



5th International Fall School
on Organic Electronics

Book of Abstracts



September 15-20, 2019
Moscow region, Russia
Soyuz Hotel
<http://www.ifsoe.ru>

5th INTERNATIONAL FALL SCHOOL ON ORGANIC ELECTRONICS – 2019 (IFSOE-2019)

Organizers

Division of Chemistry and Material Science of Russian Academy of Sciences

The Ministry of Science and Education of Russia

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

Lomonosov Moscow State University (MSU)

Printed Electronics Technologies Limited Liability Company (PrintElTech LLC)

Eklogit Limited Liability Company (Eklogit LLC)

Scientific program

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

School-conference Chairs

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

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Dr. Elena Agina – *Vice Chairman*

Victoria Chekusova – *workshop secretary*

Askold Trul

Daniil Anisimov

School program

The 5th International Fall School on Organic Electronics – 2019 Time Schedule

	Sunday September 15th	Monday September 16th	Tuesday September 17th	Wednesday September 18th	Thursday September 19th	Friday September 20th		
	School							
9:00		Luca Beverina	Sergei Tretiak	Alessandro Troisi	Yongfang Li	Fabio Biscarini	9:00	
10:00		Ruben D. Costa	Frank Schreiber	Enrico Da Como	Chihaya Adachi	Dorina Opris	10:00	
11:00	Visit to Kolomenskoe Museum (optional) Lunch Registration at ISPM RAS 16:00 Departure to Conference site	Coffee-break					11:00	
		Pavel Troshin	Anna Koehler	Maxim Shkunov	Dimitri Ivanov	Dmitri Godovsky		
12:00		Dmitry Paraschuk	Maxim Pchenitchnikov	Mikhail Nechaev	Stephan Kirchmeyer	Carlo Bortolotti	12:00	
		Artem Bakulin	Oral talks 2	Oral talks 3	Oral talks 5	Closing ceremony		
13:00		Sponsor lecture						
14:00			Lunch					14:00
15:00		Oral talks 1	Johannes Gierschner	Oral talks 4	Trip to New Jerusalem (optional)	Departure to Moscow	15:00	
16:00			Discussion lecture Johannes Gierschner				Coffee-break	
		Coffee-break		Coffee-break				
17:00	Hotel arrival.	Poster session 1	Sport activities (swimming pool, wellness, spa)	Poster session 2	Sport activities (swimming pool, wellness, spa)		17:00	
18:00	Registration							
19:00	Dinner			Conference dinner	Dinner		19:00	
20:00	Opening ceremony Guglielmo Lanzani	Evening lecture Björn Kriete	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 15th

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 opening
20:15 – 21:15	T-1. <i>Guglielmo Lanzani</i>. Organic Light Actuators for Non Genetic Cell Photo Stimulation
21:15 – 22:30	Welcome-party. The afterparty music by Crossover Classical Band.

Monday, September 16th

8:00 – 9:00	Breakfast
	Chair: <i>Artem Bakulin</i>
9:00 – 10:00	T-2. <i>Luca Beverina</i>. Bench-Top, Sustainable Access to Conjugated Materials: How Far You Can Go with Tap Water, a Stirring Plate, Very Little Palladium and a Little Soap
10:00 – 11:00	T-3. <i>Ruben D. Costa</i>. New advances in Light-Emitting Electrochemical Cells: Emitters and Operational Window
11:00 – 11:30	Coffee-break
	Chair: <i>Guglielmo Lanzani</i>
11:30 – 12:00	I-1. <i>Pavel Troshin</i>. Redox-Active Organic and Organometallic Materials for Advanced Metal-Ion Batteries
12:00 – 12:30	I-2. <i>Dmitry Paraschuk</i>. 2D Organic Semiconductor Single Crystals
12:30 – 13:00	I-3. <i>Artem Bakulin</i>. Hot-Carrier Dynamics in Lead-Halide Perovskite Nanocrystals: Role of Carrier Density, Nanoconfinement and Surface Ligands
13:00 – 13:30	Sponsor lecture. <i>Alexander Shaforostov</i>. Imaging Ellipsometry and Near-field microscopy for Organic Electronics applications
13:30 – 15:00	Lunch
	Oral talks 1. Chair: <i>Luca Beverina</i>
15:00 – 15:15	O-1. <i>Sara Mattiello</i>. Organic Semiconductors Synthesis in Water Promoted by π -Surfactants
15:15 – 15:30	O-2. <i>Igor Koskin</i>. Quantitative Topological Descriptor for Linear Co-oligomers Fusion
15:30 – 15:45	O-3. <i>Jun Liu</i>. n-Type Polymer Semiconductors Containing B\leftarrowN Unit and Their Application in OPVs and OFETs
15:45 – 16:00	O-4. <i>Maxim Skorotetcky</i>. Luminophores Based on 2,1,3-Benzothiadiazole Electron-Withdrawing Core and Their Absorption-Luminescent Properties

16:00 – 16:15	<u>O-5.</u> <i>Santosh Kumar Behera.</i> Excited State Features and Dynamics of a Highly Efficient All-Organic Photocatalyst for Polymerization Reactions
16:15 – 16:30	<u>O-6.</u> <i>Vito Vurro.</i> Cardiomyocytes Optical Pacing Mediated by Micro Patterned Polymer Interfaces
16:30 – 17:00	Coffee-break
17:00 – 19:00	<u>Poster session 1 (P-1 – P-30)</u>
19:00 – 20:00	Dinner
20:00 – 21:00	<u>Evening lecture.</u> <i>Björn Kriete.</i> Scientific Ethics

Tuesday, September 17th

8:00 – 9:00	Breakfast
	Chair: <i>Johannes Gierschner</i>
9:00 – 10:00	<u>T-4.</u> <i>Sergei Tretiak.</i> Modeling of Electronic Properties in Organic and Hybrid Materials
10:00 – 11:00	<u>T-5.</u> <i>Frank Schreiber.</i> Organic Semiconductor Heterostructures: Growth, Structure and Optical Properties
11:00 – 11:30	Coffee-break
	Chair: <i>Enrico Da Como</i>
11:30 – 12:00	<u>I-4.</u> <i>Anna Koehler.</i> Understanding and Controlling Aggregate Formation During Spin-coating
12:00 – 12:30	<u>I-5.</u> <i>Maxim Pchenitchnikov.</i> Ferroelectricity in 2D Halide Perovskites
	<u>Oral talks 2.</u>
12:30 – 12:45	<u>O-7.</u> <i>Björn Kriete.</i> Molecular Aggregate Matryoshka: 2D Spectroscopy Meets Microfluidics
12:45 – 13:00	<u>O-8.</u> <i>Dmitry Maslennikov.</i> Surface-Enhanced Raman Spectroscopy of 2D Organic Semiconductor Crystals
13:00 – 13:15	<u>O-9.</u> <i>Hui Tong.</i> Water-Dispersible Hyperbranched Conjugated Polymer Nanoparticles for Amplified Fluorescence Sensing of Trace Nitroaromatic Explosives in Aqueous Solution
13:15 – 13:30	<u>O-10.</u> <i>Daniil Anisimov.</i> Ultra-Sensitive Gas Sensors Array Based on Organic Field Effect Transistors with Tunable Selectivity
13:30 – 15:00	Lunch
	Chair: <i>Dmitry Paraschuk</i>
15:00 – 15:30	<u>I-6.</u> <i>Johannes Gierschner.</i> Highly Luminescent Organic Charge-Transfer Co-Crystals

15:30 – 16:00	Discussion lecture. <i>Johannes Gierschner</i> . Luminescence Enhancement and Quenching in Organic Solids
16:30 – 17:00	Coffee-break
17:00 – 19:00	Sport activities
19:00 – 20:00	Dinner
20:00 – 23:00	Moscow sightseeing tour

Wednesday, September 18th

8:00 – 9:00	Breakfast
	Chair: <i>Sergei Tretiak</i>
9:00 – 10:00	T-6. <i>Alessandro Troisi</i> . Searching for the Best Molecular Semiconductors
10:00 – 11:00	T-7. <i>Enrico Da Como</i> . Charge Transfer Crystals: Growth and Electronic Structure
11:00 – 11:30	Coffee-break
	Chair: <i>Alessandro Troisi</i>
11:30 – 12:00	I-7. <i>Maxim Shkunov</i> . Inkjet-Printed Polymeric 3-colour Devices Mimicking Human Retina
12:00 – 12:30	I-8. <i>Mikhail Nechaev</i> . Synthesis of High Purity Organic Materials Under Solvent-Free Conditions
	Oral talks 3.
12:30 – 12:45	O-11. <i>Maxim Kazantsev</i> . Stimuli Responsive Aggregation-Induced Emission of Bis(4-((9H-fluoren-9-ylidene)methyl)phenyl)thiophene Single Crystals
12:45 – 13:00	O-12. <i>Andrey Sosorev</i> . Simple Model for Efficient Screening of High-Mobility Organic Semiconductors
13:00 – 13:15	O-13. <i>Kostas Daoulas</i> . Generic Model for Describing Lamellar Order in Conjugated Polymers: Studying Mesoscopic Morphology and Charge-Transport
13:15 – 13:30	O-14. <i>Vladimir Nikitenko</i> . On the Description of Hopping Transport by the Multiple Trapping Model
13:30 – 15:00	Lunch
	Oral talks 4. Chair: <i>Frank Schreiber</i>
15:00 – 15:15	O-15. <i>Yuriy Luponosov</i> . Novel Donor Small Molecules for Organic Photovoltaics
15:15 – 15:30	O-16. <i>Jonathan Barsotti</i> . Ultra-Thin and Ultra-Conformable Tattoo-Like Organic Photovoltaics
15:30 – 15:45	O-17. <i>Seyed Mehrdad Hosseini</i> . Comparing Charge Generation and Extraction in ITIC and PCBM[70] Devices

15:45 – 16:00	<u>O-18.</u> <i>Maria Kotova.</i> Role of Triplet Excitons in Non-fullerene Based Organic Solar Cells
16:00 – 16:15	<u>O-19.</u> <i>Kezia Sasitharan.</i> Enhanced Performance of Bulk Heterojunction Solar Cells by Ultrathin Metal-Organic Framework Nanosheets
16:30 – 17:00	Coffee-break
17:00 – 19:00	<u>Poster session 2 (P-31 – P-59)</u>
19:00 – 23:00	Conference dinner

