalli, W. Wang, J. Perlich and P. Müller-Buschbaum, *ACS Appl. Mater. Interfaces*, 2014, **6**, 17902–17910.

Molecular dynamics simulations of nanoarchitectures based on thiophene-phenylene oligomers

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Semiconducting conjugated polymers and oligomers are of considerable interest for application in the field of organic electronic devices. In particular, the problem of developing conducting molecular wires has recently received increased attention. The aim is to create extended supramolecular pathways from short molecules interacting through noncovalent forces. Numerous experimental studies have shown the possibility to obtain such self-organized structures; however, the mobility along the chains has always been poor due to imperfect alignment of π -orbitals along the molecular nanostructure. Nevertheless, Shokri et al.¹ managed to obtain the supramolecular wires of increased conductivity based on oligomers of high planarity, rigidity and regioregularity (2,5-dialkoxy-phenylene-thiophene-based oligomers consisting of 2 or 3 monomer units, hereafter 2TBT and 3TBT, respectively).

This study aims to investigate the self-assembly of 2TBT and 3TBT oligomers on the surface of graphene monolayer at wide temperature range (300 – 600 K) using full-atomistic molecular dynamics approach. We performed simulations with the use of GROMACS 5.1 software package with the Gromos53a6 force field. To parametrize electrostatic interactions we calculated partial charges for TBT atoms with the use of quantum-chemical Hartree-Fock method with basis set 6-31G* and two approaches: Mulliken and RESP. The systems under investigation were prepared in such a way that the TBT molecules formed monolayer on the surface of graphene.

In order to study the self-assembly of the TBT molecules, we calculated the order parameter for the main-chain vectors and the density of interdigitation for the alkyl side groups. The results obtained using the Mulliken approach show that the molecules tend to adopt a liquid-crystalline type of order. However, no such organization was observed when using the RESP approach or neglecting the partial charges. To investigate the dynamic properties of the TBT oligomers we evaluated the mean-squared displacement (MSD) of the molecules centers-of-mass at different temperatures. The results obtained show that increasing the temperature leads only to enhanced mobility. On the scale of a single molecule, the following structural features were found. Noncovalent sulfur-oxygen bridges are responsible for maintaining the planarity of the molecules. The end-thiophene-rings of the molecules rotate with a dihedral angle up to 45° enabling the physical linkage of adjacent molecules and preserving the conjugation. The alkyl side groups in case of Mulliken partial charges orient predominantly perpendicular with respect to the backbones allowing for their separation and physical linkage. No major difference between 2TBT and 3TBT was observed in full accordance with the experimental findings.

All simulations were performed using the computational facilities of the Institute of Macromolecular Compounds, Russian Academy of Sciences, and the 'Lomonosov' supercomputers at Moscow State University. This work was supported by the German-Russian Interdisciplinary Science Center (G-RISC) funded by the German Federal Foreign Office via the German Academic Exchange Service (DAAD).

¹ Shokri R., Lacour M.-A., Jarrosson T., Lère-Porte J.-P., Serein-Spirau F., Miqueu K., Sotiropoulos J.-M., Vonau F., Aubel D., Cranney M., Reiter G., Simon L. *JACS*. 2013, **135**(15), 5693-5698.

Ternary solar cells based on highly soluble double-caged fullerene derivatives

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Toward efficient polymer solar cells several key challenges have to be resolved, including improvement of light absorbance, management of transport properties of free charge carriers, and nanomorphology of bulk heterojunction. Ternary systems, including the D₁:D₂:A system and D:A₁:A₂ system, is regarded as prospective approach to address these issues.¹

We previously reported novel highly soluble double-caged fullerene acceptors (dFR) providing enhanced charge transport and molecular ordering in binary systems with P3HT as a donor component.² Here we report fabrication, optimization, and testing of related photovoltaic devices with ternary active layer based on P3HT, dFR, and third component comprising a low band gap donor polymer or small-molecule/fullerene acceptors. Optimization of the fabrication protocol for ternary solar cells includes variation of donor/acceptor/third component ratio, thickness of photoactive layer, annealing temperature, and used solvent(s). Electronic properties of individual compounds as well as the active layer, including the HOMO and LUMO levels, the charge carrier mobility as well as the nanomorphology of photoactive layer will be discussed. The experimental composition-structure-property relationships for a representative series of ternary photovoltaic devices makes possible to reveal correlation between the molecular and electronic features of components of the active layer and its photovoltaic characteristics.

This work was supported by RFBR (project № 18-33-00670).

¹ Huang H., Yang L., Sharma B., *J. Mater. Chem. A*, 2017, **5**, 11501.

² Brotsman V.A. et al., *Chem. Asian J.*, 2017, **12**, 1075.

Thiophene-based monolayer OFETs with metalloporphyrin receptor layers as a perspective devices for toxic gases detection

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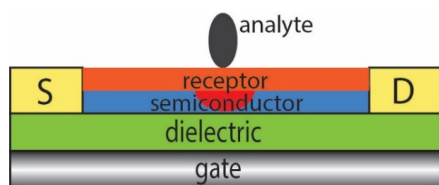
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Semiconducting monolayers of conjugated oligothiophenes and their derivatives modified by metal-containing porphyrins as an additional receptor layer are perspective functional nano-materials for creating of organic field-effect transistors (OFET) and gas sensors on their base¹.

In our work electrical properties of monolayers based on oligothiophene derivatives were studied in the presence of trace amounts of ammonia, hydrogen sulfide and nitrogen oxide depending on chemical structure of oligothiophene as well as semiconducting and receptor layers morphology. Semiconducting monolayer and porphyrin receptor layers were fabricated by Langmuir-Schaefer (LS) technique. Layer morphology was studied by polarizing optical and atomic force microscopies. Electrical and sensing properties were measured by specially constructed gas stand. Fabricated monolayer LS OFETs w/o receptor layer in bottom gate and bottom contacts geometry demonstrated p-type well-reproduced electrical behavior with a hole mobility in the range of 10^{-3} - 10^{-2} cm²/Vs, that is typical for such systems^{2,3}. Easy and scalable technology of receptor layer deposition over LS semiconducting monolayer without loss of electrical performance and OFETs stability was elaborated for the first time. It was demonstrated that hybrid OFETs with semiconducting layer modified by additional receptor layer based on metal-containing porphyrins (Fig. 1a) can be used as a gas sensors for detection of trace amounts of toxic gases in the humid air atmosphere (Fig. 1b).

a)



b)

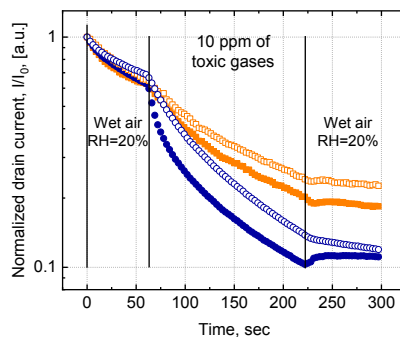


Figure 1. a) Scheme of monolayer OFETs with additional receptor layer. b) Dynamic OFETs response to 10 ppm of ammonia (filled dots) and hydrogen sulfide (unfilled dots) in wet air atmosphere: orange curves represent OFETs with TiO-TPP receptor layer and dark blue ones represent OFETs with Cu-TPP receptor layer.

This work was supported by RFBR (grant 17-03-00222) and leading science school NSh-5698.2018.33.

¹ Andringa, A.M., et al., *Organic Electronics*, 2010, **11**(5): p. 895-898.

² E.V. Agina, et al., *Spie Pros.*, 2017, **10365**.

³ A.A. Trul, et al., *J. Mater. Chem. C*, 2018, DOI: 10.1039/C8TC02447B

Self-assembled monolayers of porphyrin dyads enable light-induced switching in OFET-based optical memory devices

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Organic electronics is one of the most rapidly developing fields of science and technology. A considerable attention has been paid recently to exploration of memory devices based on bistable organic field-effect transistors. Field-effect transistor is a basic component of electronic circuits and it serves also as a versatile platform for designing memory devices, chemical sensors, photodetectors and etc. Memory effects in OFETs can be realized using different types of charge-trapping materials, ferroelectric polymers, and floating gate device architectures.¹ Optical OFET-based memory elements incorporating light-sensitive layers of photochromic materials have also been reported recently.²

In this work we report for the first time the application of the self-assembled monolayers of donor-acceptor dyads with porphyrin moieties as light-sensitive components of OFET-based optical memory elements. The monolayer of the photoactive material was grown at the interface between the semiconductor and AlO_x dielectric layers of the device as in shown in Fig. 1. We explored a series of porphyrin-based dyads with appended acceptor units based on [60]fullerene or ruthenium pyridyl complexes (Fig. 1). The device structure was completed by depositing semiconductor material (C₆₀ as n-type or pentacene as p-type) and top source and drain contacts by evaporation in high vacuum.

The designed memory elements operated at low voltages (<15 V), showed wide memory windows and reliable switching between multiple quasi-stable electrical states characterized by I_{DS} current ratios of 10²-10⁴ when measured at the same V_{GS} voltage (switching coefficients K_{sw}~10²-10⁴). The operation mechanism of the designed light-switchable transistors has been explored and will be discussed in the presentation.

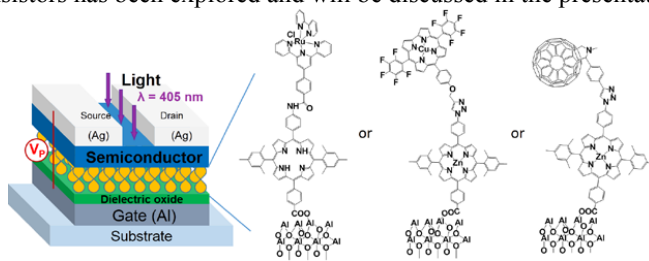


Fig. 1. Schematic illustration of the OFET-based memory device and molecular structures of the explored photoactive materials

Following investigation of the molecular structure – electrical performance relationship for the explored photosensitive materials will pave a way toward designing highly efficient memory devices possessing all the advantages of organic electronics while being cheap, flexible, biodegradable and for this reason more environmentally friendly.

This work was supported by RFBR (project № 18-33-00904).

¹ Zhou L., Mao J., Ren Y., Han S.-T., Roy V. A. L., Zhou Y., *Small* 2018, **14**, 1703126.

² Frolova, L.A., Rezvanova, A.A., Shirinian, V.Z., Lvov, A.G., Kulikov, A.V., Krayushkin, M.M., Troshin, P.A., *Adv. Elec. Mater.* 2016, **2**(3), 1500219.

Impact of the semiconductor/dielectric interface modification on the performance of OFETs and memory devices

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Memory elements based on organic field-effect transistors (OFETs) have been intensively developed during the last few years. These devices have a bistable nature, so the transistor can be reversibly switched between two distinct electrical states with different threshold voltages (V_{TH}). There are several approaches to realize two or more quasi-stable states in OFETs, which are based on using photosensitive or ferroelectric materials, as well as floating-gate device architecture. However, poor reproducibility of the electrical characteristics of the existing types of devices and/or technological problems in their fabrication make their practical application rather challenging.

In this report we address the origin of the hysteresis effects appearing in OFETs assembled using electrochemically grown aluminum oxide (AlO_x) dielectric. We show that the electrochemically grown aluminum oxide dielectric films always comprise some redox-active molecular species absorbed from the electrolyte. This contamination affects dramatically electrical performance of organic field-effect transistors (OFETs), particularly leading to the appearance of hysteresis in the current-voltage characteristics and positive shift of the threshold voltage. A strong suppression of the hysteresis was observed while reducing the concentration of the citric acid or replacing it with an alternative electrolyte based on the aminoacid (isoleucine) and its potassium salt.

The impact of the AlO_x growth conditions and surface modification on the light- and field-induced switching behavior of organic field-effect transistors and memory elements will be discussed.

This work was supported by RFBR (project № 18-33-00904).

Ultrathin solution-processed thiophene-phenylene co-oligomers field-effect transistors with electrical performance exceeding single-crystal ones

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Recent progress in organic field-effect transistors (OFET) based on ultrathin (mono- or a few layer) single crystals stimulates the interest to ultrathin light-emitting transistors. The latter need materials combining bright luminescence with efficient ambipolar charge transport, and thiophene-phenylene co-oligomers are among the most promising materials for light-emitting transistors¹.

In this work, we synthesize two thiophene-phenylene co-oligomers with PTTP and PTPTP (P stands for phenylene, and T stands for thiophene) conjugated cores and decyl terminal substituents, DD-PTTP and DD-PTPTP, and study them in ultrathin solution-processed OFETs. Ultrathin films were grown from ortho-dichlorobenzene solution, which was spin-cast at concentrations of 0.04–0.15 g/l on silicon substrates with thermally grown silicon oxide. For both oligomers, ultrathin films with lateral dimensions in the range of 300–600 μm were grown. Drain and source electrodes were plotted by PEDOT:PSS. Figure 1 shows a photograph of a typical OFET fabricated on a silicon substrate and its output and transfer characteristics. The hole mobility in OFETs based on both oligomers was in the range 0.1–0.2 cm^2/Vs , which exceeds the best charge mobilities reported for thiophene-phenylene co-oligomer single crystals^[1]. We suggest that solution-processed ultrathin films thiophene-phenylene co-oligomers are promising platform for light-emitting transistors.

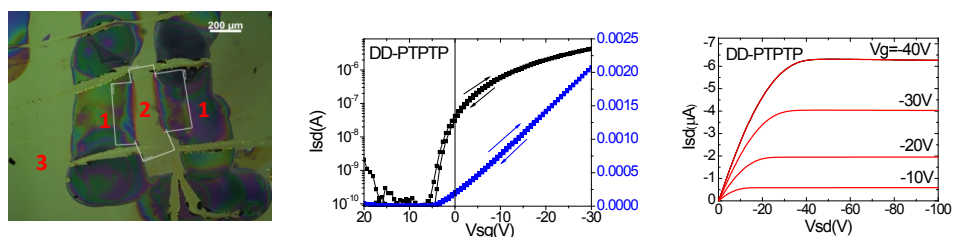


Fig. 1. OFET based on DD-PTPTP and its characteristics. (a) Optical image showing source and drain contacts (1), organic semiconductor film (2), silicon substrate (3); (b) Transfer characteristics; (c) Output characteristics.

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

¹ Hotta S., et al., *J. Mater. Chem. C*, 2014, **2**, 965-980.

Design and synthesis of bithiophene derivatives with anchoring groups for organic electronic applications

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Designed small molecules based on thiophene units often possess high charge carrier mobilities, good solution processability, oxidative and thermal stability, and other properties necessary for the development of new materials and technologies for organic electronics and nanophotonics. Thiophene-based materials were also used as self-assemble monolayers in organic thin film. Application of self-assemble monolayer modifies the electronic and morphological properties of the interfaces, which influence the response of the organic electronic devices.¹ For creation of chemical bond between an organic molecule and a dielectric layer in the organic electronic device, the presence of compatible anchoring groups is required.² Anchoring groups typically used for silica and glass surfaces which are usually used in OFET devices includes reactive silicon-based groups as SiH₃, Si(OR)₃, or SiCl₃. For metal salts and oxide surfaces used in OPV devices, phosphonic acids are often used.³ Dimethylchlorosilyl-functionalized oligothiophenes were found to be stable and reactive enough, to form semiconducting monolayers on SiO₂ surfaces by self-assembly from solution.⁴

Our aim was the synthesis of new bithiophene derivatives with different length of alkyl chain functionalized with selected anchoring groups and their OFET characteristics. Omega-bithionylated alkenes were prepared from bithiophene and were further functionalized by Pt-catalyzed hydrosilylation or Tanaka-Pd-catalyzed hydrophosphonylation of alkene, respectively (Fig. 1.).

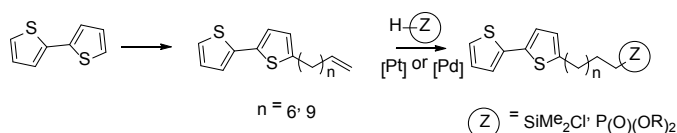


Fig. 1. Designed derivatives for SAM with different anchoring groups.

¹ Casalini S., Bortolotti C. A., Leonardi F., Biscarini F. *Chem. Soc. Rev.* 2017, **46**(1), 40-71.

² Borshchev O. V., Ponomarenko S.A. *Polymer Science* 2014, **56**(1), 32-46.

³ Queffelec C., Petit M., Janvier P., Knight D. A., Bujoli B. *Chem. Rev.* 2012, **112**(7), 3777-3807.

⁴ Ponomarenko S. A., Borshchev O. V., Meyer-Friedrichsen T., Pleshkova, A.P., Setayesh, S., Smits, E. C. P., Mathijssen, S. G. J., de Leeuw, D. M., Kirchmeyer, S., Muzafarov, A. M. *Organometallics* 2010, **29**(19), 4213-4226.

Electronic Structure at Interfaces of Hole Transport Materials

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Organic light emitting diodes (OLED) consist of multiple functional layers which are optimized to improve the device performance. A previous study by M. Kühn¹ showed that not only the individual properties of the different organic materials but also the electronic structure at the interfaces (e.g. dipole moments, band bending, barriers) strongly influences the current-voltage-(I-V)-characteristics of an OLED. Further, it was found that a thin p-doped layer between the hole injection and hole transport layer (HTL) of an OLED can increase the device performance, observable in steeper I-V-curves. For simplification our current study focuses on hole-only devices consisting of an ITO anode, a p-doped HTL, an intrinsic HTL, and an Al cathode.

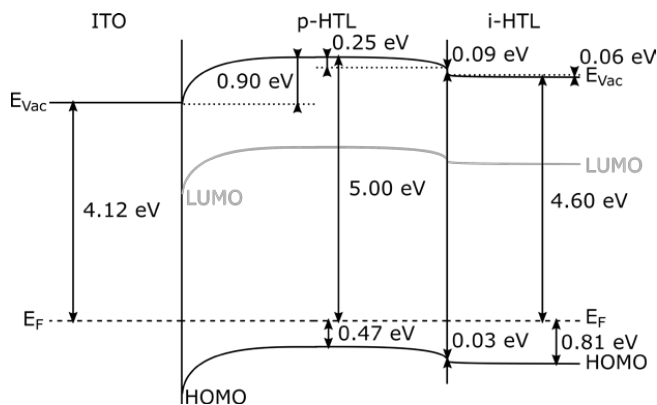


Fig. 1 Exemplary energy alignment diagram for a ITO/p-HTL/i-HTL stack obtained from PES interface experiments.

To get an understanding of the electronic interface structures in these devices, hole transport materials (HTMs) with different ionization potentials are analyzed by photoelectron spectroscopy (PES). First experiments analyze the doping behavior of the HTMs. For each HTM, thin films with different dopant concentration are deposited by thermal evaporation and analyzed by X-ray and UV photoelectron spectroscopy (XPS and UPS). As no significant differences in the doping behavior are observed among the HTMs, following experiments aim towards the interface. The interfaces are characterized by consecutive evaporation of layers, monitored by PES measurements. The first examined interfaces are the ones at the contact between ITO and the p-doped HTL. The second interfaces are then between the p-doped HTL and the intrinsic HTL. From these experiments, energy alignment diagrams for different ITO/p-HTL/i-HTL stacks are obtained (see fig. 1).

For the support of this work we thank innovationLab GmbH and Merck KGaA.

¹ Kühn M., Pflumm C., Glaser T., Harbach P., Jaegermann W., Mankel E., *Organic Electronics* 2017, **41**, 79–90.

Photothermal deflection spectroscopy as a probe of ppm-doping level in organic semiconductor single crystals

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Single-crystal thiophene-phenylene (TPCO) and furan-phenylene co-oligomers (FPCO) are in strong demand in organic optoelectronics for various light-emitting devices, since they can combine high luminescence and efficient charge transport. Doping with highly luminescent molecules is a promising way to control the luminescent properties of organic semiconductor crystals. Recently, we have found that luminescent self-dopants appear as minor byproducts in the course of TPCO chemical synthesis¹.

In this work, we report on photothermal deflection spectroscopy technique (Fig. 1a) to control small concentration ($\ll 1\%$) of molecular dopants in TPCO and FPCO single crystals. We detected dopants absorption features in single-crystal grown from vapor and solution. Using reference samples of single crystals self-doped with a longer co-oligomer and assuming that the dopant absorption is linearly dependent on the dopant content, we estimated the dopant concentration in various self-doped samples (Fig. 1b). It was observed that dopant distribution may be nonuniform in the presented materials. We compare luminescent and photothermal techniques for control of doping in organic semiconductor crystals by the lower-bandgap molecules with the sensitivity in the ppm range.

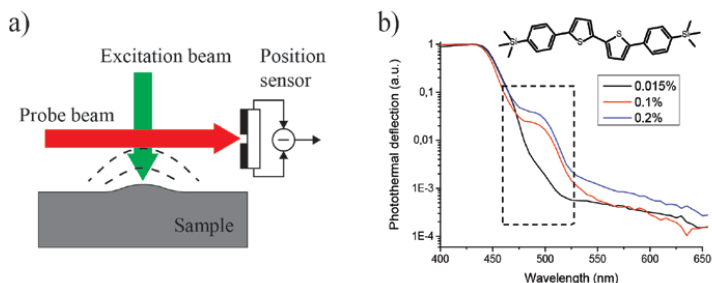


Figure 1. a) Experimental scheme of photothermal deflection spectroscopy; b) Spectra of reference samples TPCO TMS-PTTP-TMS crystals intentionally self-doped with a longer TPCO TMS-PTTTTP-TMS.

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¹ Olga D. Parashchuk et al. *Adv. Funct. Mater.*, 2018, **28**, 1800116.

Contact resistance temperature dependence of organic transistor

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Organic electronics devices based on small molecule or polymer materials like organic field effect transistor (OFET), organic light emitting diode (OLED) and organic solar cells (OSCs) have attracted a great attention due to their application as light-weight and flexible devices. The understanding of the electrical conduction mechanism in these materials and at their interfaces still represents a challenge ¹.

In the OFETs the free charge carrier mobility was identified as a main bottleneck of the charge carries transport properties of organic semiconductors. However, recent reports on the high-mobility devices pointed out the limitation by the injection properties, namely the contact resistance.

Generally, it is believed that contact resistance results in lower nominal mobility (μ_{nom}) extracted from OFETs than the intrinsic mobility (μ_{int}) of organic semiconductors. This is an important issue especially in high-mobility OFETs, in which the contact resistance would play an important role and lower the μ_{nom} significantly. However, there are few reports on clarifying how much the μ_{nom} would be lowered by contact resistance compared to μ_{int} quantitatively. As a result, a systematic work to quantitatively understand the effect of contact resistance on lowering the extracted μ_{nom} in high-mobility OFETs is necessary. Another question remaining to be answered is how the contact resistance affects the temperature dependence of mobility extracted from OFETs characterizations, which is essential for us to understand the charge transport physics in organic semiconductors².

In this study we have investigated the temperature dependency of contact resistance in organic field effect transistors. The investigated structures were top contact bottom gate OFET structures. The OFETs are based on the pentacene organic semiconductors and the source and drain electrodes are copper (Cu) prepared on highly doped Si wafer, which acts as gate electrode.

This work was supported by the Slovak Research and Development Agency (grants APVV-14-0739 and APVV-14-0740).

¹ Jurchescu O.D., Baas J., Palstra T.T.M., *Appl. Phys. Lett.* 2004, **84**, 3061.

² Yuanyuan Hu., Guodong Li, Zhuojun Chen, *IEEE Electron Lett.* 2018,**39**, 276.

Synthesis and properties of novel conjugated donor-acceptor oligothiophenes with electron-withdrawing methyldicyanovinyl groups for organic photovoltaics

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Donor-acceptor (D-A) organic conjugated systems are the most demanded type of materials being developed for organic electronics and photonics. The presence of the D-A structure makes it possible to "fine-tune" the properties of the material by varying the donor and acceptor blocks, the π -conjugated spacer length between them, and by introducing additional solubilizing groups^{1,2,3}.

In the course of this work, novel D–A oligomers consisting of 5 and 7 conjugated thiophene units with terminal electron-withdrawing methyldicyanovinyl groups were obtained. All precursors and the target compounds were characterized by ¹H and ¹³C NMR spectroscopy and size exclusion chromatography in an individual state. Variation of the thiophene bridge length as well as a number and positions of solubilizing groups allowed elucidating the structure-properties relationships for their solubility, absorption spectra, electrochemistry and phase behavior. The obtained oligothiophenes are promising candidates as donor materials for organic solar cells with a bulk heterojunction.

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¹ Meier, H., *Angew. Chem. Int. Ed. Engl.* 2005, **44**, 2482 – 2506.

² Y.N. Luponosov, J. Min, A.N. Solodukhin, O.V. Kozlov, M.A. Obrezkova, S.M. Peregudova, T. Ameri, S.N. Chvalun, M.S. Pshenichnikov, C.J. Brabec, S.A. Ponomarenko, *Organic Electronics*, 2016, **32**, 157-168.

³ Y.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.

Optical and luminescent properties of copper and silver cesium iodides

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In the last decade various types of all-solid photovoltaic cells have been developed including perovskite solar cells. Complex iodides play a role of light-harvesting compounds and obtain hole and electron conductivity properties. A significant disadvantage of most perovskite compositions is their tendency to decomposition due to oxidation when exposed to ultraviolet radiation, light, heating or because of intrinsic chemical processes. Practical application of complex iodide is limited by their stability while the optimal values of the band gap (1.2-1.8 eV) of semiconductors provide light absorption and non-equilibrium charge transfer processes. Many of advanced complex iodide compounds have a more complex structure different from perovskite cell. The object of this study was the ternary system CsI-CuI-AgI and complex iodide compounds based on cesium, copper and silver iodides. According to the literature such compositions could be a potential substitute for lead-containing iodides which are toxic and have low thermal stability¹. Optical and luminescent properties of the compounds CsCu₂I₃, CsAg₂I₃, Cs₃Cu₂I₅, Cs₂AgI₃, have been studied for the first time. Also phase equilibria and homogeneity regions in the binary system CsCu₂I₃-CsAg₂I₃ have been analyzed. Optical absorption spectra and luminescent spectra of compositions in the binary system CsCu₂I₃-CsAg₂I₃ are obtained and discussed according to the band structure of compounds. The lifetime of non-equilibrium charge carriers (τ) of individual compounds and substitution solid solutions in the ternary CsI-CuI-AgI system have been investigated. All compositions in the ternary system CsI-CuI-AgI have been synthesized using solid-phase ampoule sintering method performed at reduced pressure of 0.08 atm. Interaction of precursor compounds have been performed according to the following chemical equation: $(1 + y) \text{CsI} + x \text{CuI} + (2-x) \text{AgI} \rightarrow \text{Cs}_{1+y}\text{Cu}_x\text{Ag}_{2-x}\text{I}_{3+y}$. Analysis of optical characteristics of the compounds obtained showed the band gap (E_g) of about 2.9 eV for most the samples while for the composition CsCuAgI₃ E_g achieved just 1.8 eV that is promising for its application as a light harvesting component. According to XRD data the coherent length for the samples were of ~44 nm. The charge lifetime values τ for the samples are of 0.5-5 μs . These values exceed the lifetime characteristics for the most common lead-based perovskite iodides.

¹ Polman A., Knight M., Garnett E. C., Ehrler B., Sinke W. C. *Science*. 2016, **352**(6283), 307-318.

A new series of pyrimidine-containing chromophores - naphthalene, anthracene and cyclic imide derivatives: synthesis, investigation of spectral and electrochemical behavior

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Nowadays π -conjugated systems based on such polycyclic moieties as acenes, 1,8-naphthalimide, perylene diimide attract significant and intensive attention, first of all, as potential materials useful for application in OFETs, OLEDs, solar cells and e.g. These molecules have essential advantages, e.g., rigid planar structures, ability to form stacked structures¹, high fluorescence quantum yield, chemical, thermal and photostability².

Two different series of novel π -conjugated pyrimidine-containing chromophores have been prepared. The first one includes anthracene or naphthalene as a central core and 4,6-disubstituted pyrimidines as a terminal moieties. The second type of the synthesized compounds consists of dicarboxylic acids imides (phthalimide, 1,8-naphthalimide) substituted at imide nitrogen atom by 4,6-disubstituted pyrimidines fragments (Fig. 1). All the prepared compounds were characterized with UV-vis and photoluminescence spectroscopy, which was performed for their solutions and films, and by cyclic voltammetry, as well. The optimized structures of the prepared chromophores were obtained and visualized by quantum-chemical calculations.

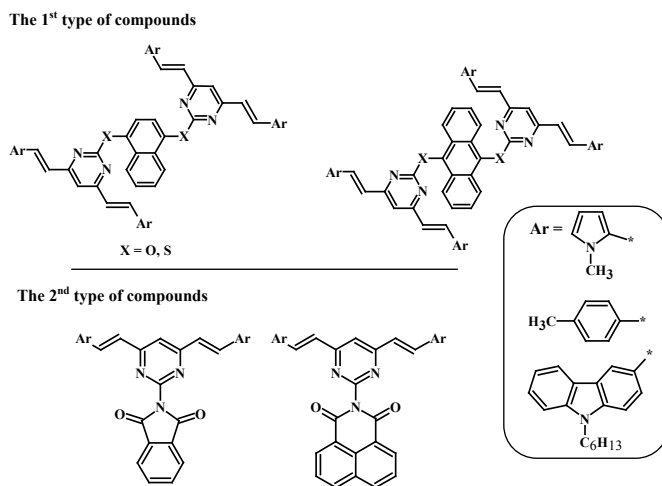


Fig. 1. The structures of the prepared compounds.

This work was supported by RFBR (project № 18-33-00323_mol_a).

¹ Anthony J. E., *Chem. Rev.* 2006, **106**, 5028–5048.

² Li Z., et al., *Synth. Met.*, 2016, **217**, 102-108.

Highly bendable thiophene-phenylene co-oligomer single crystals

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Thiophene-phenylene co-oligomer single crystals are promising optoelectronic materials for light-emitting devices because they combine the efficient charge transport and high luminescence^{1,2}. However, single crystals are usually considered to be brittle.

In this work, we study the effect of mechanical bending on photoluminescent (PL) and charge transport properties in thiophene-phenylene co-oligomer 1,4-bis(5'-hexyl-2,2'-bithiene-5-yl)benzene (DH-TTPPT, Fig. 1a) single crystals grown from solution³. DH-TTPPT single crystals demonstrated p-type conductivity with the highest hole mobility 0.065 cm²/Vs and the PL quantum yield about 17%. We found no effect of bending on PL intensity of a DH-TTPPT single crystal after 300 bending cycles (Fig. 1c). Nevertheless, an average hole mobility of the crystals exposed to bending (0.02 ± 0.01 cm²/Vs) was about twice lower than that for the neat crystals ($\approx 0.05 \pm 0.01$ cm²/Vs), which could be assigned to defects induced by bending in the near-surface layer carrying the electrical current. To conclude, DH-TTPPT solution-grown crystals could be a promising platform for highly flexible organic optoelectronic devices.

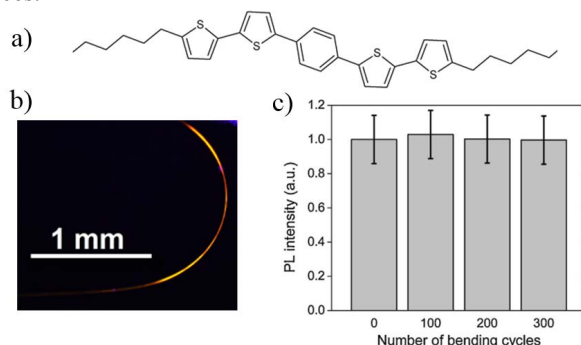


Fig. 1. a) DH-TTPPT molecular structure; b) Optical image of bent DH-TTPPT single crystal luminous under 405-nm exposure; c) PL intensity of a flat crystal after multiple bending cycles with a bent radius in the range 1.5–4 mm

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

¹ Hotta S., et al. *J. Mater. Chem.* 2011, **21**(5), 1295-1304.

² Kudryashova L.G., et al. *ACS Appl. Mater. Interfaces* 2016, **8**(16), 10088-10092.

³ Kazantsev M.S., et al. *Synth. Met.* 2017, **232**, 60-65.

Effect of counter ion on structure of thin polyaniline films on air-water interface

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The most straightforward technique for preparation of polyaniline (PANI) layer of electrochemical memristive devices is formation of thin polymeric film on air-water interface and its subsequent transfer to glass substrate. Moreover essential factor that determines performance of memristive devices is crystalline structure of such films. In current research, we studied the effect of type of counter ions in water subphase on thin films crystalline structure, morphology and conductivity.

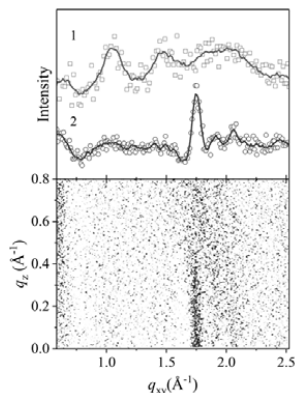


Fig. 1. GIXD scattering intensity of Langmuir layer of PANI on various surfaces: 0.01 M HCl (curve 1), 0.01 M CSA (curve 2), b) corresponding GID pattern for the film on the surface of 0.01 M CSA.

We choose the following subphase compositions: no counter ions, 0.01 M HCl and 0.01 M camphosphonic acid (CSA). Crystalline structure of thin polyaniline films on air-water interface was studied by GID (Figure a1). Polyaniline films formed in range from 12 to 20 mN/m on subphase with no counter ions are amorphous. The structure of films formed on the subphase with 0.01 M HCl corresponds to well-known ES-I emeraldine salt, and on 0.01 M CSA matches to in-plane interchain stacks of phenyl rings with domain size about 7 nm. Reciprocal GID space map of scattering diagram of PANI layer formed on the subphase comprising CSA (Figure 2b) shows the rod in q_z direction corresponding to crystalline domains in vertical direction with size about 12 Å. Such kind of X-ray patterns for PANI-CSA films are attributed to highly conductive materials with conductivity more than 10^3 S/cm and metallic conductivity-temperature dependence.¹

This work was supported by RSF (project № 16-13-00052).