Thursday, September 19th

8:00 – 9:00	Breakfast
	Chair: <i>Stephan Kirchmeyer</i>
9:00 – 10:00	<u>T-8.</u> <i>Yongfang Li.</i> Photovoltaic Materials and Devices for Polymer Solar Cells
10:00 – 11:00	<u>T-9.</u> <i>Chihaya Adachi.</i> High Performance Organic Light Emitting Devices – from TADF-OLED to Organic Semiconductor Laser Diodes
11:00 – 11:30	Coffee-break
	Chair: <i>Anna Koehler</i>
11:30 – 12:00	<u>I-9.</u> <i>Dimitri Ivanov.</i> Advanced Methods of in-situ Characterization of Organic Electronic Devices
12:00 – 12:30	<u>I-10.</u> <i>Stephan Kirchmeyer.</i> PEDOT, a Work-horse for Organic Electronics
	<u>Oral talks 5.</u>
12:30 – 12:45	<u>O-20.</u> <i>Artur Mannanov.</i> Single Component Solution-Processed Organic Solar Cells Based on Conjugated Star-Shaped Small Molecules
12:45 – 13:00	<u>O-21.</u> <i>Alexei Komolov.</i> Electron Spectroscopy Studies of Surface Deposited Conjugated Molecular Layers
13:00 – 13:15	<u>O-22.</u> <i>Vasilii Trukhanov.</i> Voltage Dependence of Light-Emitting Area Position in Channel of Oligothiophene-Phenylene Based Organic Light-Emitting Field-Effect Transistors
13:30 – 15:00	Lunch
15:00 – 19:00	Trip to New Jerusalem (optional)
15:00 – 19:00	Sport activities
19:00 – 20:00	Dinner
20:00 – 22:00	Sport activities

Friday, September 20th

8:00 – 9:00	Breakfast
	Chair: <i>Chihaya Adachi</i>
9:00 – 10:00	T-10. <i>Fabio Biscarini.</i> Neuromorphic Organic Electronics Biosensors
10:00 – 11:00	T-11. <i>Dorina Opris.</i> Functional Dielectric Elastomers: From Synthesis to Applications
11:00 – 11:30	Coffee-break
	Chair: <i>Sergey Ponomarenko</i>
11:30 – 12:00	I-11. <i>Dmitri Godovsky.</i> Redox Front Propagation in Polyaniline as a Basis for Rate-Based and Spike Neural Networks
12:00 – 12:30	I-12. <i>Carlo Bortolotti.</i> Expanding the EGOT-based Biosensor Toolbox by Materials Strategies
12:30 – 13:30	Closing ceremony
13:30 – 15:00	Lunch
15:00 – 15:15	Departure to Moscow

Poster session 1

Monday, September 16th, 17:00

Ajdari, Mohsen	P1	Investigation of N-Heteropolycyclic Molecules on Metal Surface by High Resolution Electron Energy Loss Spectroscopy
Aslandukov, Andrey N.	P2	Lanthanide Aromatic Carboxylates as Red, Green and Blue Emitters for Solution-processed OLEDs
Balakirev, Dmitry O.	P3	Novel Benzodithiophene-based Donor Oligomers for Non-fullerene Organic Solar Cells
Berens, Henning	P4	3,9-Disubstituted <i>anti-anti</i> -Bis[1]benzothieno[1,4]thiazines: Diversity Oriented Synthesis and Structure-Property Relationships of Potentially Antiaromatic Heterocyclic Donors
Borshchev, Oleg V.	P5	New Derivatives of Benzothienobenzothiophenes (BTBT) and Tetrathienoacenes (TTA) for Organic Electronics
Borshchev, Oleg V.	P6	New Organic Luminophores for Manufacturing Scintillation and Wavelength Shifting Polymer Fibers
Chekusova, Victoria P.	P7	Novel Tetrathienoacenes and Benzothienobenzothiophenes Derivatives: Investigation of Self-assembly and Thin Films Electrical Properties
Debnath, Bipasha	P8	A Study of Charge Transfer at the Interfaces of Organic Semiconductors
Dominskiy, Dmitry I.	P9	Impact of Fluorination on Crystal Packing of Di-phenyl naphthalene Diimide
Dominskiy, Dmitry I.	P10	Switching Between p- and n-type Transport in Organic Field-Effect Transistors by Terminal Substitution of Thiophene-phenylene Co-oligomers
Fedorenko, Roman S.	P11	Solution-processed High Performance 2D Field-effect Transistors Based on Luminescent BTBT Derivative
Geenen, Sarah R.	P12	Diversity-oriented Pd-Catalyzed Synthesis of Donor-Acceptor-Substituted Psoralens with Photosensitizing Properties for DNA-Intercalation
Ivanov, Konstantin S.	P13	Linear Spirocyclic Conjugated Systems as New Materials for Optoelectronics
Jacoutot, Polina	P14	Organic Infrared Photodetectors Based on Photoinduced Vibronic Phenomena
Jeong, Ahhyun	P15	Intraband Cooling Dynamics in Lead Halide Nanocrystals
Kalinichenko, Nadezhda K.	P16	Synthesis and Properties of Novel Liquid Benzothiadiazole-based Luminophores
Kalinina, Alexandra A.	P17	Polymer Muscles on the Base of Silicones
Kharlanov, Oleg G.	P18	Low Phonon Frequency Expansion for Charge Transport in Organic Crystals: Transient Localization in the Quantum Regime
Khudyshkina, Anna D.	P19	Synthesis of Poly(vinylidene fluoride-co-chlorotrifluoroethylene)-grafted-poly(acrylonitrile) Polymers for Ferroelectric Organic Field-effect Transistors

Kobeleva, Elena S.	P20	Performance of Novel Organic Semiconductors 2,2'-[2,2'-(arene-1,4-diyl)bis(anthra[2,3-b]thiophene-5,10-diylidene)] tetrapropanedinitriles as Non-fullerene Acceptors in Photovoltaics
Komarov, Pavel V.	P21	Computer Simulations of Nanocomposites Based on Conjugated Polymers and Fullerenes
Komarov, Pavel V.	P22	Mesoscale Simulations of Active Layer of Hybrid Polymer/Semiconducting Nanoparticles Solar Cell
Bretschneider, Michael	P23	Charge Transport Properties of C8-BTBT field-effect transistors
Ding, Zicheng C.	P24	Efficient and Stable Organic Solar Cells Based on Small Molecule Donor and Polymer Acceptor
Elnaggar, Mohamed	P25	Towards Understanding the Interfacial Degradation Effects in p-i-n Perovskite Solar Cells
Eskandari, Mortaza	P26	Spectral Shapes of Cyanine Dyes Mediated by Counterion Positioning in Non-/Polar Media: a Computational Study
Klimovich, Irina V.	P27	Impact of the Molecular Structure of Conjugated Block-copolymers on Their Thin Film Morphology and Photovoltaic Performance
Kolesnikov, Efim A.	P28	Optical and Luminescent Properties of Cesium-copper Iodides Thin-films.
Lypenko, Dmitry A.	P29	J-aggregate Monolayers Resulting from Non-classical Multistage Crystallization
Lypenko, Dmitry A.	P30	Effect of J-aggregate Nanocrystals on OLED Stability

Poster session 2

Wednesday, September 18th, 17:00

Konstantinov, Vladislav G.	P31	Confocal Photoluminescence Microscopy of Organic Semiconducting Ultrathin Films
Koshelev, Daniil S.	P32	The Design of Lanthanide Heteroaromatic Carboxylates for Thermometry and OLED
Koskin, Igor P.	P33	Computational Study of a Novel AIE Luminogen bis(4-((9H-fluoren-9-ylidene)methyl)phenyl)thiophene
Kriete, Björn	P34	A Microscopic View on Spectral Inhomogeneity in Molecular Nanotubes
Kuimov, Anatolii D.	P35	Doping of Furan/Phenylene Co-oligomer Single Crystals as an Efficient Way to Control Their Optoelectronic Performance
Kumar, Abhinav	P36	Coumarinacenes: Linearly π -Extended Coumarins
Kushch, Nataliya D.	P37	Structural Features and Polymorphism in New Organic Metals Based on BDH-TTP Donor and [ReF ₆] ²⁻ anion.
Lyubovskii, Rustem B.	P38	The Effect of Hydrostatic Pressure on Interlayer Charge Transport and the Electronic Structure of Metal Layers in a Two-layer in a Quasi-two-dimensional Organic Metal (BETS) ₄ CoBr ₄ (C ₆ H ₄ Cl ₂)
Lukashkin, Nikita A.	P39	Amino-Selective Gas Sensor Based on Organic Field-effect Transistor Using Porphyrin Receptor Monolayer at the Semiconductor/Dielectric Interface

Nekrasov, Nikita P.	P40	Changes of Graphene Transistors Electronic Properties by Organic Deposition
Raoufi, Meysam	P41	Influence of Light Soaking on Charge Injection Properties at Hybrid Metal Oxide/Organic Interfaces
Saunina, Anna Yu.	P42	An Analytic Model of J-V Characteristics of Quantum Dot Based and Hybrid Photovoltaic Cells
Savchenko, Petr S.	P43	Organic Photodetectors Based on Donor-acceptor Star-shaped Oligomers: Towards Artificial Eye
Schmitt, Tanja	P44	Electronic States of Pentacene Derivatives
Shao, Shiyang	P45	Bipolar Poly(arylene phosphine oxide) Hosts with Widely-Tunable Triplet Energy Levels for High-Efficiency Blue, Green and Red TADF Polymer Light-Emitting Diodes
Skorotetcky, Maxim S.	P46	Synthesis of New Tetrathienoacene Semiconductors for Organic Field-effect Transistors
Solodukhin, Aleksandr N.	P47	Donor-acceptor Triphenylamine-based Oligomers of Different Architecture for Organic Electronics
Sonina, Alina	P48	Crystal packing control of a trifluoromethyl-substituted furan/phenylene co-oligomer
Sonina, Alina	P49	Crystallization and structures of dibenzofulvene-based derivatives
Trul, Askold A.	P50	Two-layer Langmuir-Schaefer OFETs for Real-time Detection of NH ₃ and H ₂ S in Humid Air
Tukachev, Nikita V.	P51	Ground State Geometry and Vibrations of PPV Oligomers
Zaborin, Evgeniy	P52	Synthesis of Novel Silicon-containing Oligoarylenevinylenes via Heck Reaction
Lypenko, Dmitry A.	P53	Crystallography of Surface Destruction of Tubular J-aggregates of Cyanine Dye
Markina, Anastasia	P54	Molecular Design of Transport Properties and Energy Levels of Non-fullerene Organic Solar Cells
Parfenov, Alexey A.	P55	Highly Sensitive Perovskite-based Gas Sensors
Supangat, Azzuliani	P56	Highly Responsive Organic Composite Photodetector Based Small Molecules
Utochnikova, Valentina V.	P57	Lanthanide-based NIR Emitting OLEDs
Wang, Lixiang	P58	Through-Space Charge Transfer Polymers for Solution-processed OLEDs
Yusupov, Azat R.	P59	Photoconductivity of the Interface Between Two Polymer Dielectrics
Tarasenkov, Alexander, N.	P60	Dielectric Properties of Silicone Compositions Containing Metallosiloxanes

Tutorial lectures

Organic Light Actuators for Non Genetic Cell Photo Stimulation

G. Lanzani^{1,2*}

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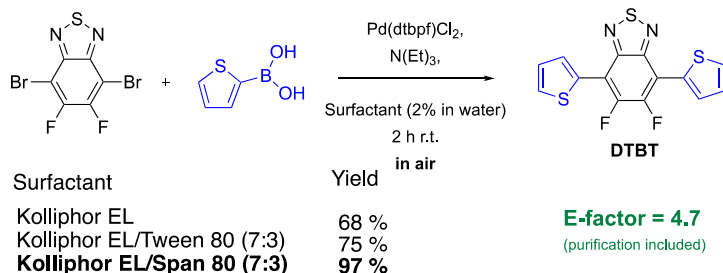
The overarching goal of the research I'm going to describe is to *induce light sensitivity in cells*. In order to achieve this, I will introduce a number of new light actuators that were recently developed based on organic molecules. In different forms, films, nanoparticles or intramembrane molecular clusters, they essentially realize abiotic/biotic interfaces that are able to transduce light signals into bio-stimulation. I will review a number of different approaches we explored, reporting both in vitro and in vivo experiments and discussing possible photo stimulation mechanisms. Eventually I will show application to the realization of a retina prosthesis for rescuing vision in blind patients affected by photoreceptors degeneration.

Bench-Top, Sustainable Access to Conjugated Materials: How Far You Can Go with Tap Water, a Stirring Plate, Very Little Palladium and a Little Soap

*L. Beverina*¹

¹Milan University

Organic (opto)electronics has played a major role in academic and industrial research in the last 30 years, eventually reaching market maturity and holding promises for sizeable further growth. Very few materials have been produced in industrially relevant scale, and the most performing ones are not amongst them. Indeed, if on the lab scale the research is still very much focused on performances, industrialization requires sustainable processes and reduction of pollutants and hazards to a level compatible with large scale production. Mostly, organic materials are not water soluble thus requiring the use of more or less flammable/toxic solvents for manufacturing and handling. As a result, only highly efficient processes featuring high yield, small number of steps and generally high concentration can satisfactorily go through the “lab to fab” evolutionary process. Modern organic chemistry methods are increasingly relying on the use of water as the main reaction medium, unregarding to the water solubility of reagents and products. The key components enabling such reactions are specifically devised surfactants that, along with water and the water insoluble reagents, lead to the formation of a range of interface rich systems the like of micellar solutions, emulsions, microemulsions and dispersions. Provided that such microheterogeneous systems are correctly handled, a wide variety of synthetically invaluable reactions like the Suzuki-Miyaura, Stille, Buckwald-Hartvig, Heck, Neghisi, Sonogashira and many more becomes accessible at room temperature, in water and sometimes even without any special precaution in keeping oxygen out of the reaction environment.¹ In this tutorial I will show how this kind of “benchtop” chemistry enables the high yield preparation of notable small molecule organic semiconductors of the diketopyrrolopyrrole, isoindigo, perylenediimides, benzothiadiazole and acenes families as well as relevant polymers like F8BT and polyfluorene.^{2,3} Relevant differences between such water based over standard organic solvent promoted reactions will be highlighted.



¹ Serrano-Luginbühl, S.; Ruiz-Mirazo, K.; Ostaszewski, R.; Gallou, F.; Walde, P. *Nature Reviews Chemistry* 2018, **1**.

² Sanzone, A.; Calascibetta, A.; Ghiglietti, E.; Ceriani, C.; Mattioli, G.; Mattiello, S.; Sassi, M.; Beverina, L. *J. Org. Chem.* 2018, **83** (24), 15029.

³ Mattiello, S.; Rooney, M.; Sanzone, A.; Brazzo, P.; Sassi, M.; Beverina, L. *Org. Lett.* 2017, **19** (3), 654.

New Advances in Light-Emitting Electrochemical Cells: Emitters and Operational Window

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Light-emitting electrochemical cells (LECs) are the leading example of easy-to-fabricate and simple-architecture devices.¹ The key-aspect of this technology is the use of a single active layer that consists of a mixture of an emitter and an ionic polyelectrolyte. The presence of mobile anions assists both charge injection and transport using air-stable electrodes. The evolution of the LEC technology has involved different stages, namely i) the search for the best combination of emitters (luminescent conjugated polymers and ionic transition complexes) and additives (ionic polyelectrolytes, ionic liquids, and neutral polymers), ii) the understanding of the device mechanism using several techniques, iii) the development of simple and up-scalable device fabrication processes and, iv) the quest for new emitters like copper(I) complexes, small-molecules, quantum dots, and perovskites.

In this contribution, we disclosed the new trends in LECs concerning the use of new emitters and the search for new ionic polyelectrolytes towards mechanically stable devices. In particular, the implementation of the third generation of materials – i.e., lighting perovskite nanoparticles,² small molecules,³ and copper(I) complexes⁴ – for LECs will be presented as new approaches to develop deep-red, blue, and white lighting sources. In addition, we will disclosed new insights into the search on new ionic electrolytes with regards to i) stability under ambient condition, ii) device lifetime, iii) performance loss upon bending in flexible devices. These aspects are regarded to the archetypal Ir(dtbbpy)(ppy)₂PF₆ emitter – i.e., [4,4'-Bis(1,1-dimethylethyl)-2,2'-bipyridine-N1,N1']bis[2-(2-pyridinyl-N)phenyl-C]iridium(III) hexafluorophosphate – in concert with traditional electrolytes.⁵

¹ E. Fresta et al. *J. Mater. Chem. C* 2017, **5**, 5643.

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³ a) M. D. Weber, et al. *Adv. Funct. Mater.* 2015, **25**, 5066; b) M. D. Weber, et al. *Adv. Funct. Mater.* 2016, **26**, 6737

⁴ a) M. Elie, et al. *ACS Appl. Mater. Interfaces*, 2016, **8**, 14678. b) M. D. Weber, et al. *Adv. Funct. Mater.* 2018 DOI: <https://doi.org/10.1002/adfm.201707423>.

⁵ E. Fresta et al. *Adv. Funct. Mater.* 2018 (submitted)

Modeling of Electronic Properties in Organic and Hybrid Materials

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Understanding and gaining control of electronic and optical properties and concurrent electron-vibrational dynamics in complex natural and man-made systems underpinning various technologies, ranging from sensing, imaging, solar energy harvesting, to future optoelectronic devices. In this talk, I will illustrate how theoretical modeling delivers a new body of knowledge by explaining and ultimately guiding experimental studies in several distinct materials. In the realm of organic semiconductors and molecules I will discuss computational results for ultrafast dynamics and exciton transport, particularly coherent vibronic dynamics important for energy and charge transport. Proposed simple model explains appearance of coherent exciton-vibrational dynamics due to non-adiabatic quantum transitions, which is universal across multiple molecular systems studied. In organic halide perovskites, I will outline the effects of electron-phonon coupling leading to polaron formation across the broad range of materials. Calculated electronic structure, charge density, changes the geometry, and reorganization energies are further related to experimentally measured specific vibrational modes, Huang-Rhys parameters and Jahn-Teller like distortions. These effects lead to formation of meta-stable deep-level charge states, which potentially responsible for photocurrent degradation in thin-film perovskite devices. The photophysics of layered perovskite materials is defined by an interplay of strongly bound excitons and lower-energy states associated with the edges of the perovskite layers. Finally, for chemically functionalized semiconducting carbon nanotubes, I will discuss modification of electronic structure introduced by chemical adducts. Our simulations suggest an association of spectroscopic features with deep trap states tied to different specific chemical species. These results suggest that covalent doping chemistry is a powerful route toward harnessing dynamics of excitons and charges in carbon nanotubes leading to new enhanced optical behaviors. Overall, observed relationships between spatial extent/properties of electronic wavefunctions and resulting electronic functionalities allow us to manipulate excited state dynamics and energy transfer pathways in a number of electronic materials.

Organic Semiconductor Heterostructures: Growth, Structure and Optical Properties

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Functional organic materials and devices are becoming increasingly complex. Their preparation and growth is, not surprisingly, similarly complex, and the resulting structure will be determined by a competition between kinetics and thermodynamics, which is not trivial to predict in particular for multi-component systems. We discuss general concepts¹ and recent examples of the thin film growth of organic semiconductors and their blends in the context of kinetic effects compared to thermodynamic (equilibrium) structure. These include unconventional structural motifs, such as a frozen-smectic structure formed in a blend of organic semiconductors, which form conventional crystals as pure compounds.² Particular attention is paid to the case of kinetically limited phase separation of a donor-acceptor pair (DIP:C60) used in organic photovoltaics.^{3,4} This leads to asymmetric domain sizes near bottom vs top electrode due to the time (thickness) dependent phase separation with important consequences for device modeling. A further class of applications is the controlled “dilution” of pentacene by DIP or picene (PIC) to tune the charge transfer.⁵ Finally, we discuss the implications for the optical and electronic properties as well as possible device applications with focus on the (generally anisotropic) coupling between donor and acceptor components in organic photovoltaics.⁶

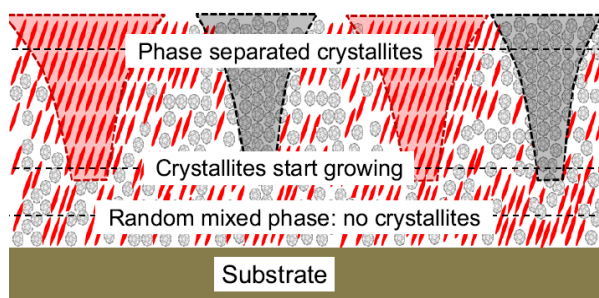


Fig. 1. Schematic of non-equilibrium structure formation for a phase separating system (DIP:C60)³.

This work was supported by the DFG, DAAD, and AvH. Contributions by numerous students and external collaborators are gratefully acknowledged.