¹ K. Lee, S. Cho, S. H. Park, A. J. Heeger, C. W. Lee and S. H. Lee, *Nature*, 2006, **441**, 65–68.

In situ impedance spectroscopy of polymer structures by resistive switching

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Development of fast, compact and low-cost electronic memory elements is one of the priority tasks of the modern microelectronics. Application of the resistive switching effect (RSE) in structures of different types can result in efficient and easy to use memory elements¹. In particular, this refers to devices based on organic materials. RSE based on organic materials is nonvolatile, fast (switching time is less than 10 ns); has over 10⁵ cycle endurance, slow degradation and high scalability potential². For further optimization of operational parameters, it is essential to understand mechanisms of RSE. In this work, we analyze different RSE stages using the impedance spectroscopy for organic based sandwich structures with a modified polymer matrix as an active element. The impedance spectroscopy was performed for a series of intermediate states formed within the switching process, as shown in fig. 1a. Analysis of the experimentally obtained impedance spectra shows that the charge transport is due to delocalized charge carriers and occurs via conducting filaments formed in a highly isolating matrix. Interestingly, the filament configuration changes during the switching. With the transition from isolating to conducting states, single filaments are reorganized into a branched network (fig.1b). In summary, we demonstrate that the impedance spectroscopy enables identification of the resistive switching mechanisms in composite organic structures.

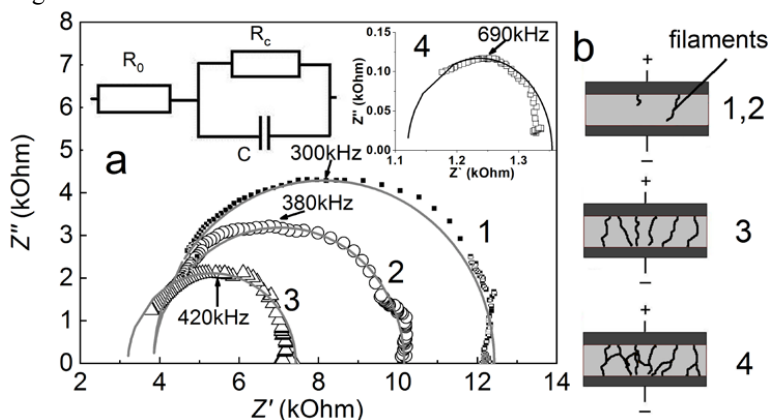


Fig. 1. a) Impedance spectra for intermediate states (numbers near the curves) of the RSE. Symbols- experimental data, curves – fitted dependencies calculated using the equivalent circuit parameters (inset) b) Illustration of the filament formation in intermediate states.

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¹ Chen, Y., et.al. *APL*. 2014, **105**, 193502.

² Kotova M.S., et.al. *Organic Photonics and Photovoltaics*. 2016, **4**(1), 17-23

Photon counting multi-channel scaler for phosphorescence spectroscopy of organic semiconductors

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The lowest excited state of typical organic semiconductor is a triplet. This paramagnetic state is unavailable to optical absorption and fluorescent spectroscopy but determines many important photophysical properties of organic semiconductors. To study the triplet excited states, phosphorescent spectroscopy is traditionally used¹. However, for many of organic semiconductor materials due to a very low efficiency of phosphorescence the experiment is very complicated¹. The most challenging problem is to study phosphorescence in an aggregated state, which may dramatically reduce the triplet lifetime and the observed signal.

Here, we present a new instrument built to increase the efficiency of the phosphorescent spectroscopy. It is field-programmable gate array (FPGA) based photon counter with a photomultiplier designed to allow photon counting during the whole phosphorescence decay time instead of one point in kinetics. This approach dramatically decreased the accumulation time needed to acquire a kinetic profile with up to 10 ns resolution allowing us to sample large arrays of data and to acquire the spectrum kinetics with great accuracy.

Fig 1. shows the spectral kinetics of organic semiconducting molecule TMS-PTTP-TMS (see Fig 1.) phosphorescence in solid polymethyl methacrylate solution at room temperature. Peak of the phosphorescence at 680 nanometers shows mono-exponential decay with 0.82ms lifetime.

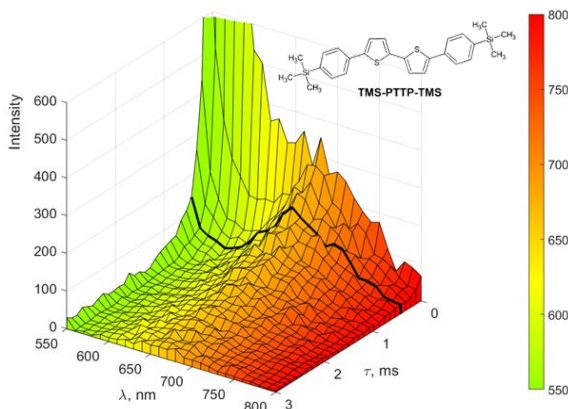


Fig 1. Room-temperature phosphorescence kinetics of TMS-PTTP-TMS molecule.

The instrument decreased the accumulation time of the spectral kinetics acquisition by about two orders of magnitude compared to common photon counting. This allowed us to eliminate the effect of photo-degradation. We suggest that the developed spectroscopic method is promising for studying phosphorescence in crystalline organic semiconductors.

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

¹ Janssen, R; Marsal, P; Wasserberg, D; *J. Phys. Chem. B* 2005, **109**, 4410-4415.

Vibronic Control of Organic Electronic Devices

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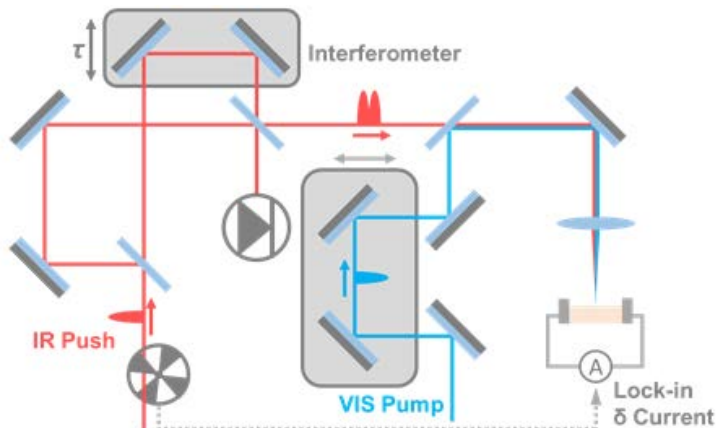


Figure 1: experimental pump-push setup, incorporating a Mach-Zehnder interferometer.

The electronic properties of materials used in Organic Electronics are strongly dependent on the overlap of molecular orbitals and are thus highly sensitive to the geometric configuration of the constituent molecules. The soft and flexible nature of organic materials thereby gives rise to coupling between the nuclear dynamics within a material and its electronic properties, termed vibronic coupling (VC).¹

Due to the timescales of electronic and nuclear motion, the observation of VC effects requires the use of ultrafast (< 100 fs) techniques. Our present goal is to observe VC phenomena using ultrafast spectroscopy and to execute a novel experimental approach of vibronic control to detect electronic signals following optical excitation of nuclear motion.

Progress so far includes development of the experimental setup for pump-push measurements with photocurrent detection (PPP, figure 1), which incorporates an interferometer for time- and frequency-resolved spectroscopy.² The PPP setup has also been redesigned for near and mid infrared (IR) experiments. Using difference frequency generation, light of 3 – 12 μm has been generated, and focus is now on attempting to use broadband IR push pulses instead of narrowband.

This work was supported by the ERC Starting Grant Programme (Grant №: 639750).

¹ M. Galperin, M. A. Ratner, A. Nitzan, A. Troisi, *Science*, 2008, **319**, 1056—1060.

² A. A. Bakulin *et. al*, *Nat. Commun.*, 2015, **6**, 7880.

COPHEE: Condensed Phase Excitation Energies Database

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Benchmark studies provide fair comparisons of accuracy and computational cost of different methods; as such, they play a critical role in forming community knowledge base. However, to date, benchmarks for methods capable of describing photochemistry in condensed phase are scarce and incomplete.

We work on development of condensed-phase photochemistry database by (i) creating and documenting model systems covering wide range of photochemical phenomena in various environments and (ii) providing benchmarks on these systems with various solvation models such as quantum mechanics / molecular mechanics (QM/MM), QM with the effective fragment potential (EFP) embedding, and fragment molecular orbital (FMO) method.

The test set will include DNA nucleic bases such as molecule of cytosine in natural environment and in water solution. A preference will be given to systems with available experimental data such as absorption, emission and transient absorption spectra.

The following information is documented and stored for general use on external website (cophee.efpdb.org): (i) gas phase geometries; condensed phase snapshots from MD trajectory, (ii) gas phase excitation energies at different levels of theory, (iii) QM/MM, QM/EFP, FMO excitation energies for specific geometry snapshots, (iv) plots of excitation energy distributions (i.e., absorption spectra) at different levels of theory, (v) statistical analysis of various sets of data, including average solvatochromic shifts and widths of spectral lines, (vi) information on reference experimental data, (vii) detailed description of all computational protocols, and (viii) sample inputs for gas phase, QM/MM, QM/EFP and FMO calculations.

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Toward the design of lanthanide heteroaromatic carboxylates

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Coordination compounds (CC) of lanthanides are used in many areas, such as bioimaging and Organic Light-Emitting Diodes (OLEDs). For each application, the requirements for the physicochemical properties of the CC are different. Therefore, OLED luminescent materials should demonstrate high photoluminescence quantum yield, charge carrier mobility, and high solubility in case of deposition from solution. Summarizing the literature data and results of previous works of our group, ways of influencing the composition and structure of CC on these properties were gathered. Thus, charge carrier mobility may be increased by introduction of a heteroatom into the highly conjugated system due to formation of electron depletion system and an increase of intermolecular interaction. The same introduction of a heteroatom and increasing of conjugation degree may also influence the quantum yield by changing the triplet level, which sensitizes lanthanide ions. Introduction of a heteroatom increase triplet level while increase of conjugation degree decrease it. The introduction of heteroatoms into α -positions with respect to the carboxylic group also increases solubility due to the decrease of polymerization degree. Based on these dependence it was chosen benzofuran-2- (H(bfc)), benzoxazole-2- (H(boz)), benzothiazole-2- (H(btz)) and naphthothiazole-2-carboxylic (H(ntz)) acids, whose anions have two- or three-rings conjugated systems and heteroatoms in α -positions with respect to the carboxylic group, in order to obtainment soluble effectively luminescent materials possessing charge carrier mobility and testing them as host-free emitting layers in OLED.

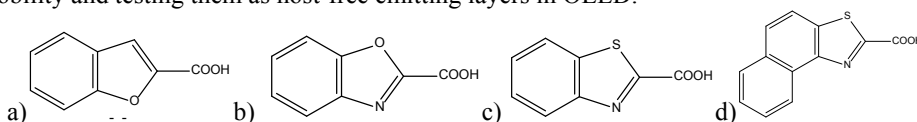


Fig.1. Structural formulae of a) benzofuran-2- carboxylic b) benzoxazole-2- carboxylic c) benzothiazole-2- carboxylic d) benzothiazole-2-carboxylic acids

Syntheses of carboxylic acids were described in literature, but we optimized and improved methods of obtaining such compounds. Since H(boz) and H(btz) were unstable under the normal conditions, they were obtained and further used in the form alkali salts. CCs with above mentioned carboxylate anions were obtained, and all the europium complexes demonstrated high intensity of europium ionic photoluminescence. It turned out that three-ring conjugate system possess low triplet level and small back energy transfer is observed on luminescence spectra $\text{Eu}(\text{ntz})_3 \cdot 3\text{H}_2\text{O}$ as small ligand emission band. At the same time, all the terbium complexes including two-ring conjugate systems possessed intense ligand emission band indicating effective back energy transfer, which is explained by high excited state energy of Tb^{3+} .

All the complexes demonstrate solubility in several solvents up to 16 g/ml in chloroform, though complexes with three-ring ligand were less soluble that with two-ring ligands. All the complexes $\text{Eu}(\text{L})_3 \cdot n\text{H}_2\text{O}$ ($\text{L}=\text{bfc}$, boz, btz, ntz) were tested as emission layers in host-free solution-based OLEDs and demonstrated europium ionic luminescence due to enough electron mobility, witnessed by OLED I-V curves.

Thus, the design of the lanthanide coordination compounds by means of changing degree of conjugation and introduction of a heteroatom leads to the obtainment of soluble highly luminescent complex with charge carrier mobility.

This work was supported by RFBR (project № 18-33-00250).

New bifunctional organic conductor (BETS)₂Cu(dca)₃ and semiconductor (BEDT-TTF)₂Cu¹⁺Cu²⁺(dca)₄ with the dicyanamidocuprate anions

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The cation radical salts based on organic chalcogen-containing π -donors with the magnetic counter-ions combine conductive and magnetic properties in the same molecule. Conductivity in these compounds is provided by the π -electrons of the organic cation radical layers and the magnetic properties are associated with the localized spins of the metals from the anionic layers. The presence of different functional blocks in one molecule opens the way for the control one of the properties, affecting the other by external factors.

The present work is a development of our previous researches on the synthesis of new radical cation salts using as counter-ions the complex dicyanamidocuprate anions.

Electrocrystallization of bis(ethylenedithio)tetraselenafulvalene (BETS) and bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) in the presence of the electrolyte (Ph₄P)[Cu(dca)]₃ has been studied, using different solvents. A new superconductor (BETS)₂Cu(dca)₃ [(dca) = [N(CN)₂]₃⁻] (**1**), and the first radical cation salt with dicyanamidocuprate anion, incorporating diamagnetic Cu¹⁺ and paramagnetic Cu²⁺ atoms, (BEDT-TTF)₂Cu₂(dca)₄ (**2**) have been obtained. The crystal structure, electronic structure and conductivity of both salts as well as the electronic structure of **2** and its structural analog (BEDT-TTF)₂CuMn(dca)₄ (**3**) were analyzed. The salt **1** has a layered structure in contrast to the structure of the BEDT-TTF radical cation salt **2**. The latter is characterized by the presence of a polymeric anion built into the BEDT-TTF radical cation layers. At ambient pressure the crystal of **1** undergoes a metal-insulator transition at T~30 K, which however can be suppressed by applying relatively low external pressure, giving way to a superconducting state. The salt **2** undergoes a semiconductor I-semiconductor II phase transition, which manifests in a jump of the resistivity and a hysteresis in the R(T) curves in a very large temperature range (250 - 185 K). The phase transition is accompanied by changes in the charge state of the BEDT-TTF molecules as well as notable changes of the structure of the anion layer especially in the environment of Cu²⁺ atom. For the salt **3**, structures determined at five temperatures allow detailed electronic structure calculations. The selfconsistent charges show a sharp increase of charge order between 291 K and 285 K. Before, in this temperature range in the salt **3** was observed the semiconductor I-semiconductor II phase transition.

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Novel low molecular weight semiconductor materials based on rhodanine, thiophene and benzothiadiazole for organic electronics

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A considerable attention of the researchers has been paid to low molecular weight compounds as promising semiconductor materials for organic electronics. Small molecules have numerous advantages over the polymer-based materials such as improved crystallinity, well-defined chemical composition/molecular structure and easy purification.¹ Therefore, it is not a big surprise that low molecular weight electron donors and acceptors are actively developed to boost both the efficiency and stability of organic solar cells.

In this work, we report two new promising organic semiconductor materials **M1** and **M2** (Fig. 1). Recently we showed that conjugated compounds with extended DADAD system of donor (D) and acceptor (A) blocks demonstrate improved optoelectronic properties as compared to the materials with classical DAD units.² In particular, DADAD-type conjugated polymers provided higher efficiencies in organic solar cells. Following the same strategy, we synthesized small molecules **M1** and **M2** featuring the A₁D₁ADAD₁A₁ type architecture with peripheral rhodanine A₁ fragments and alternating thiophene (D, D₁) and benzothiadiazole (A) blocks.

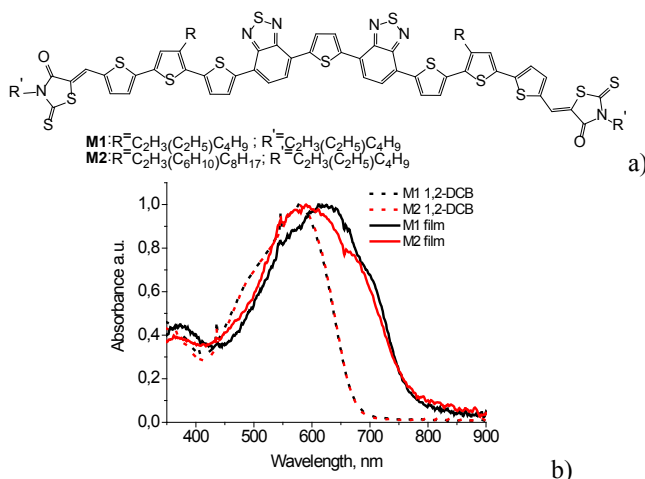


Fig.1 Molecular structures of **M1** and **M2** (a) and their absorption spectra in 1,2-dichlorobenzene (1,2-DCB) and in thin films

Bathochromic shift (~110 nm) of the absorption bands while going from solution to thin films indicates efficient self-assembling and strong intermolecular coupling of molecules in the solid state (Fig. 1b). Both **M1** and **M2** have optical band gaps ($E^{\text{opt}}_{\text{g}}$) of ~1.58 eV and HOMO energies of -5.48 eV, as estimated from the optical spectra and cyclic voltammetry data. The optoelectronic properties of the designed small molecules allow one to consider them as promising materials for organic electronics and, in particular, photovoltaics. Preliminary results on the performance of **M1** and **M2** in organic solar cells and transistors will be presented and discussed.