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⁶ V. Belova et al., Evidence for anisotropic electronic coupling of charge transfer states in weakly interacting organic semiconductor mixtures, *J. Am. Chem. Soc.*, 2017, **139**, 8474.

Searching for the Best Molecular Semiconductors

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We present several approaches to screen a large database of molecular materials in search for known compounds with selected optimal properties. In the first part, after reviewing our recent work on the prediction of charge mobility in molecular crystals¹ we discuss approximated methods to enable the rapid computational screening of many thousands of materials.^{2,3} We then present the results of such screening and try to identify the maximum achievable charge mobility within this class of compounds. In the second part, we tackle the search of optimal materials for singlet fission. After a new calibration of the computational procedure, we show that hundreds of good candidates can be easily identified among known compounds.⁴

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³ T. Nemataram, S. Ciuchi, X. Xie, S. Fratini and A. Troisi, *J. Phys. Chem. C*, 2019, **123**, 6989.

⁴ D. Padula, O. Omer, T. Nemataram, A. Troisi, *Energ. Environ. Sci.*, 2019, DOI: 10.1039/C9EE01508F.

Charge Transfer Crystals: Growth and Electronic Structure

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In this tutorial lecture, I will explain the relevance of studies on single crystals of organic semiconductors considering both single component and bi-component charge transfer cocrystals. I will start with a survey of the growth methods with particular emphasis on purification of materials and vapor phase techniques for growing large size high-quality single crystals. I will also describe spectroscopic methods capable of investigating the electronic structure and the phonon/molecular vibrations spectrum. Examples of materials covered in this tutorial will be mainly small molecule semiconductors such as acenes and charge transfer cocrystals with TCNQ based acceptors. For charge transfer crystals, recent results on the impact of ground-state charge transfer degree and molecular dynamics on the electronic structure and properties will be covered.

Photovoltaic Materials and Devices for Polymer Solar Cells

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Polymer solar cells (PSCs) are composed of a blended active layer of a *p*-type conjugated polymer as donor and an *n*-type organic semiconductor (*n*-OS) as acceptor, sandwiched between a transparent electrode and a top metal electrode.¹ The PSCs have attracted great attention in the past two decades, because of their advantages of simple device structure, light weight and capability to be fabricated into flexible and semitransparent devices. Recently, the low bandgap *n*-OS acceptors^{2,3} and the absorption-complementary polymer donors^{4,5,6} have promoted the research progress of the PSCs significantly, and the power conversion efficiency of the PSCs has reached over 15% recently.⁷ Here I will talk about the device structure, working mechanisms, developing history and recent research progress of the photovoltaic materials and devices of PSCs.

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High Performance Organic Light Emitting Devices – from TADF-OLED to Organic Semiconductor Laser Diodes

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After the great success of thermally activated delayed fluorescence (TADF) technology, the importance of charge transfer (CT) states has been widely recognized in organic luminescence materials.¹ Finely controlled donor-acceptor strength in TADF molecules could realize almost 100% quantum efficiency of electron-photon conversion in OLEDs by tuning the singlet-triplet energy gaps, upconversion rates from T₁ to S₁ states and radiative decay rates from S₁ states. Recently, further delicate control of CT interaction leads to long range exciplexes² and long persistent luminescence (LPL).³ In my first talk, we will introduce the diversified possibilities of organic CT states which open novel optoelectronic device applications.

In my second talk, we introduce our recent state-of-the-art organic semiconductor laser diodes (OSLDs). The devices incorporate a mixed-order distributed feedback (DFB) SiO₂ grating in an organic light-emitting diode structure. This device architecture allows lasing by direct injection of current into an organic thin film. It is critical to have a high-gain organic semiconductor layer showing clear separation of the lasing wavelength from significant triplet⁴ and polaron absorptions and design of a proper feedback structure to suppress losses at high current densities. We demonstrate a current driven OSLD and discuss the requirements of laser materials design and device architectures.⁵

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³ R. Kabe and C. Adachi, *Nature*, 2017, **550**, 384.

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Neuromorphic Organic Electronics Biosensors

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⁴Consiglio Nazionale delle Ricerche-ISMN

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 sensing device is operated in frequency as a "synapse-like transistor", either in a two terminal or a three-terminal device. The characteristic time scale of the synapstor is used as the signal correlate to the concentration. DA levels in the brain of healthy people are in the nanomolar range of concentration and decrease to 100-picomolar range in patients with Parkinson's disease (PD). 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. We also assessed the sensor against the whole series of DA catabolites, showing the capability of the sensor to discriminate sub-molecular changes of the chemical structure, or non-covalent interactions. 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.

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Functional Dielectric Elastomers: From Synthesis to Applications

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Soft materials that respond to either an electric stimulus by generating a mechanical stress or to a mechanical stress by generating an electric signal are of great technological importance and may find applications in actuators, sensors, generators, soft robotics, and implants.¹ However, even after years of research it is still challenging to achieve such responsive materials, which are also easily accessible, environmentally friendly, up scalable, and easily processable.

To achieve soft elastomers that deform under a low electric field, polymethylvinylsiloxane was used as starting material and was modified with different amount and type of polar groups, whereby the very efficient thiol-ene reaction was used. This allowed us creating a library of polymers and selecting some of the most promising ones for further investigations. Eventually, using appropriate starting polymer, polar groups, and appropriate processability and cross-linking into thin films, dielectric elastomer actuators responsive to unprecedentedly low voltages of 200 V are available.^{2,3}

To achieve elastomers that generate an electric signal when mechanically stressed, a composite approach was used. For this specially designed polymer nanoparticles with high T_g and side groups with large permanent dipoles were embedded in a chemically crosslinked polydimethylsiloxane matrix. The initially randomly oriented polar groups in the nanoparticles were poled in a strong electric field, while the film is heated above the T_g of the nanoparticles. The polar groups orient in the direction of the electric field and the achieved orientation is subsequently frozen-in by cooling the material back to room temperature. A permanent polarization responsible for the piezoelectric response is induced in the elastomers.^{4,5}

Thus, this presentation gives an overview of novel elastomers developed at Empa and the challenges faced during their synthesis and their incorporation in devices.

*This work was supported by SNF, Sciex and Empa.*¹

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Invited lectures

Redox-Active Organic and Organometallic Materials for Advanced Metal-Ion Batteries

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Using organic redox-active molecules provides a new paradigm for future development of metal-ion batteries. Indeed, organic materials are usually based on light elements (C, H, N, O, S) and, therefore, can enable much higher specific capacities compared to the salts and oxides of heavy transition metals. Most of organic materials are non-toxic and environment friendly, which makes easy their recycling as a common household waste. In contrast to crystalline inorganic cathodes and anodes, organic materials are soft and, therefore, can operate at high charge and discharge rates thus leading to design of ultrafast batteries. Mechanical properties of polymeric cathodes and anodes enable their application in truly bendable batteries for emerging generation of portable electronics.

Lithium-ion batteries currently represent one of the mainstream energy storage technologies. However, lithium is a scarce element and the available resources are definitely not matching the rapidly growing demand for energy storage. Therefore, sodium- and potassium-ion batteries (SIBs and PIBs) are now considered as promising scalable metal-ion battery technologies. In that context, organic redox-active materials are particularly important since they can operate efficiently with multiple mobile ions, while most of inorganic cathodes are constrained to only one specific ion matching the crystal lattice.

In this talk, we will highlight our recent results on the design of organic and metal-organic cathode and anode materials for lithium, sodium and potassium batteries. In particular, we will present ultrafast potassium-ion batteries delivering specific capacities of 169 mA h g⁻¹ at an impressive current density of 10 A g⁻¹ (charging/discharging in ca. one minute) and 245 mA h g⁻¹A at a lower current density of 50 mA g⁻¹. Specific energy of ~550-600 W h kg⁻¹ is reached for the best organic cathodes in potassium batteries. The polymer-based devices also demonstrated record-high cycling stability with no capacity decay after 10 000 cycles, thus outperforming all previously reported non-aqueous K-ion batteries.

The obtained results suggest that organic electrode materials, while being at the infancy of their development, start to show commercially interesting performances thus paving a way to implementation of a new generation of post-lithium metal-ion batteries.

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

2D Organic Semiconductor Single Crystals

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Organic light-emitting transistor (OLET) — one of the "youngest" organic electronics devices — has a number of advantages over the more traditional organic light-emitting diodes (OLEDs), which are already widely used in displays of portable devices and advanced TV screens. For example, OLET can be much brighter, and the light can be outcoupled from it much more efficiently. Moreover, OLETs are the most promising platform for injection organic lasers, which have still to be demonstrated. An ideal OLET is *per se* an ambipolar organic field-effect transistor (OFET) with a totally emissive active layer and Ohmic contacts. Taking in account that the charge transport in OFETs occurs within a few semiconductor monolayers adjacent to the semiconductor-dielectric interface, a perfect OLET active layer would be a molecularly thin (2D) single crystal of brightly luminescent ambipolar semiconductor. Indeed, the high structural quality of semiconductor single crystals provides their superior electrical performance, and the 2D active layer is very beneficial for OLET to get rid of waveguiding effects that reduce the light output from thin film and 3D-single-crystal devices. In addition, 2D OLETs have a high potential for various sensing applications.

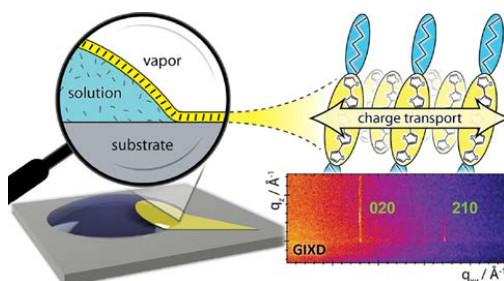


Fig. 1. Illustration of growth mechanism and x-ray diffraction pattern for a 2D organic semiconductor crystal.¹

However, combination of bright luminescence and efficient ambipolar charge transport in one material is not easy to achieve. Moreover, 2D emissive semiconductor single crystals are an almost unexplored field of research. In this presentation, recent development of 2D semiconductor single crystals will be overviewed. The most attention is paid to single crystals based on highly emissive thiophene-phenylene co-oligomers (TPCO). Monolayer single crystals of TPCO showing the electrical performance not inferior to that of the 3D ones will be presented.¹ Hurdles on the way to efficient 2D OLETs will be discussed.

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

¹ Bruevich V.V., et al., *ACS Appl. Mater. Interfaces*, 2019, **11**, 6315.