¹ S.D. Collins, N.A. Ran, et al., *Advanced Energy Materials*, 2017, **7**, 1602242.

² A. V. Akkuratov, D. K. Susarova, et al., *Macromolecules*, 2015, **48**, 2013–2021.

***p*-Doping of poly(3-hexylthiophene-2,5-diyl)/carbon nanotubes composites with strong acceptor C₆₀F₄₈**

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Extensive research in the field of organic semiconductors demonstrates their great potential for different electronic applications. Enhancement of charge transport properties of organic semiconducting materials is still challenge which can be overcome by effective controlling molecular doping.¹ A large variety of organic molecules can serve as dopants, however, doping mechanism and efficiency still cannot be reliably predicted because of complexity of composite materials, high level of energetic disorder, strong effects of film nanomorphology, etc. Fluorinated fullerenes are one of the scantily explored strong electron acceptors which can be easily obtained via direct fluorination of fullerenes with molecular fluorine or metal fluorides.² Having in hands fluorinated fullerene C₆₀F₄₈ (Fig. 1), which is a strong acceptor with the LUMO energy of 5.2 eV and yet found to be an effective dopant for small-molecule benzothiophene derivative,³ we start our research with doping of widespread conjugated polymer, poly(3-hexylthiophene-2,5-diyl) (P3HT) and its composites with carbon nanotubes. We investigate influence of dopant concentration, P3HT/carbon nanotubes ratio on optic properties, electronic characteristics and morphologies of fabricated *p*-doped materials.

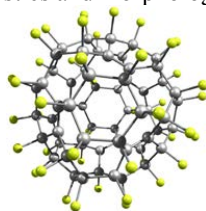


Fig. 1. Fluorinated fullerene C₆₀F₄₈ (*D*₃-symmetrical isomer).

UV-Vis absorption spectra of P3HT and fluorinated fullerene in *o*-dichlorobenzene solutions demonstrate appearance and arising of new absorption features in linear dependence with acceptor concentration due to absorption either of fluorinated fullerene anions or formation of charge transfer complexes between donor and acceptor species. Further evidence of interactions comes from quenching of P3HT fluorescence upon addition of C₆₀F₄₈. The devices with ITO/*p*-doped material/Ag architecture are constructed, and their morphology is studied by means of AFM. Space-charge limited current measurements demonstrate enhancement charge mobility in P3HT and P3HT/CNT composites of ca two order of magnitude through addition of even a small amount of C₆₀F₄₈ (ca 2 wt%).

The reported study was funded by RFBR according to the research project № 18-53-06009.

¹ Jacobs I.E., Moule A.J. *Adv.Mater.* 2017, **29**, 1703063.

² Goryunkov A.A., Ovchinnikova N.S., Trushkov I.V., Yurovskaya M.A., *Russ. Chem. Rev.*, 2007, **76**, 289.

³ Paterson A.F. et al. *Adv.Mater.* 2016, **28**, 7791–7798.

Photophysical behavior of *meta*-aminophenol in the hydrophobic environment of β -cyclodextrin nano-cage: An experimental and theoretical approach

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Meta-aminophenol (*m*-AP) is incorporated into the hydrophobic nano-cavity of β -cyclodextrin (β -CD) to form host-guest inclusion complex in aqueous medium through fluorescence spectroscopic titration method followed by gradual addition of β -CD to the aqueous solution of *m*-AP of fixed concentration (0.23 mmol L⁻¹). The fluorescence intensity of *m*-AP increases gradually, according to the increased concentration of β -CD with a hypsochromic shift of the peak energy position. These observations confirm the inclusion of *m*-AP into the hydrophobic nano-cavity of β -CD¹. The observed fluorescence intensities and values of β -CD concentration satisfy the Benesi-Hildebrand¹ equation for 1:1 inclusion complex with an association constant of 21.83 L mol⁻¹. The time-resolved spectroscopic data reveal that the average fluorescence lifetime of *m*-AP increases from 0.17 ns (in absence of β -CD) to 3.69 ns (in presence of β -CD at the highest concentration of 19.8 mmol L⁻¹). The DFT computation is done to investigate the inclusion manner of *m*-AP into the β -CD cage in gas phase in two possible orientations 'A' and 'B' as shown in the figure.

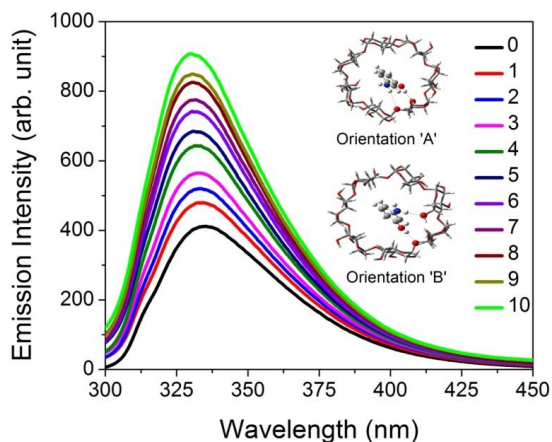


Fig. Steady state fluorescence emission spectra of *m*-AP (0.23 mmol L⁻¹) in aqueous medium in presence of β -CD at different concentrations (in mmol L⁻¹): 0 - 0; 1 - 2.11; 2 - 3.96; 3 - 5.95; 4 - 7.97; 5 - 9.87; 6 - 11.8; 7 - 13.9; 8 - 15.9; 9 - 17.8; 10 - 19.8.

¹ Chen Y., Xu T., Shen X., Gao H. *J. Photochem. Photobiol. A: Chem.* 2005, **173**, 42-50.

Nonwoven materials in the development of organic memristive element based on polyaniline/polyethylene oxide

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Memristive elements could be based on semiconductor materials, which are able to change resistance reversibly¹. An organic memristive element based on a thin polyaniline (PANI) film was firstly described by Erokhin at al². Resistivity of those elements depends on the oxidation state of the PANI via its electrochemical reaction with a silver chloride electrode, accompanied by $\text{Li}^+\text{ClO}_4^-$ ion migration through a separating polyethylene oxide (PEO) layer³. Compared with inorganic semiconductor materials, organic PANI-based memristive elements could be assembled not only by laboratory-scale thin-film technologies but also by electrospinning – a easy scalable technique for the preparation of nonwoven 3D fibrous materials⁴. Thereby the transition from planar thin-film to 3D fibrous architecture is perspective for creating stochastic neural networks.

In this work three possibilities to use a nonwoven materials or fibers in the development of memristive element will be described. Commonly in an organic PANI-PEO memristive element a PANI-contained material contacts with two electrodes and a PEO-contained material, which besides contacts with silver chloride electrode. Firstly, a PANI-contained material could have 3D fibrous morphology, conductance and wettably with PEO aqueous solution. Nonwoven PANI-contained material may be electrospun by the mixture of PANI with PEO⁵ or with other polymers and also PANI may be synthesized onto 3D fibrous matrix. Secondly, an organic memristive element could be based on a single PANI-contained fiber⁶. Prototype assembly of an organic memristive element based on single PANI/PA-6 hybrid fiber showed the possibility of using 3D nonwoven materials for creating stochastic networks of organic memristive elements on this basis. Thirdly, a nonwoven material could be electrospun by PEO solution⁷. Spinning of a nonwoven material from an aqueous PEO solution is a promising procedure for applying a polymer electrolyte layer onto memristive devices, e.g., through a template, or for uniformly coating complex 3D surfaces.

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¹ Ouyang J. *Nano Rev.* 2010, **1**, 5118.

² Erokhin V., Berzina T., Fontana M.P. *J. Appl. Phys.* 2005, **97**, 064501.

³ Demin V.A., Erokhin V.V., Kashkarov P.K., Kovalchuk M.V. *J. Appl. Phys.* 2014, **116**, 064507.

⁴ Erokhin V., Berzina T., Smerieri A., Camorani P., Erokhina S., Fontana M.P. *Nano Commun. Networks* 2010, **1**, 108–117.

⁵ Malakhova Y.N., Korovin A.N., Lapkin D.A., Malakhov S.N., Shcherban V.V., Pichkur E.B., Yakunin S.N., Demin V.A., Chvalun S.N., Erokhin V.V. *Soft Matter* 2017, **13**, 7300–7306.

⁶ Lapkin D.A., Malakhov S.N., Demin V.A., Chvalun S.N. *Tech. Phys. Lett.* 2017, **43**, 1102–1104.

⁷ Malakhova Y.N., Malakhov S.N., Kamyshinskii R.A., Belousov S.I., Chvalun S.N. *Russ. J. Appl. Chem.* 2017, **90**(9), 1540–1544.

Charge generation and recombination in single material organic solar cells based on donor-acceptor star-shaped molecules

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The performance of small-molecule organic solar cells (OSC) has been dramatically increased for the recent years. Soluble small conjugated molecules combine the advantage of a well-defined chemical structure, ease of synthesis and purification, reproducibility, and straightforward analysis of structure-property relationships. Donor-acceptor oligomers are promising materials for small-molecule organic solar cells, e.g., bulk heterojunction OSC based on star-shaped oligomers (SSO) with a triphenylamine donor core and dicyanovinyl acceptor terminal groups show the efficiency up to 5.4%¹. It was recently shown that efficient exciton-to-charge conversion occurs in SSO films even without external acceptor². This is beneficial for the operation of both bulk heterojunction OSC and single material OSC. These results stimulate further studies of such SSO molecules as a material of the active layer of highly efficient OSC. In this work, we study charge generation in single material OSCs based on N(Ph-nT-DCV-R)₃ (see Fig. 1). Charge generation, recombination and photovoltaic properties were investigated in solution-processed OSC in the structure: glass/ITO/PEDOT:PSS/N(Ph-nT-DCV-R)₃/Ca/Al. These single material OSC demonstrate the external quantum efficiency up to 23.2%, high open circuit voltage exceeding 1.1 V, as well as power conversion efficiency up to 1.1% and good shelf-life stability without encapsulation. Charge generation mechanism and recombination losses are analyzed and discussed.

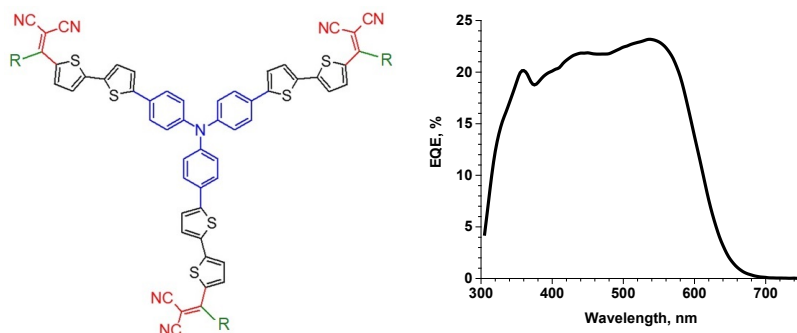


Fig. 1. Structural formula of SSO and EQE spectra for N(Ph-2T-DCV-Et)₃ solar cell.

This work was supported by Russian Science Foundation (grant 14-13-01380) and performed in the framework of leading science school NSh-5698.2018.3.

¹ Jie Min, et al. *Advanced Energy Materials*. 2014, 1400816.

² Oleg V. Kozlov, et al. *Advanced Optical Materials*. 2017, 1700024.

Fullerene derivatives as promoters or inhibitors of the photo-oxidation of conjugated polymers used in organic solar cells

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The electron spin resonance (ESR) spectroscopy was shown to be an efficient method for monitoring the quality and stability of organic semiconductor materials.¹⁻² In particular, we showed that photodegradation of conjugated polymers under inert atmosphere results in accumulation of free radical species, which can be quantitatively detected by ESR. More recently, we applied this technique for monitoring the light-induced degradation of both conjugated polymers and fullerene derivatives under natural outdoor illumination conditions at Negev desert.³⁻⁴ All these studies were performed with organic materials well sealed under argon environment and isolated from the ambient atmosphere.

In the present work, we applied ESR spectroscopy for monitoring the photooxidation of a series of conjugated polymers **P1-P5**, fullerene derivatives **F1-F3** and their composites. The samples were exposed to white light illumination for 2000 hours in the atmosphere of dry air and their oxidation behavior was assessed by periodic measurements of their ESR spectra. It has been shown that the introduction of **F1** ([60]PCBM) and **F2** ([60]ICBA) into the composites with conjugated polymers **P1-P4** leads to a minor decrease in the accumulation rates of the radical species. At the same time, the conjugated polymer **P5** comprising benzodithiophene unit in its molecular framework, undergoes accelerated degradation in the presence of fullerene derivatives **F1** and **F2**. It is quite remarkable that the addition of bispyrrolidinofullerene **F3** to all conjugated polymers **P1-P5** leads to a significant suppression of their degradation.

In conclusion, we have shown that the rate of the oxidation of conjugated polymers and fullerene derivatives, reflected in the accumulation of free radical species, depends on the peculiarities of their molecular structures. Mixing polymers with the conventional fullerene derivatives **F1-F2** might either inhibit or facilitate their photodegradation. On the contrary, fullerene derivative **F3** can be considered as efficient and highly promising stabilizer for all conjugated polymers suppressing strongly their light-induced oxidation in air. Fullerene derivative **F3** and other emerging antioxidants might play an important role in further commercialization of organic solar cells.

This work was supported by RFBR (project № 18-33-01086_mol_a).

¹ L. A. Frolova, N. P. Piven, D. K. Susarova, A. V. Akkuratov, S. D. Babenko and P. A. Troshin, *Chem. Commun.*, 2015, **51**, 2242.

² D. K. Susarova, N. P. Piven, A. V. Akkuratov, L. A. Frolova, M. S. Polinskaya, S. A. Ponomarenko, S. D. Babenko and P. A. Troshin, *Chem. Commun.*, 2015, **51**, 2239.

³ A. I. Shames, L. N. Inasaridze, A. V. Akkuratov, A. E. Goryachev, E. A. Katz and P. A. Troshin, *J. Mater. Chem. A*, 2016, **4**, 13166.

⁴ L. N. N. Inasaridze, A. I. I. Shames, I. V. V. Martynov, B. Li, A. V. V. Mumyatov, D. K. K. Susarova, E. A. A. Katz and P. A. A. Troshin, *J. Mater. Chem. A*, 2017, **5**, 8044.

Electrochemical formation of ZnO(Al) films for photoanodes in photovoltaic devices

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Transparent conductive oxides, such as indium tin oxide (ITO), ZnO, SnO₂, have a high transmittance in the visible region combined with good conductivity, which attract the attention of scientists for their use as electrodes in solar cells. Materials based on doped ZnO are an alternative to ITO due to the high cost of indium. Also topical tasks are the improvement of industrial technologies and laboratory methods for obtaining such doped films, increasing the efficiency of existing equipment for applying films to large-area substrates and parts with a complex developed surface with good reproducibility, with a high degree of homogeneity.

The purpose of the present work is the electrochemical preparation of doped semiconductor ZnO(Al) films and the study the correlation of film microstructure with optical characteristics. This approach allows to monitor the synthesis by chronoampero/coulometry and vary the morphology and composition of the sample by changing the parameters of electrodeposition. The thickness of the formed structure can be precisely controlled by varying the charge of deposition.

In the work the following electrolyte compositions and parameters for obtaining ZnO films were developed: 1) a non-aqueous DMSO electrolyte of the composition: Zn(Ac)₂, LiTFSI, H₂O₂; precipitation potential: -1.6 V; 2) aqueous: Zn(Ac)₂, NaNO₃, C₂H₅OH, NaEDTA; deposition potential: -1.05 V. It should be noted that one of the criteria for the desired results is film parameters such as continuity, as well as optimum optical characteristics, also the lifetime and mobility of charge carriers depend on the grain size. The most continuous ZnO films were formed from an acetate nonaqueous electrolyte, with a grain size of 150 ± 50 nm, calculated from microphotographs. According to the EDX data, the metal is uniformly distributed over the whole area of the sample. According to XRD data, the presence of Zn and ZnO phases in the film is confirmed despite the use of H₂O₂ and acetate ions in the electrolyte to form oxide films without a metal phase during electrodeposition. The obtained samples were annealed at 500 °C for 3 hours in order to oxidize the films. According to XRD data, the size of the coherent scattering region was about 250 nm.

To obtain doped samples, a non-aqueous acetate zinc electrolyte with the addition of Al(NO₃)₃ was chosen. In the work, several series of samples with an Al content of 1 to 10 atom% were obtained. To determine the influence of the synthesis temperature on the structural and optical properties of ZnO(Al) films, the resulting films were annealed at a temperature of 350 °C, 450 °C, 500 °C. The increase in temperature leads to the sealing of the film by decreasing the grain to 100 nm, which leads to an improvement in optical properties of the films.

Optical transmittance is an important optical parameter for transparent conductive oxides. The optical transmission spectra of ZnO films showed that all films are transparent in visible regions. The obtained ZnO (Al) films are characterized by a high transmittance in the visible range. For films with a thickness of about 300 nm the light transmission values are in the range of 60-90 % at 550 nm, which is comparable with the best literature data, and the best values belonging to doped films, reaches 90% in the case of 4 at.% Al content. Such optical characteristics and continuity of these oxide films are promising for their application in photovoltaic cells.

Investigating the influence of morphology on the charge-carrier mobility in organic field-effect transistors

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For organic semiconductors it is well known that the charge-carrier mobility depends sensitively on the morphology of the organic semiconductor film. The charge-carrier mobility, however, is one of the most important properties for the application of organic semiconductors as it determines the performance of devices such as organic solar cells and field-effect transistors (OFETs). Yet, there is no comprehensive theoretical description available for this complex morphology-mobility relationship. Here, we use a kinetic Monte Carlo model to simulate charge transport in OFETs in order to investigate the interplay between the morphology of the semiconductor and the charge-carrier mobility. We find that the charge-carrier mobility increases with the length of conjugated segments. It is especially enhanced if the conjugated segments are randomly displaced, i.e. with a more disordered morphology. Moreover, we show that charge transport mainly takes place in the first and second layer of the semiconductor and therefore impacts on the charge-carrier mobility in ordered layers.

This work was supported by German National Science Foundation DFG (GRK 1640), the Bavarian State Ministry of Science, Research, and the Arts for the Collaborative Research Network “Solar Technologies go Hybrid” and the Volkswagen foundation for funding in the framework of the “Trilaterale Partnerschaften”.

Assessment of charge transfer reorganization energy for organic semiconductors by Raman spectroscopy

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In recent years, the fabrication of flexible, transparent and cheap electronic devices based on organic semiconductors is interesting for researching. High mobility of charge carriers is necessary for efficient operation of such devices. The interaction of charges with intra – and intermolecular vibrations is one of the key factors influencing the mobility of carriers in organic semiconductors. Raman spectrum is sensitive to changes in the polarizability of molecules and intermolecular interactions. Thus, Raman spectroscopy can investigate the role of vibrations in the charge transport. High frequency spectral region is associated with intramolecular vibrations¹.

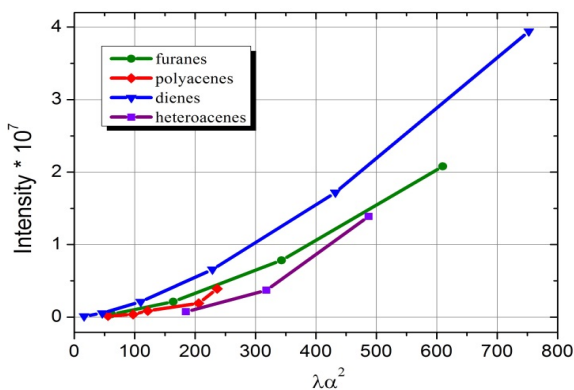


Fig.1 Correlation between integral intensity, energy of reorganization and polarizability for different series of molecules.

In this work, for the first time it was revealed theoretically that the integral intensity of Raman scattering in the high-frequency region (above 200 cm⁻¹) is directly related to the polarizability of the molecule α and the reorganization energy λ . Reorganization energy is estimate of impact of vibrations on the charge transport. On the basis of the density functional theory (DFT) calculations is revealed that Raman intensity increases monotonically with the $\lambda\alpha^2$. The established correlation can be used for estimation of reorganization energy from experimental Raman spectrum.

This work was supported by RFFI (project № 17-02-00841).

¹ Myers A.B. *Chemical Reviews*, **96**, 911-926, 1996.

Photoactive layer / metal electrode interface as one of the origins of the burn-in degradation of organic solar cells

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Organic photovoltaics (OPVs) represents an exciting solar energy conversion technology¹. Organic semiconductor materials can be solution-processed onto flexible substrates, enabling fast and inexpensive manufacturing of OPV modules. Both the capital expense and energy payback period of OPVs are projected to be less than that of other photovoltaic products^{2,3,4}. The efficiencies of the best laboratory prototypes of organic solar cells have reached 13.2%⁵, while their commercial application is hampered severely by a number of factors. Low operation stability of organic solar cells is considered as the main limitation to the moment^{6,7,8}.

There are three major degradation regimes observed in OPVs: an initial period of rapid superlinear efficiency decay, which slows down with time (burn-in), a period of relatively slow linear degradation that lasts for the most of the solar cell's usable lifetime (long-term), followed up by a rapid and complete device failure (failure). Although the length of the burn-in period usually stays within a few hundred hours, the decrease in the device efficiency can be dramatic and amount up to 50% of the initial values. The mechanisms and origins of the burn-in process are intensively discussed in OPV community, while no clear and universal model has been elaborated to date.

In this work, we focused on the investigation of the interfacial effects occurring between the photoactive blend and top metal electrode of the device in the context of their impact on the burn-in degradation behavior of organic solar cells. We have found that interfacial degradation at the metal/organic interface is a cause of the rapid drop in the efficiency of the solar cells based on a certain group of photovoltaic materials. Particularly remarkable was the discovery of the opposite behavior: depositing metal cathode on top of photoactive blend can slow down remarkably the burn-in degradation of the devices based on some conjugated polymers as compared to the samples, which were aged under identical conditions without top electrodes. Thus, we show that the nature of the metal/organic interface can govern the operation behavior of organic solar cells leading either to improved device stability or complete failure depending on the realized physicochemical mechanisms. The results of the performed experiments and some details of the revealed mechanisms will be discussed in this presentation.

¹ D. M. DeLongchamp et al, *Springer*, 2016, pp. 25–74.

² S. B. Darling et al, *RSC Adv.*, 2013, **3**, 17633

³ P. C. Dastoor et al, *Sol. Energy Mater. Sol. Cells*, 2014, **120**, 9.

⁴ F. C. Krebs et al, *Sol. Energy Mater. Sol. Cells*, 2013, **119**, 84.

⁵ F. C. S. P. Thanks, M. Pfeiffer, "Heliatek sets new Organic Photovoltaic world record efficiency of 13.2%," <http://www.heliatek.com/en/press/press-releases/details/heliatek-sets-new-organic-photovoltaic-world-record-efficiency-of-13-2> 2016 (accessed: Nov 2016).

⁶ J. Nelson et al, *Adv. Mater.* 2013, **25**, 1847

⁷ P. C. Dastoor et al, *Sol. Energy Mater. Sol. Cells*, 2014, **120**, 9.

⁸ J. Nelson et al, *Energy Environ. Sci.*, 2011, **4**, 3741.

Infrared spectroscopic study on solution-processed metal oxides as efficient charge transport layer in organic photovoltaic cells

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Organic photovoltaic cells (OPVs) have received increasing attention over the past years as potentially printable low-cost alternatives to silicon based semiconductor devices. The performance of OPVs is significantly influenced by the properties of the interfaces between the layers. Increasing the interfacial compatibility especially between the transparent conductive oxide electrode and the organic semiconductor layer can improve the charge carrier transport through the stack and thus the efficiency of the device. Thin films of nickel oxide (NiO) have shown promising characteristics as hole extraction layers in OPVs.^{1,2}

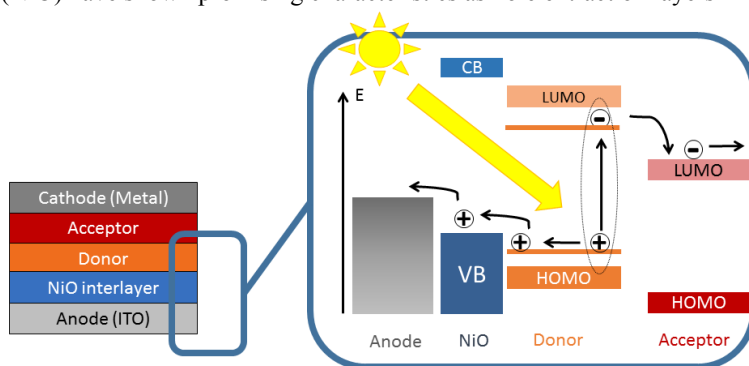


Fig. 1. Schematic view of the organic photovoltaic cell (OPV) layer stack and the corresponding energy diagram. The nickel oxide (NiO) interlayer improves the band alignment between the anode and the organic semiconductor.

In our studies, solution-processed NiO surfaces were passivated by self-assembled monolayers (SAMs) to tune the work function and to reduce the surface reactivity.³ Infrared spectroscopy gives insight into the composition of the investigated material and can monitor orientation of characteristic vibrations or functional groups. We studied the influence of oxygen plasma treatment and annealing temperature on bulk and surface properties. The results show that nickel hydroxide and nickel oxyhydroxide play an important role for the binding mechanism of SAMs on the NiO surface.

The work was financially supported by the German Federal Ministry of Education and Research (BMBF) within the INTERPHASE project and the German Science Foundation (DFG) within the collaborative research center SFB 1249. V.R. acknowledges financial travel support from the Heidelberg Graduate School for Fundamental Physics (HGSFP).

¹ Manders et al, *Adv. Func. Mater.*, 2012, **22** (2), 405-414.

² Steirer et al, *J. Mater. Chem. A*, 2015, **3** (20), 10949-10958

³ Hietzschold et al, *ACS Appl. Mater. Interfaces*, 2017, **9** (45), 39821–39829

Application of spectral technique for accurate efficiency measurements of organic and perovskite solar cells

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As the power conversion efficiency (PCE) is a key driver of solar photovoltaics, accurate PCE measurement is of key importance. PCE of a solar cell is calculated from its current–voltage characteristic measured under illumination of standard solar spectrum (AM1.5G). However, in laboratory conditions the standard spectrum is usually simulated with noticeable deviation (Fig.1). As a result, the short-circuit current (and hence, PCE) under simulator illumination differs from that of standard illumination. In this work, we applied the spectral technique¹, which takes into account the cell spectral response and a spectral mismatch between the standard solar (AM1.5G) and the simulator spectra. As a result, we obtained the correction factor for the measured short-circuit current (Table 1).

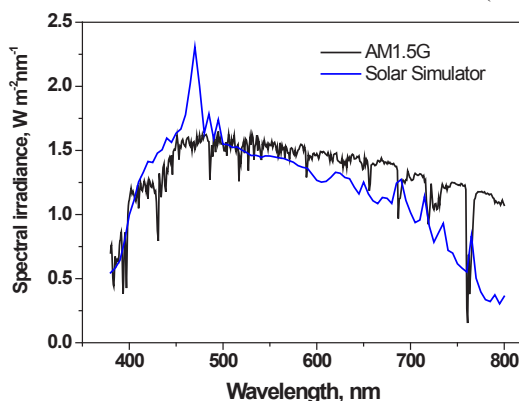


Fig. 1. Spectral irradiance of AM1.5G and Newport 67005 solar simulator spectra.

We studied active materials for solar cells with different absorption spectra: perovskite and donor-acceptor small molecule:PC₇₁BM blend (Table 1). The results showed that the spectral technique is a convenient and reliable tool to compensate the spectral mismatch between the simulator and standard solar spectra and, therefore, to evaluate the PCE under true AM1.5G in the laboratory conditions.

Solar cell	J_{sc} , mA/cm ²	V_{oc} , V	FF, %	PCE, %	$K = \frac{J_{ss}}{J_{AM1.5G}}$
N(Ph-2T-DCV-Et) ₃ : PC ₇₁ BM	7.25	0.96	52.1	4.13±0.16	1.02
Perovskite	13.66	1.02	65.6	9.01±0.35	1.06

Table 1. Photoelectrical characteristics of measured solar cells.

This work was supported by Russian Science Foundation (grant 14-13-01380). The authors would like to thank P. Troshin and S. Tsarev for perovskite solar cell samples, S. Ponomarenko and A. Solodukhin for provided materials.

¹ A.Yu. Gavrik, et al. *Book of abstracts (IFSOE-2014)*. 2014, p. 55.

Excited States Dynamics in TIPS-Pentacene Studied with Femtosecond Time-Resolved Second Harmonic Generation

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Understanding the ultrafast excited state dynamics in organic semiconductors after optical excitation is a key requisite on the road towards the design of efficient organic solar cells (OPV). Recently, the singlet fission process has gained much attention since it may improve the energy conversion efficiency in OPVs. In this work we monitored the ultrafast (sub-picosecond) excited states dynamics in TIPS-Pentacene (TIPS-Pn) using time-resolved second harmonic generation (TR-SHG). Sapphire was used as non-interacting substrate to analyse the dynamics of excitonic species in TIPS-Pn films. Thereby the dynamics of singlet fission process could be resolved. The process consists of the generation of singlet excitons localized on a single molecule followed by the fission into two triplet excitons on two TIPS-Pn molecules. While the overall singlet fission process occurred within 200fs, we could also resolve the transfer from the singlet exciton state to the mediating multiexciton state.

This work was supported by the German Research Foundation (DFG) through the collaborative research center SFB 1249 (project B06).

Langmuir films of organosilicon conjugated oligomers: thermodynamics of their self-assembly on the water surface

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Recently self-assembled monolayer field effect transistors (SAMFETs) have gathered much attention. High charge carrier mobility demonstrated by monolayer films¹ in conjunction with ultralow semiconductor thickness enable SAMFETs to become a universal platform for various sensor applications.² A number of effective strategies for dense monolayer formation has been demonstrated up to date. Among them Langmuir techniques are notable because of their simplicity, fast deposition, scalability and possibility of precise control of the monolayer formation process on the subphase.^{3,4} Chemical structure of the molecules used for the Langmuir monolayer formation has a dramatic impact on both film morphology and its electrical properties.⁵ Considering that the self-assembly of Langmuir films is heavily governed by the thermodynamics of the system, it is actual to find a relationships between thermodynamic parameters of organosilicon conjugated oligomers and their Langmuir monolayer formation and properties.

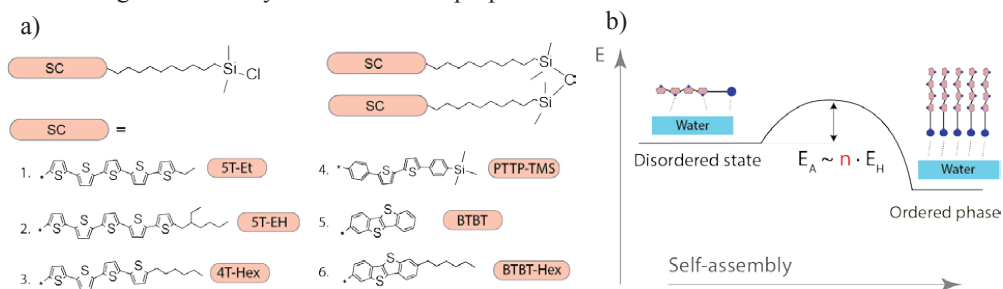


Fig. 1. Chemical structure of investigated organosilicon conjugated oligomers (a); energy diagram of the self-assembly process of the Langmuir film (b).

In this work we suggest a simple model considering thermodynamic characteristics of conjugated amphiphilic molecules and allowing to describe formation of their Langmuir monolayers on the water surface under the external barrier pressure. To prove the model validity, we apply it to a series of organosilicon conjugated oligomers (Fig. 1a). In order to evaluate the Gibbs energy of the Langmuir film, we use the thermodynamic parameters of the bulk films, additionally taking into account the impact of the subphase (Fig. 1b). It was found, that the model successfully predicts the morphology of Langmuir films of organosilicon conjugated oligomers based on their DSC data and chemical structure. We suggest the model to be universal and therefore applicable for the design of novel monolayer semiconductors.

This work was performed in the framework of leading science school NSh-5698.2018.3. Authors are also grateful to RFBR (grant 18-33-01210) for financial support.

¹ M. Li, D. K. Mangalore, J. Zhao, et al. *Nat Commun* 2018, **9**, 451.

² B. Peng, S. Huang, Z. Zhou, et al. *Adv Funct Mater* 2017, **27**, 1700999.

³ E. V. Agina, A. A. Mannanov, A. S. Sizov, et al. *ACS Appl Mater Interfaces* 2017, **9**, 18078.

⁴ O. V. Borshchev, A. S. Sizov, E. V. Agina, et al. *Chem Commun* 2017, **53**, 885.

⁵ E. V. Agina, A. S. Sizov, D. S. Anisimov, et al. *Proc. SPIE* 2015, **9568**, 95680Z.

New nanostructured luminophores based on 1,3,5-benzene

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The demand for organic luminophores is due to their wide range of applications in modern high-tech devices - organic light-emitting diodes, luminescent concentrators for photovoltaic cell, lasers with optical pumping, chemo- and biosensors, plastic and liquid scintillators, spectroscopic optical fibers, etc.

Recently, we have developed nanostructured organosilicon luminophores (NOLs), consisting of two types of covalently bonded via silicon atoms organic luminophores with efficient Förster energy transfer between them [1-3]. They combine the best properties of organic luminophores and inorganic quantum dots. On the other hand, it is known that the addition of conjugated fragments to the positions of the 1,3,5 benzene ring leads to a disruption of the conjugation between them [4-5]. Therefore, the use of the 1,3,5-benzene ring as branching center instead of a silicon atom is an interesting scientific task.