Hot-Carrier Dynamics in Lead-Halide Perovskite Nanocrystals: Role of Carrier Density, Nanoconfinement and Surface ligands

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The major efficiency limit in conventional solar cells is imposed by the rapid relaxation of above-bandgap “hot” carriers via electron-phonon coupling. Lead-halide perovskites (LHPs) currently hold the efficiency record for solution-processable solar cells, and previous observations of slow hot-carrier cooling in these materials have piqued a deeper interest into their application in disruptive next-generation photovoltaics. Here we implement an ultrafast “pump-push-probe” technique^{1,2} to study the sub-ps cooling dynamics in LHP thin films and nanocrystals (NCs) (fig.1a). We demonstrate that cooling in the all-inorganic CsPbBr₃ is slower than its hybrid counterparts (e.g. FAPbBr₃) in the high carrier density regime, owing to the relative abundance of optical phonon modes associated with the organic cation. We scrutinise the thermal equilibration between cold and hot states in the single- and multiple-exciton-per-NC cases (fig.1b), and remark on the effect of surface ligands on the cooling dynamics.

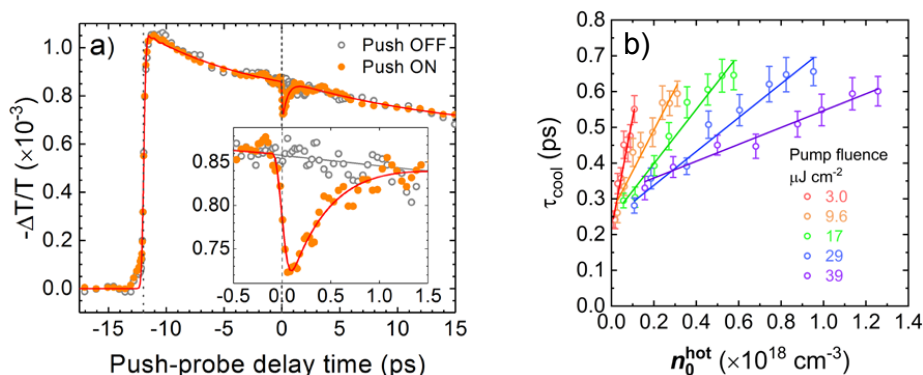


Fig. 1. (a) Observation of carrier cooling in pump-push-probe experiment. (b) The influence of hot and cold carrier concentration on the cooling dynamics in CsPbBr₃ nanocrystals.

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Understanding and Controlling Aggregate Formation During Spin-coating

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In this presentation, I shall discuss what we can learn from comparatively simple spectroscopic measurements regarding the formation of aggregates in polymers and oligomers when spin-coating. I will demonstrate that the aggregation process is preceded by a planarization of the polymer backbone, and that it can be described like a coil-globule transitions.¹ In particular, the nature of the resulting aggregates can be controlled through the substrate temperature^{2,3} which changes the nucleation process. This is illustrated for a range of widely used polymers such as P3HT, PFO, PCPDTBT, PCE11 and others.

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Ferroelectricity in 2D Halide Perovskites

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Ferroelectricity is the characteristic of a dielectric material when its polarization induced by an external electric field persists even after the electric field is removed. Ferroelectricity has a strong influence on spatial charge separation and carrier transfer, thus affecting the performance of perovskite devices. Here we discuss ferroelectricity in 2-phenylethyl-ammonium (PEA) and methylammonium (MA) Ruddlesden-Popper (RP) perovskite $(\text{PEA})_2(\text{MA})_{\bar{n}-1}\text{Pb}_{\bar{n}}\text{I}_{3\bar{n}+1}$ obtained with piezo force microscopy and polarization-electric field measurements. Extensive Molecular Dynamics simulations support the experimental results and identified ion translations and correlated reorientation of MA molecules as the source of ferroelectricity. Our findings present fresh insights into the origin of the ferroelectric properties in RP perovskites essential for developing new functionalities in perovskite optoelectronics.

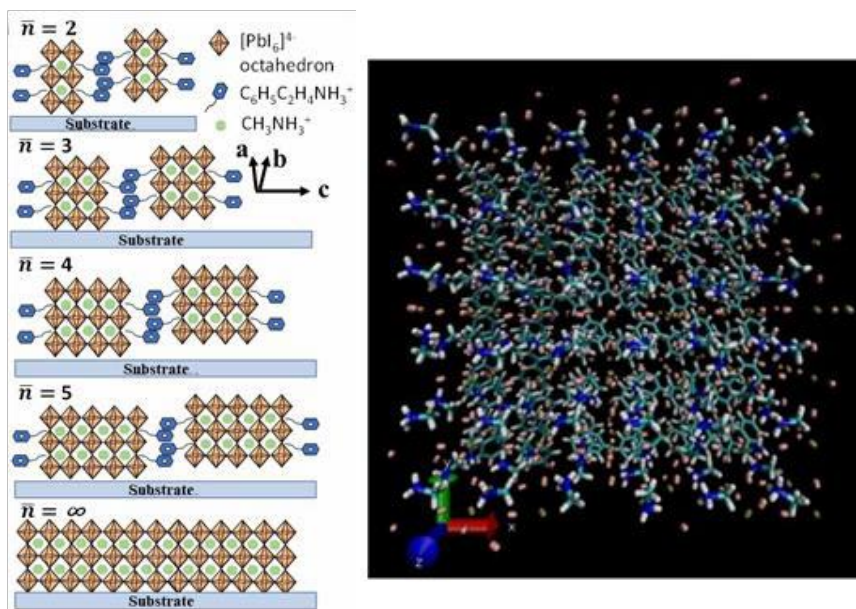


Figure. Left: Structural orientation of RP perovskites $(\text{PEA})_2(\text{MA})_{\bar{n}-1}\text{Pb}_{\bar{n}}\text{I}_{3\bar{n}+1}$ (where $\bar{n} = 2$ to ∞), on conducting substrate. Right: Illustration of the simulation box for $\bar{n} = 3$. Lead atoms are shown in golden colors, iodine in pink, carbon in cyan, nitrogen in blue and hydrogen in white. The red, green, and, blue arrows illustrate the axes of the cubic simulation boxes.

¹ Q. Zhang, A. Solanki, M. Li, D. Giovanni, K. Parida, P.S. Lee, Th. Jansen, M.S. Pshenichnikov, T.C. Sum, *ACS Appl. Mater. Interface*, 2019, **11**, 13523.

Highly Luminescent Organic Charge-Transfer Co-Crystals

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Co-crystals of conjugated organic compounds have attracted much attention as next-generation composite materials for organic optoelectronics. The vivid interest is driven by targeted materials design concepts inter alia via the isometric approach¹ creating segregated or mixed-stacked co-crystal systems. Reversible segregated-mixed stack conversion can be induced by external multi-stimuli, generating large color changes by switching between localized exciton vs. charge-transfer (CT) emission.² Combined pump-probe, low-temperature PL and atomistic quantum-chemical studies reveal the spectral signatures and kinetics of exciton generation, transport and deactivation.^{3,5} Switching from 1D to 2D mixed-stacking motif gives rise to well-balanced ambipolar charge transport materials, being a prerequisite for optimized electrically driven light emission, and allowing for the first CT-crystal-based OLET.⁴ opening new pathways in the field. Targeted crystal design allows for systematic color variation and intermolecular TADF characteristics while keeping the structural characteristics.⁵

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⁵ S. Oh et al, **to be submitted**

Inkjet-Printed Polymeric 3-colour Devices Mimicking Human Retina

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Conjugated small molecules, polymers and extended pi-systems such as graphene, represent a promising platform for visual prostheses offering novel retinal biocompatible devices.¹⁻⁴ Polymers, in particular, with high absorption coefficients, chemically tuneable bandgaps, the ability to be processed at room temperatures on flexible substrates, and signal transduction mechanisms that do not require external power sources, make them ideal materials for retinal prosthetic applications. Despite ongoing research efforts in artificial retina field with organic semiconductor materials, full-colour sight restoration remains very challenging.

We propose a novel inkjet-printed, tri-colour Artificial Retina optoelectronic devices based on photoactive conjugated polymers mimicking human retinal photoreceptors activities. These are based on biocompatible thin films of three different polymers interfaced with a biological electrolyte solution. Photo-response of these devices is demonstrated with long-pulse excitation from monochromator-filtered light source. We compare polymers' films response with retinal photoreceptors colour sensitivity and discuss the role of polymer-electrolyte interface for photo-transduction mechanisms. Ink-jet printed devices are demonstrated in the form of arrays of semiconducting $\approx 80\mu\text{m}$ diameter-polymeric round 'pixels-photoreceptors' with specific red, green and blue colour sensitivity. The devices do not require wiring or external bias to operate, and are stable in aqueous physiological conditions. Due to biological compatibility of organic semiconductors, high absorption and wide spectral tuneability, this device technology is expected to find medical applications as retinal bio-engineered prosthesis towards the restoration of human vision lost due to common eye diseases, including Age Related Macular Degeneration and Retinitis Pigmentosa.

¹ Yang J.-W. et.al. *Adv. Healthcare Mater.* 2018, **7**, 1800365.

² Rand D. et.al. *Adv. Mater.* 2018, **30**, 1707292.

³ Gautam V. et.al. *Adv. Mater.* 2014, **26**, 1751-1756.

⁴ Ghezzi D. et.al. *Nat. Photonics* 2013, **7**, 5 400-406.

Synthesis of High Purity Organic Materials Under Solvent-Free Conditions

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One of the most important requirements for organic materials in electronic applications is their purity. Of special importance is the contents of transition metals that should not exceed ppm or even ppb values. Admixtures of transition metals can influence semi-conductor properties of organic materials and/or catalyze unwanted chemical transformations under photo- or electro-activation leading to degradation of the organic layer, and, consequently, the whole device.

Last several years our group was involved in contract research projects with LG Chem, one of the world leaders in development and production of organic materials for various electronic applications. We performed the search for new efficient approaches for synthesis of organic materials which are used as electron-, hole-transporting layers, as host materials, or as light emitting materials. The main customer's demands were: high yields of synthetic methods, scalability, robustness, high selectivity, and, finally, high purity of materials with special emphasis on purity from transition metals.

Many organic materials of interest for electronic applications are synthesized using transition metal catalyzed reactions:

- Palladium catalyzed Suzuki C-C, and Buchwald-Hartwig C-N cross-coupling reactions.
- Copper catalyzed alkyne-azide cycloaddition.
- Gold catalyzed additions of nucleophiles to alkynes.