In this work, silicon less analogues of NOLs based on 1,3,5-benzene will be obtained (fig.1), their properties will be studied and compared with the properties of NOLs both in dilute solutions and in polymer thin films.

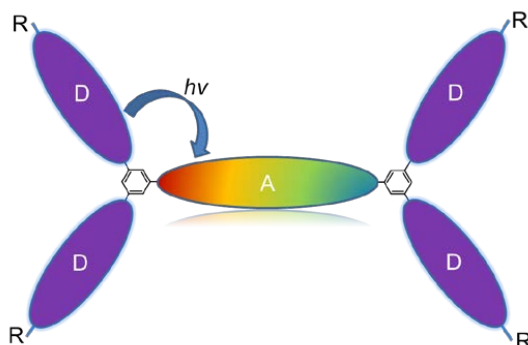


Fig.1. Representative structure of nanostructured luminophores based on 1,3,5-benzene.

Also, model compounds will be obtained. Studying their electronic absorption and fluorescence spectra will help to establish the structural fragments responsible for the absorption and luminescence in molecules based on 1,3,5-benzene.

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

² S.A. Ponomarenko, O.V. Borshchev, N.M. Surin et al., *Proc. of SPIE* 2017, **103440**

³ S.A. Ponomarenko, N.M. Surin, O.V. Borshchev et al., *Proc. of SPIE* 2015, **9545**

⁴ S.A. Ponomarenko, S. Kirchmeyer, A. Elschner et al., *Adv. Funct. Mater.* 2003, **13**, 591

⁵ M. H. van der Veen, M. T. Rispens, H. T. Jonkman, J. C. Hummelen *Adv. Funct. Mater.* 2004, **14**, 215

Novel organosilicon luminophores based on arylenevinylenes for organic photonics

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A special place among the materials for organic photonics and electronics is occupied by various arylenevinylenes. After the discovery of electroluminescence in poly(arylenevinylenes) [1], they have been successfully used in organic light-emitting diodes (OLED), organic field effect transistors (OFET), organic photovoltaic cells and others devices. The good optical properties of such conjugate building blocks and synthetic versatility make them particularly interesting for application in NOLs (Nanostructured organosilicon luminophores) [2].

In this work, a number of new organosilicon oligo - and poly(arylenevinylenes) linear and branched structures will be developed and synthesized (Fig.1). Several approaches to the synthesis of organosilicon arylenevinylenes will be reviewed during the execution of work. The advantages and disadvantages of each method will be discussed. The main aims of the work are to develop approaches to the synthesis of new organosilicon oligo - and poly(arylenevinylenes) linear and branched structures, and to identify the relationship between their molecular structure and physicochemical properties (solubility, optical properties and phase behavior).

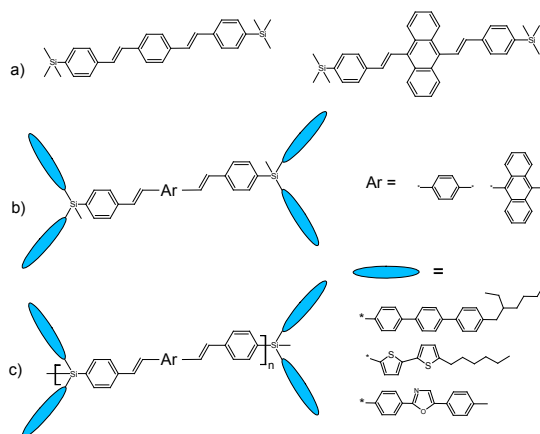


Fig.1. Representative structure of luminophores based on arylenevinylenes.

This work was performed in the framework of leading science school NSh-5698.2018.3 under support of grant of RFBR 18-03-00699

¹ J.H. Burroughes, D.D.C Bradley, A.R. Brown et al. *Nature*. 1990, **347**, 539

² S.A. Ponomarenko, N.M. Surin, O.V. Borshchev et al., *Scientific Reports* 2014, **4**, 6549.

Influence of the carboxylic acid anhydride substitution on the electronic properties of the ultra thin naphthalene films

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Ultra thin films made from perylene-tetracarboxylic dianhydride (PTCDA) and naphthalene-tetracarboxylic dianhydride (NTCDA) are known as electron acceptor materials in organic electronics¹. One of the possibilities to tune the materials' and the devices characteristics is to attach various substituent groups to the aromatic core of the molecules.

In the present work the conduction band electronic structure of dicarboxylic-substituted naphthalene (NDCA) films deposited onto the surface of oxidized Si was studied and measured using the total current spectroscopy (TCS) technique in the electron energy range from 5 eV to 20 eV above the Fermi level. Based on the experimental and theoretical results, the energy position of the main DOUS peaks of the NDCA film was established and a comparison with the position of the DOUS peak of the tetracarboxylic-substituted naphthalene (NTCDA) film was made. Theoretical analysis included the calculation of the energies and spatial distribution of molecular orbitals using the DFT method at the B3LYP/6-31G (d) level and the subsequent correction method of the calculated values of the orbital energies, developed particularly for the small conjugated organic molecules.

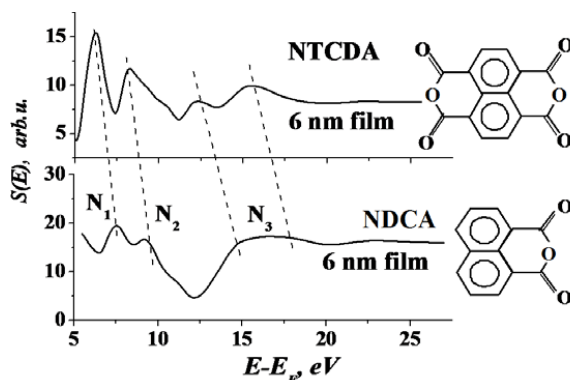


Fig.1. The TCS fine structure of the NTCDA and NDCA films. The relative energy shifts of the corresponding TCS peaks are shown by the dashed lines.

The work was supported by the RFBR grants 18-03-00020 and 18-03-00179. The measurements were performed partly at the Centre "Physical methods of surface investigation" of the Research park of St. Petersburg State University.

¹ R. Tonner, P. Rosenowa, P. Jakob. *Phys. Chem. Chem. Phys.*, 2016, **18**, 6316.

Modification of the work function and of the conduction band density of states profile using end substituents in thiophene/phenylene co-oligomers

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Ultrathin thiophene/phenylene co-oligomer (TPCO) films have previously shown their potential for diode like and OLED device applications as one-layer and as multilayer structures. The difference in the electronic properties of the layers is achieved by the layer doping and by using substituted thiophene/phenylene molecules.

In the present work the potential barrier formation (Fig. 1) and the conduction band density of the unoccupied states (DOUS) were studied using the total current spectroscopy (TCS) technique at the interfaces of the dimethyl-TPCO and of the bis-trifluoromethyl-TPCO films of 5-10 nm thickness deposited by means of thermal evaporation on the surface of the oxidized Si. The work function values of the two types of the TPCO films studied differed approximately 0.6 eV.

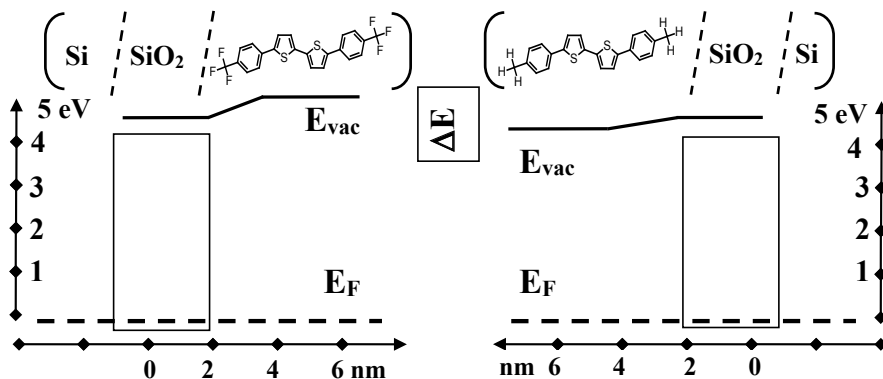


Fig.1. The schematic illustration of the work function value formation in the structures studied. The organic layers were made from CF_3 -phenylene-thiophene-thiophene-phenylene- CF_3 and from CH_3 -phenylene-thiophene-thiophene-phenylene- CH_3 molecules reported earlier.¹

The work was supported by the RFBR grants 18-03-00020 and 18-03-00179. The measurements were performed partly at the Centre "Physical methods of surface investigation" of the Research park of St. Petersburg State University.

¹ V.A. Postnikov, Y.I. Odarchenko, A.V. Iovlev, V.V. Bruevich, A.Yu. Pereverzev, L.G. Kudryashova, V.V. Sobornov, L. Vidal, D. Chernyshov, Y.N. Luponosov, O.V. Borshchev, N.M. Surin, S.A. Ponomarenko, D.A. Ivanov, D.Yu. Paraschuk. *Cryst. Growth Des.*, 2014, **14** (4), 1726–1737.

Novel donor-acceptor triphenylamine-based oligomers of different architecture for organic photovoltaics

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Donor-acceptor oligomers based on electron-donating triphenylamine are promising semiconductor materials for organic photovoltaics^{1, 2, 3, 4, 5, 6, 7}. In this work novel donor-acceptor oligomers having 1, 2 or 3 oligothiophene arms attached to triphenylamine core and end-capped with electron withdrawing either alkyl- or phenyldicyanovinyl or pristine dicyanovinyl groups were synthesized, investigated and compared to each other (Figure 1).

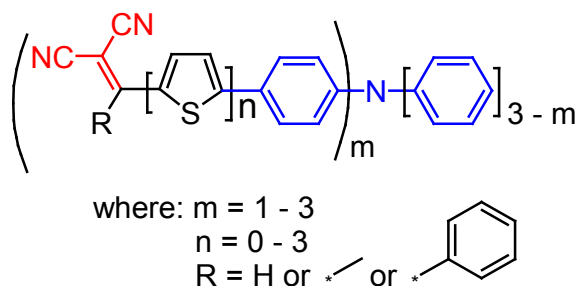


Fig. 1. Schematic representation of donor-acceptor oligomers based on triphenylamine.

Variations of different parameters of their chemical structures such as length and number of oligothiophene blocks and type of substituents at the acceptor group were used to study the structure – properties - device performance relationships and in this new type of molecules.

The work in the part of synthesis and investigations of star-shaped oligomers was supported by Russian Science Foundation (14-13-01380), whereas unsymmetrical molecules were supported by Russian Science Foundation (17-73-10485). The work was performed in the framework of leading science school NSh-5698.2018.3.

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

² Ponomarenko S.A., Luponosov Y.N., Min J. et al. *Faraday Discuss.*, 2014, **174**, 313-339.

³ Do K., Kim C., Song K. et al. *Solar Energy Materials & Solar Cells*, 2013, **115**, 52–57.

⁴ Kozlov O.V., Luponosov Y.N., Solodukhin A.N. et al. *Organic Electronics*, 2018, **53**, 185-190.

⁵ Kozlov O.V., Luponosov Y.N., Solodukhin A.N. et al. *Adv. Optical Mater.*, 2017, **5**(7), 1700024.

⁶ Luponosov Y.N., Solodukhin A.N., Mannanov A.L. et al. *Organic Electronics*, 2017, **51**, 180-189.

⁷ Kozlov O.V., Liu X., Luponosov Y.N. et al. *J. Phys. Chem. C*, 2017, **121**, 6424–6435.

The impact of the molecular structure of conjugation polymers on the indoor operation stability of solar cells

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An important aspect for the practical application of organic solar cells is the long-term operational stability of the devices. This parameter depends on a variety of factors, such as the photochemical and thermal stability of semiconductor materials and their composites, interfacial adhesion and compatibility of functional layers in solar cells, the quality of encapsulation of prepared devices with respect to elimination of harmful effects of the ambient environment. Among all the aforementioned factors, the characteristics of the photoactive layer have the greatest impact at the stable solar cell operation. Therefore, degradation processes occurring in electron donor conjugated polymers play a key role in ensuring long-term stability of the devices.

Here we explored the operation stability of organic solar cells assembled using a panel of structurally different conjugated polymers. The experiments were carried out in the inert atmosphere of the MBraum glove box under continuous illumination provided by metal halide lamps in a special experimental chamber. The power of the light flux at the sample holder was about 60 mW/cm², the temperature in the sample chamber was 82-85 °C to reproduce, as closely as possible, the real operation conditions of the encapsulated solar cells.

We compared the behavior of four different conjugated polymers (P1-4) in the blends with the fullerene derivative [60]PCBM against the reference P3HT/[60]PCBM system. The obtained results showed that devices based on conjugated polymers comprising fluorene (P1), benzodithiophene (P2) and silafluorene (P3) structural blocks exhibit higher operation stability under inert atmosphere conditions as compared to the cells based on P3HT. In particular, continuous aging of the devices under open circuit for 3000 hours leads to a decrease in the efficiency of their by less than 20%.

The obtained results strongly suggest that the designed conjugated polymers are promising materials for development of efficient and stable organic solar cells.

This work was supported by RFBR (project № 18-33-01086_mol_a).

Novel D- π -A chromophores based on the hydrazonocyclopentadiene accepting moiety

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Synthesis of π -conjugated systems with the donor- π -acceptor structure (D- π -A) is one of the important directions in the development of organic materials that can be used to create molecular electronic devices. We focused our investigations on the development of novel acceptor moiety for this type of chromophores, particularly on the use of previously unexplored electron-deficient hydrazonocyclopentadienes. This fragment is interesting due to its polarization, similar to that in fulvenes, where the negative charge is stabilized not only by the cyclopentadienyl moiety, but also by electron-withdrawing substituents in it¹.

We have developed three approaches for the synthesis of dyes containing a hydrazonocyclopentadiene fragment which include the decarboxylative azo-coupling reaction of cyclopentadienides, derivation of cyclopentadienones and the reaction of organometallic compounds with diazocyclopentadienes. The last one is especially important for thiophene containing dyes which are not available via the other two. Additionally, a number of precursor dyes containing functionalizable fragments were synthesized and were further used in the synthesis of extended conjugated systems. Using this approach, we obtained donor-linker tandems containing either biphenyl or stilbene linkers and a triphenylamine donor part.

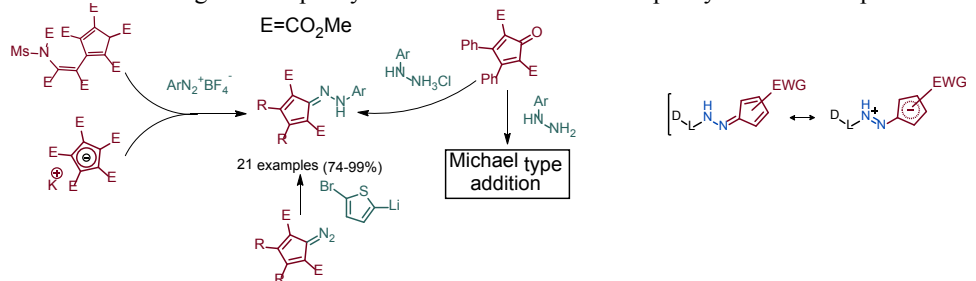


Fig. 1. Synthesis of hydrazonocyclopentadienes

All products were investigated in terms of their optical properties and demonstrated intense absorption within 450-550 nm and mild solvatochromism. A derivative containing four ester groups at the acceptor fragment showed considerable blue shift in the presence of sodium methylate as a base which can find application in pH dependent on-off sensors. Electrochemical properties investigations as well as thermogravimetric analysis of the most promising compounds were carried out.

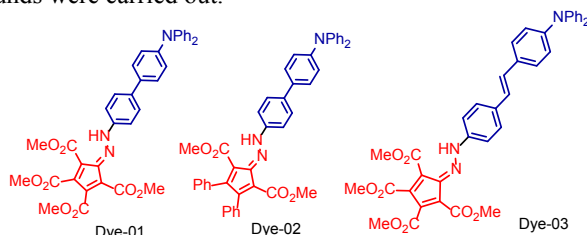


Fig. 2. Linker containing chromophores

¹ Platonov D. N., Okonnishnikova G. P., Salikov R. F., Tomilov Y. V. *Tetrahedron Lett.* 2015, **57**, 4311–4313.

Light-induced processes in the multilayer structures incorporating molecular and perovskite-type materials

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Perovskite-like photoabsorbers are the most probable candidates for the next generation photoconvertors due to the unique combination of optoelectronic properties, processability and relatively small manufacturing costs. Nonetheless, singularities of solid-state arrangement and chemical composition underpin the instability of device performance, which is besides affected by environmental factors. Degradation mechanisms in the hybrid (organic/inorganic) or in more stable inorganic perovskite structures for solar cells are increasingly studied in the last years¹.

In the previous work², we investigated the light induced degradation of hybrid and inorganic perovskites in thin films and in the HTL/perovskite/ETL multilayer structures. It was found out that in absence of the environmental factors, current and/or temperature stress, the light-induced degradation of perovskites occurs within the characteristic time of few hours, being facilitated by the internal (chemical) sources that inherently exist in the multilayer structure.

In this work, we report on analytical studies of the archetypical thin-film perovskite-based photoconverters using X-ray diffraction and reflectometry (GIXRD, XRR), mass-spectrometry (ToF-SIMS with depth profiling) and optical spectroscopy. The all-inorganic perovskite thin-films with lead iodide as a matrix and molecular functional layers were deposited on the different substrate materials (transparent and opaque for the UV-Vis irradiation) using the vacuum evaporation technique. For thus obtained structures, the static and dynamic J-V measurements were carried in the laboratory conditions or in the inert atmosphere using illumination sources with varying intensity and spectral range. In parallel, the chemical composition, thin-film morphology (surface relief, crystal arrangement) and optical absorbance were controlled.

The most representative results are discussed and conclusions on the possible degradation mechanisms in multilayer structures with the vacuum-deposited perovskites are made.

This work was supported by RSF (project № 17-79-10397)

¹ Ono L.K., Leyden M.R., Wang S., Qi Y. *J.Mat.Sci.* 2016, **4**, 6655–7074.

² Travkin V.V., Pakhomov G.L., Yunin P.A., Drozdov M.N. *Acta Phys.Pol.A.* in press.

Organic single-crystal light-emitting transistors with polycrystalline under-electrode interlayers

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Organic light emitting transistors (OLETs) are perspective optoelectronic devices that combine the light-generation capability with the switching ability of organic field-effect transistors (OFETs). OLETs can overcome equivalent OLEDs by external quantum efficiencies¹ and have a potential application in lighting, displays and injection lasers technologies. Light generation in OLETs requires recombination of holes and electrons making efficient injection/transport in the active layer of both necessary. Considering difference in HOMO and LUMO energy levels, widely used approach is the combination of two different metals with low and high work functions for injection of holes and electrons, respectively. Widely used low work function metals as Ca and Al are unstable and being rapidly oxidized in air. Achieving low electron and hole injection barriers from air-stable electrodes is a challenging task. Recently, a novel concept of efficient electrode composed of polycrystalline organic semiconductors (pc-OSC), which is the same as the single crystal (sc-OSC) active layer, covered by a metal (Ca or Au) layer was proposed².

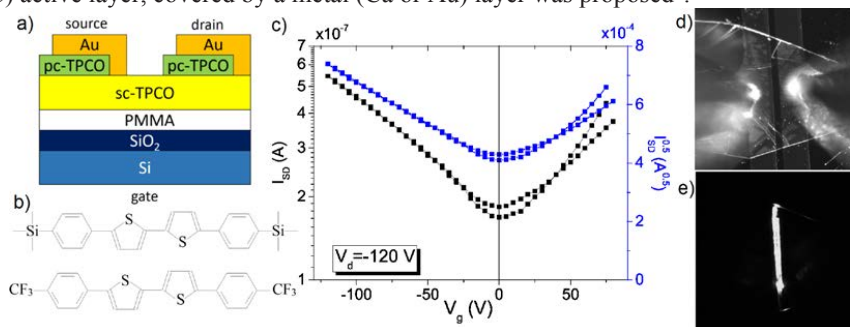


Fig. 1. (a) Structure of OLET with under-electrode polycrystalline interlayers. (b) Structural formulas of some of the studied OSCs. (c) OLET transfer characteristics. (d) OLET image. (e) Light emission from the OLET channel.

In this work, we develop this concept by using under-electrode pc-OSC, whose chemical structure is different from the sc-OSC used as the active layer, the proposed OLET structure is shown in Figure 1a. Specifically, we use OSC oligomers with the same conjugated moiety, but different terminal substituents (Fig. 1b). The interlayer allows efficient ambipolar injection from gold electrodes (Fig. 1c) resulting in strong light emission (Fig. 1e), while OFETs with conventional gold electrodes demonstrate only unipolar hole transport without light emission. We compare OLETs with different combinations of sc-OSC (active layer) and pc-OSC (interlayer) and study the influence of the interlayer on the apparent mobility, threshold voltage, contact effects and light emission.

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

¹ Capelli R., et al, *Nature Materials*, 2010, **9**, 496.

² Kanagasekran T., et al, *Nature Comm.*, 2017, **8**, 999.

Toxic gas detection with fully printed organic field-effect transistor

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The aim of the work was to investigate the influence of toxic gases presence in air atmosphere on electrical properties of recently developed fully printed organic field-effect transistors (OFETs)¹. Fully printed OFETs were fabricated in bottom gate bottom contact architecture by inkjet printing of functional inks: silver gate, source and drain electrodes from Ag nanoparticles; dielectric layer from cross-linked poly(4-vinyl phenol); passivation layer from pentafluorothiophenol and semiconducting layer from FS-0096 (Flexinks Inc.).

Such devices demonstrate good electrical behavior, which is typical for p-type semiconductors (Fig. 1a). Saturated mobility, threshold voltage and on-off ratio were found to be in range of 10^{-3} - 10^{-2} $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, $-3\dots+3$ V and 10^2 - 10^3 , correspondingly.

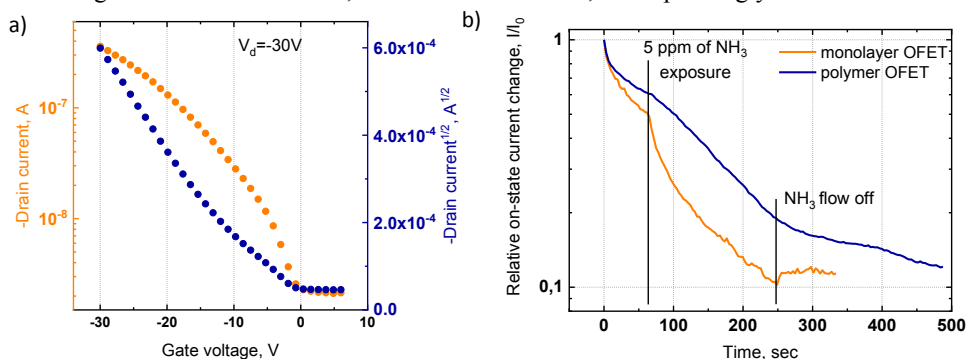


Figure 1. a) Typical transfer characteristics of fully printed polymer OFETs; b) Dynamic response of monolayer and polymer OFETs on 5 ppm of ammonia.

It was found that polymer OFETs can be utilized as highly sensitive gas sensors for detection of extremely low concentration of toxic gases. Figure 1b demonstrates dynamic response of fully printed OFET on 5 ppm of ammonia in dry air. The lowest measured concentration of toxic gases was 100 ppb of ammonia and theoretical limit of detection was found to be 30 ppb, that is almost the same value for sensors based on monolayer Langmuir-Schaefer OFETs recently developed by our group. However, it should be noted that response time of polymer OFETs is much higher than for monolayer OFETs. Probably, slow diffusion of toxic gas molecules into thick semiconducting layer to the semiconductor-dielectric interface is the reason of observed behavior.

Concentration dependence of sensor response to ammonia and hydrogen sulfide as well as repeatability and reproducibility of sensor response were thoroughly investigated. The obtained data are compared with the same for the sensors based on monolayer OFETs.

The work was performed in the framework of leading science school NSh-5698.2018.3 and supported by RFBR (project № 17-03-00222).

¹ E. Sowade, E. Ramon, K. Y. Mitra, et al., *Sci Rep*, 2016, **6**, 33490.

On theoretical prediction of electronic properties of novel conjugated polymers

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Conjugated polymers are seen as perspective materials for solar cell industry due to the relative simplicity of the material fabrication and almost infinite potential for fine-tuning properties of the device by changing the chemical structure of the polymer. Having in mind the amount of possible structures, one can easily understand the importance of the computational screening procedures allowing to predict the most appropriate candidates for the following experimental and in-depth theoretical investigation.

We develop three-level screening procedure for computer aided design of conjugated polymers. 1) The first level of screening predicts conformational preferences and electronic structure of an ideal isolated polymer using computed data for short oligomers (up to 3-5 monomers). The approach is based on our previous studies of flexible dihedrals in oligomers¹ and estimation of tight binding Hamiltonian of polymers². 2) Secondly, DFT computations are used to evaluate the key parameters (such as energy gap, ionization potential etc.) for properly centered oligomers to define the most promising candidates for further experimental investigation. 3) Finally, in-depth theoretical study is carried out, aiming to reproduce the experimental results as accurately as possible.

Our theoretical results are tested using series of donor-acceptor polymers recently synthesized for solar cell application³, utilizing the perspective (X-DADAD)_n motif (Fig. 1) with different acceptor unit.

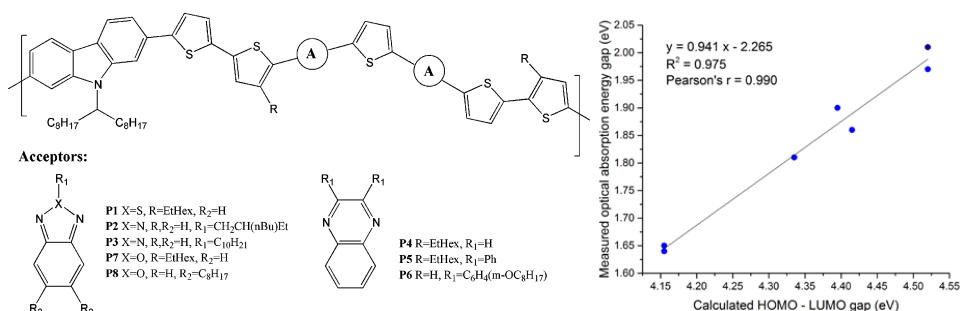


Fig. 1. Structures of some polymers under consideration

Fig. 2. Correlation between the calculated values of HOMO-LUMO energy gap for properly centered fragments of polymer chain and experimentally observed optical absorption energy

Using computationally inexpensive approach (namely, DFT CAM-B3LYP in 6-31G* basis set for relatively small fragments) we manage, as shown on Fig. 2, to correctly reproduce experimentally observed trends for energy gap; however, according to our analysis, ionization potential for that similar structures could not be used as a reliable criterion to choose more prominent polymer.

This work is supported by Volkswagen Foundation (A115678).

¹ Coughlin J.E., Zhugayevych A., et al., *Phys. Chem. C* 2014, **118**(29), 15610-15623.

² Coughlin J.E., Zhugayevych A., et al. *Chem. Sci.* 2017, **8**(2), 1146-1151.

³ Akkuratov A.V., Susarova D.K., et al.. *Macromolecules* 2015, **48**(7), 2013-2021.

Molecular Orientation in Thin Films of Conjugated Polymers

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The physical, electronic and optical properties of conjugated polymers (CPs) are strongly influenced by intra- and intermolecular order and the characterization and control of molecular orientation in thin CP films is an important step in optimizing high performance polymer based devices. For example, molecular orientation effects present a limiting factor for realizing electrically-pumped polymer laser devicesⁱ - an aligned polymer layer leads to increased charge carrier mobility due to intermolecular electronic couplingⁱⁱ but photon scattering at domain boundaries cause severe optical losses. Nevertheless, the mechanisms responsible for generating a preferred orientation in a polymer layer are not fully understood and are a topic of current research.

Several methods have been developed to control the molecular orientation of CPs, such as mechanical stretching, liquid crystalline self-organization or rubbing, where the latter is the most common method for liquid crystal (LC) alignment in LC displaysⁱⁱⁱ. Nevertheless, this method suffers from several drawbacks, such as surface contamination, producing static charged dust and scratches. To overcome these limitations, photo-alignment methods are becoming increasingly important with the great advantage of not requiring expensive or elaborate instruments^{iv}. Using linear polarized UV-light a preferred orientation may be directly created in UV-sensitive polymers or a photo-aligned surface can be used to introduce orientation to a polymer layer on top.

Scanning transmission soft X-ray microscopy (STXM) is ideally suited to the task of mapping bulk molecular orientation with high spatial resolution. Using linear polarized soft X-ray radiation provided at the PolLux beamline^v at the Swiss Light Source (Villigen, Switzerland) both the 285.2 eV spectral resonance and images recorded at this photon energy are sensitive to molecular orientation due to the interaction between the electric field vector of the linearly polarized X-rays and the C 1s- π^* transition dipole moment perpendicular to the plane of conjugation in the polymers.

We will present recent results about the evolution of molecular orientation in F8BT thin films during thermal annealing and its dependence on different molecular weights and preparation methods such as spin- and blade-coating. Furthermore, we will provide an overview of our efforts to control the molecular orientation of CPs based on a functionalized pre-aligned surface to reach the goal of an electrically-pumped polymer laser device.

This project has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No 701647. PolLux is funded by the BMBF (project no. 05K16WED).

ⁱ Bisri, S. Z., Takenobu, T., Iwasa, Y. *J. Mater. Chem. C* 2014, **2**, 2827-2836.

ⁱⁱ Bae, J. W., Song, K. *Organic Electronics* 2016, **30**, 143-148.

ⁱⁱⁱ D. Berreman, *Phys. Rev.* 1972, **28**, 1683.

^{iv} Seki, T., Nagano, S., Hara, M. *Polymer* 2013, **54**, 6053-6072.

^v J. Raabe et al., *Rev. Sci. Instrum.* 2008, **79**, 113704.

Functional environments for precision humidity sensors based on dielectric nanoparticles in a hydrophilic polymer

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At present the using of the special properties of nanoscale materials is topical for alternative energy. Due to the difference between the electron emission energy of materials of the dispersed phase and gas molecules of the atmosphere (dispersion medium) in the heterophase boundary occurs electric fields of several billion volts per meter. For example, the difference between the electron emission energy of nanoparticles material and chemisorbed water molecule for ZrO_2 is at least 9eV. For the bond lengths $0.33 \div 0.51$ nm of the (111) and (110) ZrO_2 - crystal planes, the electric field will be not less than $9 \cdot 10^9$ V/m. Such large value of field provides conditions for charge exchange between the nanopowder system and outside gas environment by for example, "ballistic" transport mechanism. Thus, the conditions for precision sensing of humidity are performed.

The idea of a humidity sensor obtaining working through the so-called chemo-electronic conversion process¹ in nanostructured systems was realized practically. The appearance of the planar device is shown in the Image 1. The purposes of this work were to investigate of the mechanism of interfacial electronic exchange and establish its relationship with the stability of the crystal structure of the surface layer of nanoparticles.

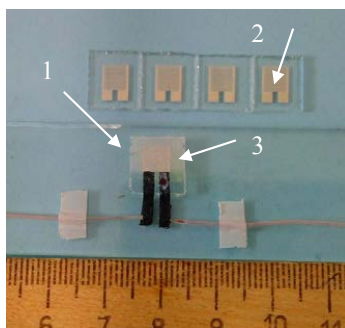


Image 1. Appearance of a sample of a planar nanoionic sensor where: a glass substrate (1), electrode grid with an interdigitated topology (2), functional layer made of a PVA polymer filled with ZnO_2 -3mol% Y_2O_3 nanopowders (3).

The work was supported through the project H2020/MSCA/RISE/HUNTER/691010, JINR-Romania Cooperation Program Project of 2018 Order No. 220 / 55 is acknowledged.

¹ Styrov V V, Tyurin Yu I, 2003 *Non-equilibrium chemo-effects on the surface of solids* (Moscow: Energoatomisdat)

Photoinduced degradation of a series of conjugated polymers under different oxygen level conditions

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Conjugated polymers used as active materials in organic solar cells (OSC) undergo rather facile degradation under the device operation conditions. A considerable attention was paid to the photochemical degradation of conjugated polymers under ambient conditions. However, the conjugated polymers are known to be highly sensitive to the oxygen and moisture as well as many inorganic photoactive materials. Therefore, organic solar cells have to be protected from the environment by using appropriate barrier coatings. At the same time, we cannot protect the active layer of OSC from the action of light and elevated temperatures and, probably, trace amounts of oxygen since encapsulation on industrial scale is supposed to be done in air.

We have shown that ESR spectroscopy represents a highly sensitive tool which is ideally suitable for studying photothermal degradation of conjugated polymers.¹ Here we report a systematic investigation of photostability of a series of >20 conjugated polymers comprising TBT and TTBTBTT units (T - thiophene, B - benzothiadiazole) in combination with different building blocks such as carbazole, silafluorene, fluorene, indolocarbazole, benzodithiophene and cyclopentadithiophene under both anoxic and low oxygen level (900 ppm) conditions. The correlations between the molecular structures of conjugated polymers and their photochemical stability will be presented and discussed.

This work was supported by RFBR (project № 18-33-01086_mol_a).

¹ L. A. Frolova, N. P. Piven, D. K. Susarova, A. V Akkuratov, S. D. Babenko and P. A. Troshin, *Chem. Commun.*, **2015**, 51, 2242.

Synthesis of unsymmetrical 2-[2-vinyl-chromen-4-ylidene]-malononitrile dyes via Knoevenagel reaction

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Recent time the development of organic nonlinear optical (NLO) materials is generated a huge interest owing to their potential applications in information processing, fiber communications, optical switching and information storage. The increasing of transmitted information volume requires the use of high-speed electro-optical (EO) modulators operating at a frequency of more than 100 GHz. These frequencies are achieved using only organic nonlinear optical (NLO) materials. Organic NLO materials are based on the push-pull organic chromophores, which include the donor and acceptor fragments connected by a p-conjugated bridge (D- π -A). In the previous work we have shown the prospects of using 4-oxo-4H-chromene-3-carbonitrile moiety as acceptor for push-pull organic chromophores¹. In this paper, we synthesized new 2-[2-vinyl-chromen-4-ylidene]-malononitrile acceptor-based chromophores containing a vinylthiophene bridge structure. Synthesis was carry out via Knoevenagel reaction of 2-(2-methyl-chromen-4-ylidene)-malononitrile with appropriate aldehydes in presents of piperidine as catalyst (Fig. 1). Compounds **3a-d** have absorption maxima at 547-594 nm, that suitable for signal modulation at datacom(0.84 μ m) and telecom wavelength (1.3 μ m).