Strict industrial requirements prompted us to develop new approaches for the known catalytic reactions – transition metal mediated reactions under solvent-free conditions. Apart from applied importance new methods are of high fundamental interest. We succeeded to develop new synthetic procedures that yield high purity products. Reactions under study proceed in absence of solvent, in melt. After completion of the reaction the product can be sublimed-off directly from the reaction vessel under reduced pressure. Such isolation procedure secures us from impurities such as transition metals, bases, and etc. due to their low volatility. Moreover, new synthetic methodologies turned out to be high yielding, selective, scalable and robust. Finally, these methods are highly atom economical and “green”, since produce low amount or virtually now waste. Sheldon's E-factor values for most examples are below 1.0, and in some cases reach unprecedented values of 0.1-0.01.

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Advanced Methods of in-situ Characterization of Organic Electronic Devices

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Detailed information on the morphology of the active layers of organic electronic devices can be one of the key issues for optimizing their performance. In the talk, the capacities of several advanced characterization methods will be dwelled upon. In particular, we will discuss on the recent developments of synchrotron-based nano- and micro-focused X-ray scattering applied to studies of polymer micro-structure.¹ We will also address combinations of structural characterization such as grazing-incidence X-ray diffraction (GIXD) with electrical measurements^{2,3} (cf. Fig. 1). Such *in-operando* approaches constitute a powerful tool for studies of correlations between the microstructure and charge transport in thin organic films.

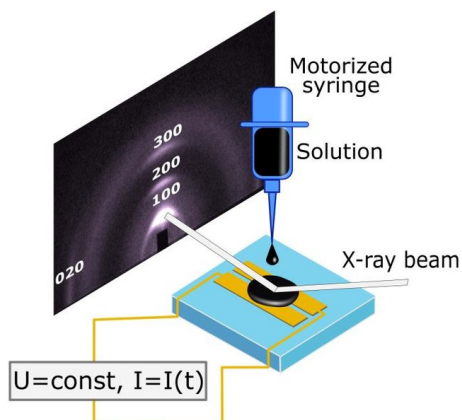


Fig. 1. Schematics of the setup allowing for simultaneous in-situ electrical and structural measurements.

This work was performed in accordance with state task No. 0074-2019-0014.

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PEDOT, a Work-horse for Organic Electronics

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PEDOT or poly[3,4-ethylenedioxythene] has been used in industry for more than 20 years, in the printed circuit industry, for capacitors and as antistatic layers in polarizers. 10 years ago commercial grades having much higher conductivity became available which were suitable to build transparent electrodes in OLED, solar cells, and other printed electronic devices. The lecture will give an overview on organic conductors, their function as transparent electrode and other functional layers in various printed electronic devices as well as the understanding of effects originating from electronic, chemical, and morphological manipulations of PEDOT.

Redox Front Propagation in Polyaniline as a Basis for Rate-Based and Spike Neural Networks

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The redox front propagation phenomenon in conductive polymers immersed into liquid electrolyte, changing their conductivity from insulator to conductor was known before¹ and several analytical models of front propagation were introduced e.g.², stressing the role of counter-ions movement as a limiting stage of front velocity. We were first to observe the redox front propagation in polyaniline³, which is also known for its memristive behaviour⁴ meaning that redox front changed conductance is memorized after front propagation. The spikes propagation in polyaniline, interfaced with solid polymer electrolyte is soliton-like with low dissipation and high speed, just resembling the signal propagation along nerves of biological system, due to concerted change of redox states, electron transfer and local change of counter-ions concentration.

The combination of fast propagation speed (1 mm/200 millisecc) observed in thin LB films of PANi and memristive property makes polyaniline ideal for use in neural networks, both 2nd generation (rate-based) and 3^d generation (spiking).

The simple polymer all-memristor multi-layer neural networks were manufactured, comprising neural network itself – made of gold contacts and polyaniline memristive bridges, layer of polymer electrolyte on top and counter-electrode with polyaniline buffer – only one for the whole system and used both as counter- and reference electrode.

In case of rate-based neural networks we developed the concept of Hebbian or non-linear networks, including the introduction of error back-propagation algorithm method. In case of spiking neural networks we found spike propagation mechanism to be similar to biological nerve and found mechanism of network plasticity

We also propose large scale spiking network concept, where the metal contact plays the role of Leaky Integrate and Fire (LIF) neuron and VLSI is possible, just combining the metal contacts and polymer bridges between them. If combining only metal pads and polymer bridges neural networks with the number of neurons 10⁹ is not a big problem. The rate-based networks require Schottky-type contacts between metal and polyaniline to realize the non-linear transfer function, the ability to make Schottky-contact based 2nd generation VLSI neural networks is also discussed.

¹ Olle Inganäs *et al*, *J. Electrochem. Soc.*, 2004, **151**, 119-124.

² J.C.Lacroix, K.Fraoua, P.C.Lacaze, *J. Electroanal. Chem.*, 1998, **444**, 83-93.

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⁴ V.Erokhin *et al*, *Journal of Applied Physics*, 2009, **105**, 124.

Expanding the EGOT-based Biosensor Toolbox by Materials Strategies

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Electrolyte Gated Organic Transistors (EGOTs) are three-electrode organic electronic devices that feature an electrolyte solution serving as the gate dielectric.¹ Although not fully understood, the accepted working mechanism of EGOTs relies on electrolyte ions migration upon application of a gate voltage, accumulating either at the interface between the organic semiconductor and the electrolyte or within the OSC bulk. In the former case, the corresponding devices are named EGOFETs (Electrolyte Gated Organic Field Effect Transistors), while in the latter we are dealing with OECTs (Organic Electrochemical Transistors). Both EGOFETs and OECTs are rapidly emerging as novel tools for a wide range of applications including bioelectronics, neuromorphic computing, integration into logic circuits and energy storage. EGOTs appear to be particularly suited as ultra-sensitive biosensing tools for label free detection of biological species across a large length scale range. Following successful demonstration of EGOT-based biosensors for the detection of neurotransmitters², inflammatory biomarkers³ and plant viruses⁴, we are currently exploring new device architectures and novel schemes for integration of biorecognition elements either at the gate/electrolyte or at the OSC(Organic Semiconductor)/electrolyte interfaces. We also investigated how the choice of materials largely impacts on the operational regime of EGOTs, highlighting some guidelines to tailor the device properties for selected biosensing applications.

This work was supported by FAR2015 “PRODE”, FAR2017, FAR 2018 “E-MAP” and by EuronanomedIII Project “AMI”

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³ Berto et al., *Adv. Biosyst.* 2018, **2**, 1700072

⁴ Berto et al., *Sens. Actuat B-Chem* 2019, **281**, 150-156

Discussion,
evening and
sponsor lectures

Luminescence Enhancement and Quenching in Organic Solids

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The last years have seen a boost in small molecule based luminescent materials for innovative (opto)electronic applications. Targeted design of such materials requires nevertheless a systematic understanding of structure-property relationships; this however can only be achieved if all intra- and intermolecular parameters are understood which control the radiative and non-radiative decay processes. The discussion lecture addresses these parameters in a systematic manner based on a library of structurally similar materials with largely differing photophysics, discussing non-/radiative deactivation in fluid and solid solution, to then turn to nano-, poly- and single crystalline materials. By this a holistic view on non-/luminescent solids is achieved.

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³ J. Shi et al, J. Gierschner, *J. Phys. Chem. C* 2017, **121**, 23166.

⁴ J. Shi et al, J. Gierschner, *Adv. Opt. Mater.* **2017**, **5**, 1700340.

⁵ J. Gierschner et al, *Adv. Opt. Mater.* 2016, **4**, 348.

⁶ J. Gierschner, S. Y. Park, *J. Mater. Chem. C* 2013, **1**, 5818.

⁷ J. Gierschner et al, *J. Phys. Chem. Lett.* 2013, **4**, 2686.

Scientific Ethics

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Over the past decades science has become increasingly competitive which is mainly linked to a declining success rate for scientific funding. In order to secure the next iteration of funding, international recognition plus an impressive publication track record have evolved to become key factors for a scientist's future existence. This has led to an enormous pressure on scientists to publish in prestigious journals like *Science* or *Nature*, a trend that is often condensed in the phrase '*publish or perish*'. As a consequence, some scientists felt compelled to manipulate or even to forge scientific data which immediately raises an issue of scientific ethics. While these acts are obvious violations of good scientific practice, there are also more subtle cases of scientific misconduct. In other words, there is a large grey zone between unquestionably correct and incorrect ethical behavior.

In this evening lecture we will venture on a journey to the grey zone of scientific ethics in natural sciences. We will explore the entire ethical spectrum of scientific practice by presenting a series of famous cases of scientific misconduct. Highlighting the consequences and implications for all involved parties will underline the importance of ethical guidelines for the whole scientific community, from individual PhD students all the way up to funding and government agencies.

Imaging Ellipsometry and Near-field Microscopy for Organic Electronics Applications

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Imaging ellipsometry (Accurion) combines the unique sensitivity for thin film thickness and tiny changes in optical properties, respectively of ellipsometry with the lateral resolution and visualisation properties of optical microscopy. The technique offers information on thickness (0.1 nm – 10 µm ± 0.01 nm) and optical properties for micro-structures down to 1 µm size. Imaging Ellipsometry uses imaging optics to record micro-maps and measure multiple regions simultaneously. Spectroscopic Imaging ellipsometry can be performed making use of spectral range from 190 nm to 1700 nm. The primary data are microscopic maps of the ellipsometric angles Delta and Psi that can transformed to parameters like Thickness and complex refractive index by optical modelling.

Neaspec near field technology is one of the most recent contribution to the scientific imaging tools. What this microscopes do, is a full optical measurement, but below the diffraction limit. Let's imagine we have a semiconductor structure, with different doping – but our probing wavelength is much larger than the actual structure – so with standard widefield methods, we are not able to resolve this structure at all – esp not different regions and areas of interest on it. To enable this, we have to use neaspec's nearfield technology.

Oral talks

Organic Semiconductors Synthesis in Water Promoted by π -Surfactants

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Sustainability is rapidly becoming a key priority in synthetic chemistry, with reduction of organic solvents consumption and energy intake of reactions representing critical aspects. A variety of strategies are being developed to overcome these issues, in many cases relying on the use of benign solvents like water.¹ Synthesis of organic semiconductors could greatly benefit from these methods. In fact, an important reason preventing organic electronics to reach the market is the difficult synthetic access to performing materials, whose large-scale production is so far unsustainable.²

Micellar coupling reactions count among sustainable methodologies applicable to synthesize π -extended derivatives: industrial surfactants like Kolliphor EL allow Suzuki-Miyaura and Buchwald-Hartwig coupling for the synthesis of such molecules, although at the expenses of the use of cosolvents to push the reactions to full conversion.^{3,4} An alternative approach consists in the development of designer surfactants containing aromatic moieties capable to feature π - π interactions with conjugated building blocks. We here describe how original aromatic designer surfactants, like PiNap-750M (Figure 1), enable carrying out micellar couplings on relevant organic semiconductors precursors in water alone, at room temperature and with remarkably short contact times, affording the target compounds with unprecedented high simplicity and sustainability.