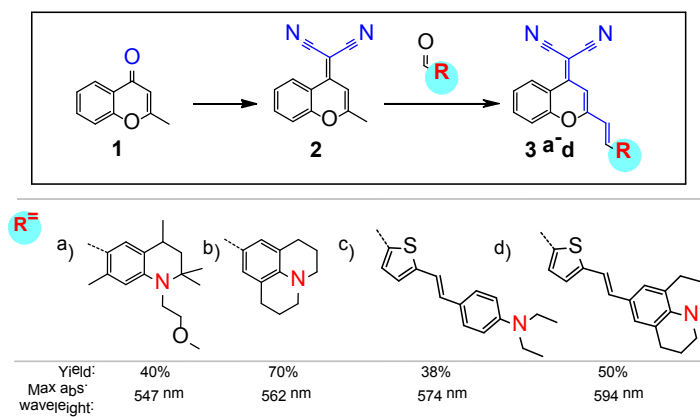


Fig. 1. Scheme of synthesis of new 2-(2-methyl-chromen-4-ylidene)-malononitrile. Reagents and conditions: (i) CH₃CN, pip, r.t.-reflux, 3-5 h.

The results of this work provide access to a new chromophores that may be useful for NLO devices and other applications.

This work was supported by RSF (project № 17-73-10433).

¹ Levchenko K.S., Chudov K.A., Poroshin N.O., Zinoviev E.V., Chicheva P.A., Shohina E.A., Shmelin P.S., and Grebennikov E.P. *VII International Conference on Photonics and Information Optics, KnE Energy & Physics*, 2018, 138–146.

New materials in CsI-SnI₄-GaI₃ ternary system

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Nowadays perovskite solid state photovoltaic devices are of great interest. New light-harvesting compounds are the most promising materials in ambitious pathway towards high efficiencies and long-life devices^{1,2}. Recently Sn(II)-based iodides have been investigated however demonstrated rather poor stability to oxidation and hydrolysis processes³. Later Cs₂SnI₆ with a perovskite-like structure of the compos was suggested. This compound contains Sn(IV) which is more resistant to air and moisture. Iodostannate (IV) cesium is the direct-gap p-type semiconductor with a bandgap of ~ 1.6 eV and is the promising material in solar cells that can replace toxic lead-based perovskite compounds³.

The aim of this project is to investigate new compositions and compounds based on cesium, tin and gallium iodides, which can be used as light-harvesting components in solar cells. Analysis of literature sources showed possible quasi-chemical equilibria in Cs₂SnI₆-CsGaI₄ and Cs₂SnI₆-CsGa₂I₇ binary systems. That was found that doping of Cs₂SnI₆ compound with a trivalent metals (M = Ga, In, Sb) initiate the appearance of donor levels in the bandgap and increase the electronic conductivity of the material. As the main synthesis approach solid phase ampoule sintering was applied varying both temperature and duration of calcinations. Sintering products are all black color molts. Ranges of solid solutions were analyzed by X-ray diffraction and Raman spectroscopy. Thermal stability was studied by TG-DTA with MS analysis of gaseous products. Diffuse reflectance spectroscopy showed appropriate bandgap values.

Some compositions were synthesized by wet-chemistry route as thick films. Micromorphology of the films was investigated by optical and scanning electron microscopy.

¹ X. Qiu, Y. Jiang, B. Cao, S. Y. X. Chen, Z. Qiu, G. Mercuri. *Solar Energy Materials & Solar Cells*, 2016, **159**, 227–234.

² B. Saparov, F. Hong, J.-P. Sun, H.-S. Duan, W. Meng, S. Cameron, I. G. Hill, Y. Yan, D.B. Mitzi. *Chem. Mater.*, 2015, **27**, 5622–5632.

³ B. Lee, C. C. Stoumpos, N. Zhou, F. Hao, C. Malliakas, C.-Y. Yeh, T. J. Marks, M.G. Kanatzidis, R.P.H. Chang. *Chem. Soc.*, 2014, **136**, 15379–15385.

Synthesis of perovskite of methylammonium triiodide and study of structural degradation

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The creation of photovoltaic converters of the third generation on the basis of the perovskite structure of ABX_3 is currently one of the active developing directions in photovoltaics. In a short time, the efficiency of hybrid organo-inorganic perovskite solar cells (SC) reached 20-22% in laboratory conditions [1].

The main advantages of perovskite materials in comparison with traditional materials are a high absorption coefficient (105 cm^{-1}) and a long lifetime of charge carriers ($1 \mu\text{s}$) [2]. To date, one of the problems of practical application of hybrid organo-inorganic perovskites in photovoltaics is their low resistance, as well as the presence of lead in the composition of the material.

The work is devoted to the synthesis of lead methylammonium triiodide $\text{CH}_3\text{NH}_3\text{PbI}_3$ on the basis of $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 precursors in a N, N-dimethylformamide (DMF, $\text{C}_3\text{H}_7\text{NO}$). It should be noted that studies of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films are hampered by insufficient thermal stability and photostability of hybrid organo-inorganic perovskites, including under conditions of removal of Raman spectra. To overcome this difficulty, it is necessary to use a low intensity of the exciting radiation. It is rather difficult to accurately correlate individual strips of thin films of $\text{CH}_3\text{NH}_3\text{PbI}_3$, their spectra are similar to the Raman spectra of PbI_2 , which can be a product of degradation of a sample of hybrid organo-inorganic perovskites before or during Raman spectra measurements.

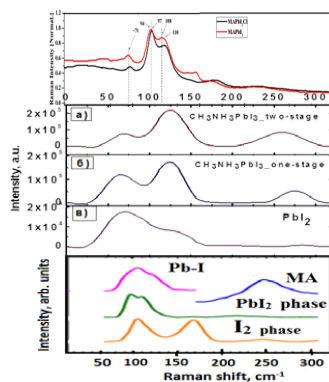


Figure 1. Comparison of Raman spectra of PbI_2 and $\text{CH}_3\text{NH}_3\text{PbI}_3$ films obtained experimentally: a) one-stage; b) two-stage methods) with literature data.

¹ J.-P. Correa-Baena, A. Abate, M. Saliba, W. Tress, T. J. Jacobsson, M. Gratzel, and A. Hagfeldt., *Energy Environ. Sci.* 2017, **10** (3), 710–727.

² Paul Pistor., *Scientific Reports.* 2016, **6**, 1–8.

Thiophene-phenylene co-oligomer single crystals: effect of molecular end-groups on structural and electronic properties

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Single crystals of thiophene-phenylene co-oligomers (TPCO) are promising optoelectronic materials for light-emitting devices as they combine efficient charge carrier transport and high luminescence^{1,2}. These electronic properties are controlled by the chemical structure of the molecules and their crystal packing; however, the structure-property relationships in TPCO single crystals have not yet been properly understood^{3,4}.

Here, we study the impact of molecular end-groups (H, F, CH₃, CF₃, Si-(CH₃)₃, C-(CH₃)₃, O-CH₃) on the structural and electronic properties of vapor-grown TPCO single crystals with the same phenylene-thiophene-thiophene-phenylene (PTTP) conjugated core using optical/atomic force microscopy, x-ray diffraction, DFT and other calculations, and field-effect transistor (FET) measurements.

Our experimental data show that the variation of the end-group types results in a significant impact on the crystal habit and on the molecular orientation vs their basal plane, thus not affecting much the herringbone packing itself. Almost all the molecules tend to form layered plate-like crystals, which is confirmed by morphology simulations. TPCOs with H and F, CH₃ and CF₃, Si-(CH₃)₃ and C-(CH₃)₃ have similar crystal habit, respectively. Calculated energies of frontier molecular orbitals of the TPCOs show their small variation with the end-group type; however, the static dipole moment of half TPCO changes its direction, probably affecting charge injection. FETs based on non-fluorine TPCO single-crystals exhibited p-type semiconductor behavior with charge carrier mobility in the range 0.03–0.1 cm²/Vs, while other TPCO single crystals (with F and CF₃ end-groups) worked as n-type FETs. We discuss the FET performance in relation with structural features of the TPCO single crystals.

This work was supported by RFBR (project № 17-02-00841).

¹ S. Hotta et al., *Journal of Materials Chemistry*, 2011, **21**(5), 1295-1304.

² L. Kudryashova et al., *ACS Applied Materials & Interfaces*, 2016, **8**(16), 10088-10092

³ C. Reese et al., *Advanced Materials*, 2009, **21**, 3678-3681

⁴ G. Schweicher et al., *Advanced Materials*, 2015, **27**, 3066-3072

Electrochemical preparation of MoO₃ buffer layer deposited

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The use of organic materials appears as an alternative to produce low-cost solar cells and make them competitive in the electricity market. These cells are not yet commercially competitive because of their low power conversion efficiency. However, the huge choice in chemical composition and layer structure and technical advances, ensure continuity in the development of these devices.

Stable, reproducible and weakly reduced molybdenum oxide films were obtained on ITO electrodes employing potentiostatic techniques and using a concentrated molybdic acid solution in a sulfuric medium, and citric acid as a complexing agent. These films have been successfully tested as anodes in a two-layer heterojunction solar cell arrangement improving the surface properties of the device. Further characterization of the deposit shows that amorphous molybdenum oxide films of appropriate thickness have been prepared. The films deposited by the potentiostatic technique are more homogeneous than those deposited by cyclic voltammetry. XPS analysis indicates that the improvement in solar cell performance is mainly due to the correct oxidation state of the film, comparing these results with vacuum molybdenum oxide deposits.

The Application of Viologen Materials in Organic Electronics

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Viologens, which are usually named as 1,1'-disubstituted-4,4'-bipyridinium salts, are one of the most frequently utilized organic functional materials¹. The unique color change, easy preparation and extraordinary stability are the main features that the applications were attracted to. As shown in Fig. 1 below, viologen undergoes two successive reduction processes, which contain two single electron transfer steps. There are three redox forms of viologen (V): a dication (V^{2+}), a radical cation ($V^{+\bullet}$) and a neutral form (V^0), each of them has own properties and applications. The dication salt is the most stable one and usually is colorless. The radical cation ($V^{+\bullet}$) is intensely colored, which is owing to the intramolecular optical charge transfer process, and it is highly stable among organic radicals. The neutral form of viologen is extremely reactive so it can work as reductive agent. By modifying the substituent group, the redox potentials and colors of the viologens can be adjusted.

The viologens have been widely utilized in different applications, such as electrochromic devices, sensors, biofuel cells and so on. In recent years, the application of viologen materials in energy storage devices has attracted more and more attentions, due to their bulk redox charge storage and good stability². In the previous research of my PhD. thesis work, different kind of polyviologen materials has been synthesized and characterized. The polyviologen materials has shown huge potential to be applied as the functional materials in various of organic electronics.

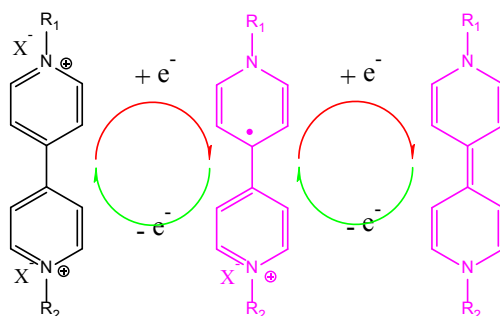


Fig. 1. The redox process of viologens, from left to right: V^{2+} , $V^{+\bullet}$ and V^0

¹ Monk, P. M. S., *The viologens: physicochemical properties, synthesis, and applications of the salts of 4,4'-bipyridine*. Wiley: 1998.

² Chun, S. E.; Evanko, B.; Wang, X.; Vonlanthen, D.; Ji, X.; Stucky, G. D.; Boettcher, S. W., *Nat Commun* 2015, **6**, 7818.

Understanding the Photophysics of Efficient Nonfullerene Acceptors

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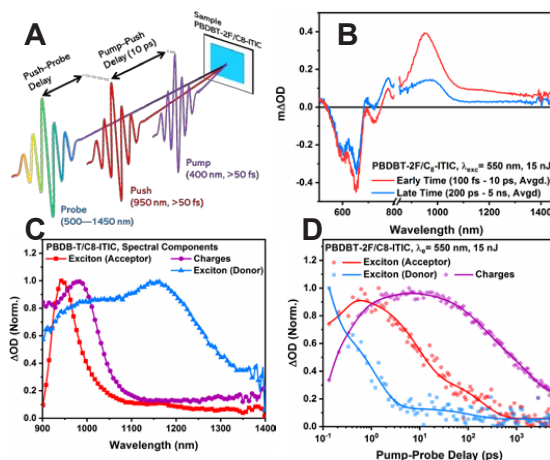


Figure 1: (A) Pulse sequence employed in pump-probe and pump-push-probe experiments; (B) Full-range Pump—Probe spectrum at early (0.1—10 ps, red) and late delay times (200—5000 ps, blue); (C) Spectra and (D) kinetics extracted using global analysis.

One of the key areas of study in organic photovoltaics is the development of so-called 'nonfullerene acceptors' (NFAs), which enjoy several benefits over older, fullerene-based acceptors, including: low open circuit voltage losses, low cost, high absorptivity, and broad tuneability. However, these advantages come at the expense of light harvesting efficiency. A recent report Fei *et al.* demonstrated conversion efficiencies of 13% in donor acceptor blends comprising a fluorinated derivative of the common donor PBDB-T and an alkylated derivative of the ITIC (C₈-ITIC) acceptor species¹.

In order to understand the processes underlying this remarkable efficiency, we performed ultrafast transient absorption studies on the donor:acceptor blend PBDBT-2F/C₈-ITIC. Long-lived excitons form at the acceptor regardless of whether the donor or acceptor is pumped, suggestive of rapid energy transfer from the donor to the acceptor. A distinct change in exciton decay characteristics was observed at longer timescales in tandem with spectral drift in the acceptor localised excitonic peak. We use global analysis methods to elucidate the mechanism behind this feature. Furthermore, using 3-pulse "Pump-Push-Probe" spectroscopy, we are able to track the dissociation of interfacial charge transfer states within the material. Our results will help to shed light on the remarkable efficiency of this material and aid the development of more efficient and effective non fullerene acceptors.

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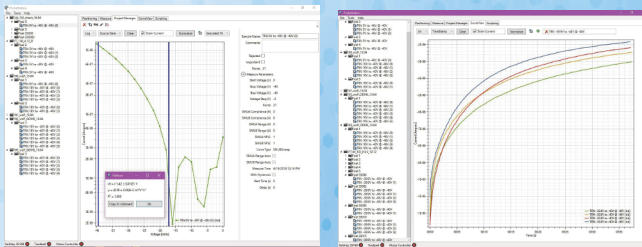
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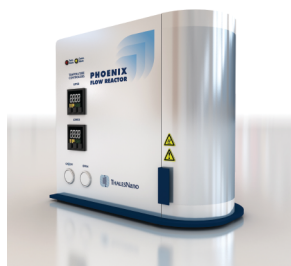




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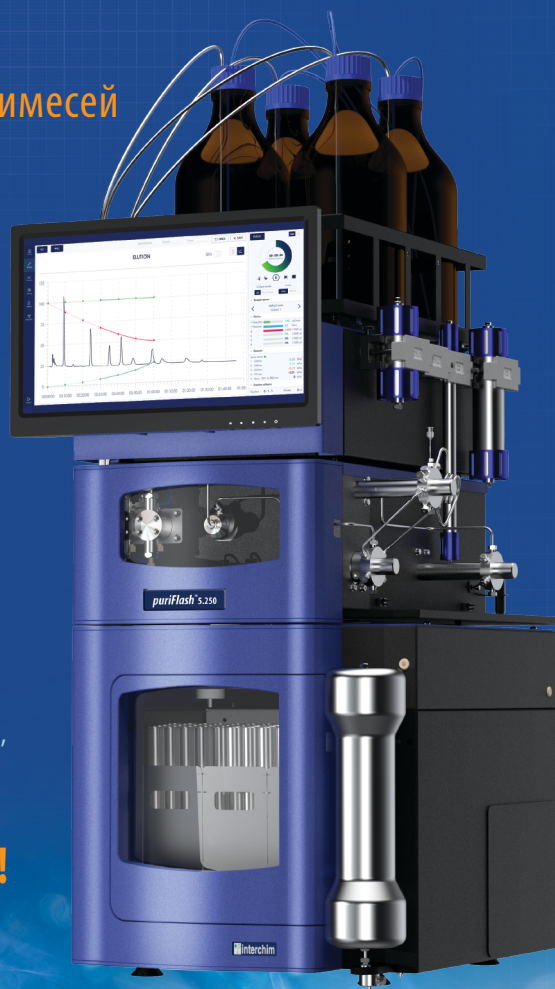
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