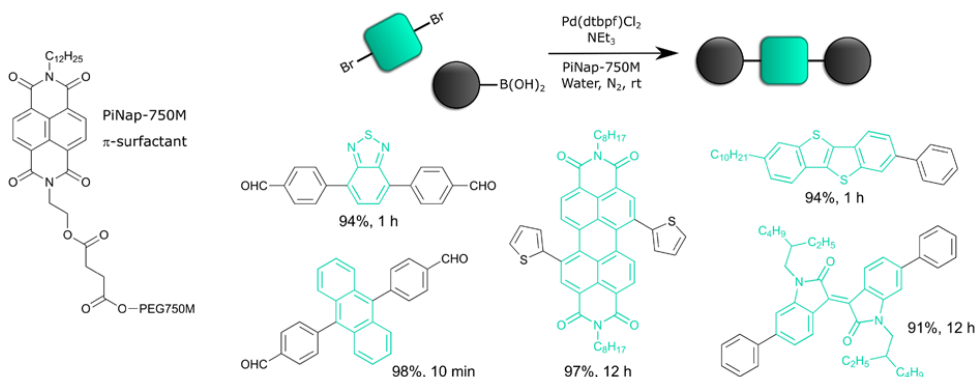


Fig. 1. Conditions for Suzuki-Miyaura coupling reactions with PiNap-750M π -surfactant, and examples of synthesized organic semiconducting derivatives

This work was supported by the Italian Ministry of University and Research (MIUR) through grant “Dipartimenti di Eccellenza 2017 Materials For Energy”.

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Quantitative Topological Descriptor for Linear Co-oligomers Fusion

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Conjugated organic molecules are versatile compounds for numerous bio-medicinal and optoelectronic applications. Previously, conjugated rod-like co-oligomers (distyrylbenzenes, thiophene/ and furan/phenylene co-oligomers) were reported as highly-emissive semiconductors with moderate charge mobility.¹ However on the opposite, rigid, planar and closely-packed annulated conjugated systems (acenes, fused polycyclic furans and thiophenes) were reported to show very high charge carrier mobility, albeit low emission efficiency due to aggregation quenching.² Thus, searching (even in silico) an optimal (fully or partially) annulated system with balanced optoelectronic performance is still a great challenge and hence strict and quantitative definition of annulation concept is required.

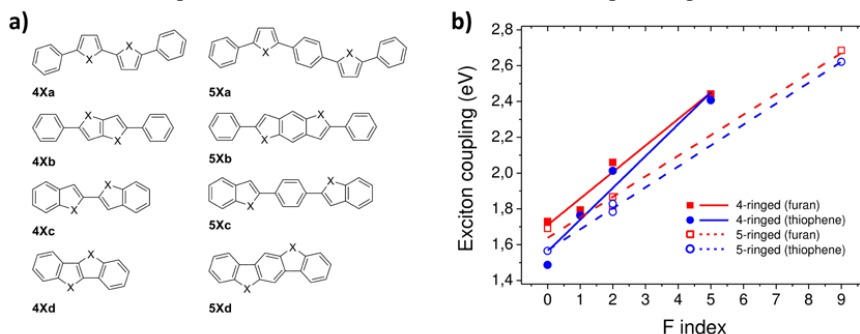


Fig. 1. (a) Chemical structure of studied compounds; (b) example of correlation between F-index and exciton coupling evaluated for model π -stacking dimers

In this work we propose F-index: intuitive, quantitative definition of annulation based on molecular topology applicable to the materials of strategic importance in organic optoelectronics, viz. linear quasi-one-dimensional centre-symmetrical heterocyclic molecules originated from the fusion of furan/ and thiophene/phenylenes.³ F-index evaluated for investigated compounds (Fig. 1a) showed excellent correlations with HOMO-LUMO gap, absorption energies, exciton coupling (Fig. 1b), electron affinity. Thiophene/phenylenes were shown to be very sensitive to annulation due to the ~ 2 -3 decrease in the charge reorganization energy whilst it remains almost unchanged for furan/phenylenes. Although some properties (single-point energy and energy of boundary orbitals) did not exhibit good correlations, further generalisation of the definition of F-index, with addition of other structural properties and electronic effects, may allow to apply it to a wider classes of conjugated compounds to estimate their optoelectronic performance without heavy quantum chemical calculations.

The work was supported by the Ministry of Education and Science of the Russian Federation (grant number 4.7154.2017/8.9).

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n-Type Polymer Semiconductors Containing B←N Unit and Their Application in OPVs and OFETs

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Conjugated polymers as semiconductors are widely used in organic opto-electronic devices, such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic solar cells (OSCs). Compared with inorganic semiconductors and organic small molecular semiconductors, conjugated polymer semiconductors have the great advantage of solution processing with low cost and flexibility. There are much less n-type conjugated polymers than p-type conjugated polymers. Moreover, most of n-type conjugated polymers are based on imide-containing unit, such as naphthalene diimide unit or perylene diimide unit. We propose to design n-type conjugated polymer semiconductors using boron-nitrogen coordination bond (B←N) and develop a new family of n-type conjugated polymers containing B←N unit. In this talk, I will show you the principle of B←N unit, the molecular design of n-type conjugated polymers containing B←N unit, the functions of B←N in these polymers, and the unique electronic structures of these polymers. I will also show you how to use molecular design to tune the absorption spectra, energy levels and electron mobilities of these polymers.

All polymer solar cells (all-PSCs), which use blend of p-type polymer electron donor and n-type polymer acceptor as the active layer, are a promising photovoltaic technology. The n-type conjugated polymers containing B←N unit can be used as polymer electron acceptors of All-PSCs. These all-PSCs always exhibit high open-circuit voltage of 1.0-1.3 V. I will show you how we enhance the power conversion efficiency of the all-PSCs from 0.1% to more than 9%.

This work was supported by the National Key Basic Research and Development Program of China (973program, Grant No. 2015CB655001) Founded by MOST, and the Natural Science Foundation of China (No.21625403).

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Luminophores Based on 2,1,3-benzothiadiazole Electron-withdrawing Core and Their Absorption-Luminescent Properties

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Luminophores as functional materials are successfully applied in many fields of science and technology. Among them, 2,1,3-benzothiadiazole (BTD) derivatives play an important role due to their unique optical and electronic properties. Typically, BTD-based materials are symmetrical molecules composed by a donor-acceptor-donor (D-A-D) framework. The main advantage is that absorption-luminescent properties of such molecules can be easily tuned by the electronic properties of the extended donor substituents. On the other hand, introduction of silicon atoms into conjugated organic compounds can lead to the some specific electronic effects^{1,2}.

In this work a series of new linear π -conjugated oligomers based on BTD core and various combinations of 2,5-thiophene and 1,4-phenylene electron-donating units with terminal trimethylsilyl groups has been synthesized and characterized³. Investigation of their absorption-luminescent properties revealed that all of them possess high photoluminescence (PL) quantum yield and large Stokes shift both in diluted solutions and polymer matrix, while in the solid state their PL efficiency decreases. It was found that the main factor influencing the optical properties of the molecules obtained is the type of aromatic fragment directly attached to the central BTD moiety. Changing the chemical structure of the donor aromatic fragments from allows tuning the PL spectral maximum of the luminophores in wide range from 510 to 660 nm. It was shown that the presence of trimethylsilyl groups is responsible for their increased solubility, enhanced molar extinction coefficients and shortening the excited state lifetime without decreasing the PL efficiency.

This work was supported by Russian fund for basic research (grant 18-33-20050) and performed in the framework of leading science school NSH-5698.2018.3

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Excited State Features and Dynamics of a Highly Efficient All-Organic Photocatalyst for Polymerization Reactions

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Homogeneous organic photocatalysis has found increasing interest for energy and materials conversion. For this, redox, optical and photophysical properties of the photocatalysts (PCs) have to be controlled; this concerns in particular a long-lived excited triplet (T_1) state to permit effective diffusion of the reaction partners. Therefore, transition metal-based PCs are commonly used, which exhibit high intersystem crossing (ISC) owing to facile spin-orbit coupling triggered by the heavy atom. However, applications are limited due to metal contamination and toxicity. As an alternative, organic PCs (OPCs) have emerged, which however require a precise control of the ISC by tuning character and energies of the singlet (S_n) and triplet manifolds (T_n). An efficient design concept was demonstrated through strongly twisted donor-acceptor (D-A) systems, which exhibit a strong charge-transfer (CT) character of S_1 and small singlet-triplet gaps.¹

Here, we investigate a particular efficient OPC (4DP-IPN; Fig. 1) for RAFT polymerization,² by an in-depth transient absorption & luminescence study, combined with TD-DFT calculations, to quantify the complete excited state features and dynamics of the molecule. Key to the superior performance of the compound is indeed the combination of matching redox properties, good light absorption and control of character and energy of the S_n , T_n manifolds. In fact, a high ISC yield of 82% and long T_1 lifetime is achieved; this concept may pave the road to future computer-aided molecular design concepts of highly efficient OPCs for precisely tailored applications.

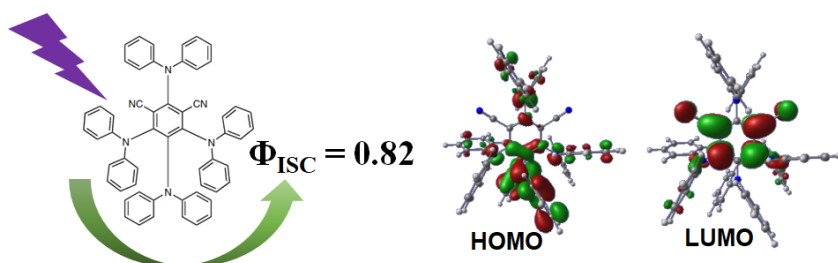


Fig. 1. Chemical structure of 4DP-IPN with Φ_{ISC} and frontier molecular orbitals.

¹ V. K. Singh et al, *Nature Catalysis*, 2018, **1**, 94–804.

² Y. Song et al, **in submission**.

Cardiomyocytes Optical Pacing Mediated by Micro Patterned Polymer Interfaces

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²Department of Physics, Politecnico di Milano

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Nowadays the research on human machine interface is constantly attracted by the idea to act in a contactless and wireless way. In particular biological and medical areas can benefit from optical method for introducing innovative ways to probe and stimulate the biological matter¹. Conjugated molecules and polymers offers a promising platform to interface with cells and living organisms thanks to their high optical absorption/emission cross section, chemical synthesis' easiness and relatively low toxicity.

In this work, we are developing a simple and fast method to fabricate and pattern an interface with a double functionality given by the presence of photoactive poly(3-hexylthiophene) and polyethylene blended together. The pattern on the surface of the film is designed to mimic the physiological condition and to help living cells to organize in a tissue. At the same time, the active component is able to transduce light into a stimulus for excitable cells. The mechanical properties and easiness of process are due to the presence of polyethylene while the optoelectronic properties are given by the poly(3-hexylthiophene)^{2,3}. We demonstrate the all optical modulation of the contraction rate of cardiomyocytes by visible light mediated by our interface. This modulation was monitored via a repeated acquisition of videos followed by a mathematical analysis performed exploiting of an algorithm based on the Motion Vector Field⁴. Both stimulation and contraction analysis of cardiomyocytes were conducted via optical methods only, although the semiconducting properties of the substrate permits possible applications of such a system in optoelectronics (i.e. bioelectronics). The ultimate goal of this project is to produce an artificial tissue for future applications in the robotic, pharmacological and regenerative medicine fields. At the same time the fabrication methods and the stimulation process make it appealing also for different applications (i.e. tissue and neural regeneration).

Molecular Aggregate Matryoshka: 2D Spectroscopy Meets Microfluidics

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Inspired by the remarkable quantum efficiencies of natural light-harvesting complexes (LHCs), double-walled tubular aggregates have attracted considerable interest as artificial LHCs.¹ At the core of their efficient energy transfer is a dense array of thousands of strongly coupled molecules giving rise to highly delocalized and mobile excitons. Unravelling the nature of exciton delocalization as well as exciton diffusion is inevitable for potential applications, yet inherently challenging to measure due to congested spectroscopic signatures.

Here we employ a novel spectroscopic lab-on-a-chip approach to first simplify the supramolecular hierarchy of our model system, multilayered C8S3 nanotubes, and then directly probe multi-exciton interactions via 5th order 2D spectroscopy.² The outer layer is selectively removed in a microfluidic channel thereby providing a sufficient time window for 2D spectroscopy. This allowed us to obtain an unobscured view on the exciton dynamics of the isolated subspecies and allowed us to unambiguously identify the exciton delocalization and mobility.

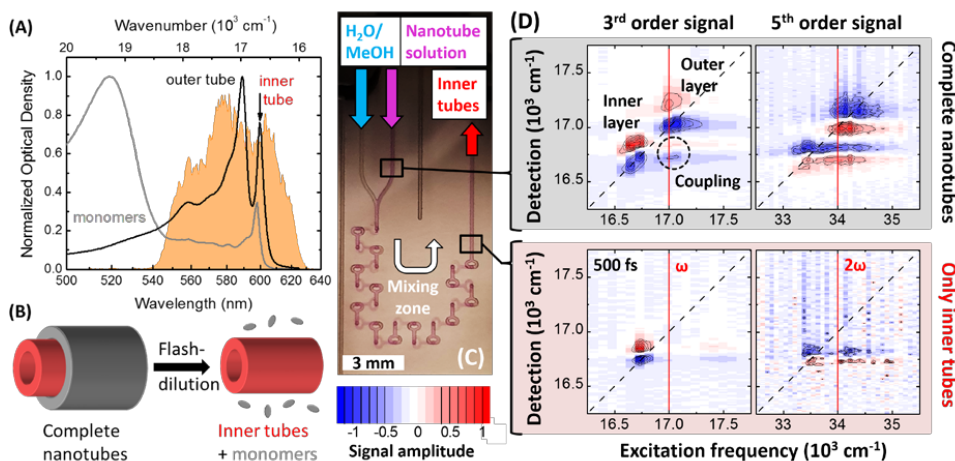


Fig. 1. (A) Linear absorption spectrum of (flash-diluted) nanotubes and laser excitation spectrum. (B) Selective Stripping of outer tube due to flash-dilution. (C) Cuvette for microfluidic flash-dilution. (D) Normalized 3rd and 5th order 2D spectra.

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Surface-Enhanced Raman Spectroscopy of 2D Organic Semiconductor Crystals

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Recently developed ultrathin two-dimensional (2D) organic semiconductor crystals are a promising platform for advanced organic electronic devices. Remarkable quality of such crystals results in charge-carrier mobilities comparable to those of bulk crystals¹, but their structure and orientations are hard to study because of their extremely small thickness. Here, we applied surface-enhanced Raman spectroscopy (SERS) to investigate the thinnest 2D single crystals — monolayers, which are based on thiophene-phenylene co-oligomers promising for light-emitting transistors: 1,4-bis(5'-decyl-2,2'-bithiene-5-yl)benzene (DD-TTPPT) and 1,4-bis(5'-hexyl-2,2'-bithiene-5-yl)benzene (DH-TTPPT) (Fig 1, a).

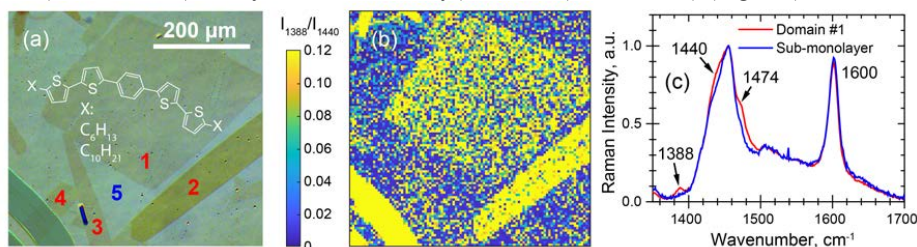


Fig. 1. (a) C-DIC microscopy image of the DD-TTPPT sample: monolayers grown on a SERS substrate. Red numbers are for crystalline domains, and a blue one indicates the interdomain area. Inset: structural formula of the studied oligomers. (b) SERS map of 1388, 1440 cm^{-1} relative intensities (I_{1388}/I_{1440}). (c) Comparison of Raman spectra averaged over domain #1 and sub-monolayer area #5: difference in peak intensities are marked with arrows.

The Raman spectra were calculated as a function of the molecule orientation (Raman anisotropy), and SERS microscopy maps were acquired (Fig 1, b). We found that the anisotropy of the SERS signal coming from variously oriented 2D crystals of DD-TTPPT is rather small but sufficient to distinguish the various orientations of 2D crystalline domains. Furthermore, SERS microscopy allowed us to detect the presence of a sub-monolayer — amorphous material between the crystalline domains, which is practically inaccessible to optical or conventional atomic force microscopies (AFM). The sub-monolayer was also studied by lateral-force AFM, which showed notably higher friction and adhesion. Very similar results were obtained for DH-TTPPT. We present the data indicating different conformations of the molecules in 2D crystals and sub-monolayers as compared to 3D (powder) samples. We discuss the possible reasons of low experimental Raman anisotropy as compared to the calculated one.

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

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Water-Dispersible Hyperbranched Conjugated Polymer Nanoparticles for Amplified Fluorescence Sensing of Trace Nitroaromatic Explosives in Aqueous Solution

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Sensitive and Selective detection of nitroaromatic explosives, in particular 2,4,6-trinitrotoluene (TNT) and 2,4,6-trinitrophenol (picric acid, PA), are of great current interest in both national security and environmental protection because they are not only explosives but also recognized as toxic pollutants. Recently, amplified photoluminescence (PL) quenching of conjugated polymers (CPs) based on photoinduced electron transfer (PET) is considered as one of the most sensitive explosive vapor detection methods. However, their applications for TNT and PA detection in aqueous solutions are limited because of their low sensitivity and selectivity.¹ In addition, high hydrophobicity of CPs limited their sensory application in aqueous media.²

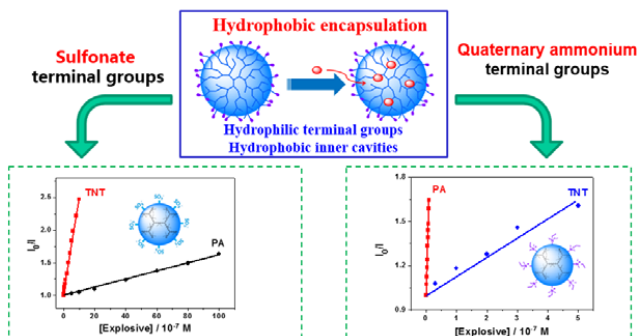


Fig. 1. Schematic illustration of fluorescence sensing based on HCPNs

Herein, we have developed two water-dispersible hyperbranched conjugated polymer nanoparticles (HCPNs) with hydrophobic CP cores and hydrophilic terminal groups, HCPN-S and HCPN-QA, which have sulfonate terminal groups³ and quaternary ammonium salt⁴ terminal groups, respectively. Based on the combination of hydrophobic encapsulation and electrostatic interaction, HCPN-S and HCPN-QA can highly sensitive and selective sensing of TNT and PA in aqueous solution, respectively. For HCPN-S, the quenching constant for TNT reaches $1.21 \times 10^6 M^{-1}$ and the detection limit is 0.80 ppb; For HCPN-QA, the quenching constant for PA is up to $6.36 \times 10^7 M^{-1}$ and the detection limit is 0.18 ppb.

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Ultra-sensitive Gas Sensors Array Based on Organic Field Effect Transistors with Tunable Selectivity

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Thin film organic field effect transistors (TF-OFETs) are known to be very sensitive to different polar molecular species present in the environment because major charge transport occurs in the thin monomolecular layer close to the semiconductor-dielectric interface and sorption of polar analytes directly to the current-carrying layer strongly affects the charge density.^{1,2} 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 that means slight response selectivity. Covering the sensor by receptor layer can provide semi-selective response keeping high sensitivity and allowing to distinguish different target gases via analysis of sensor array.

We have used Langmuir-Schaefer and spin-coating techniques with different functionalized tetramethyldisiloxane derivatives of BTBT-containing amphiphilic semiconducting molecules to fabricate TF-OFETs and study influence of the molecule structure and film morphology to sensor sensitivity. Devices have showed sensor response to different polar gases but single sensor selectivity was poor.³ While some progress could be obtained using multiparametric detection with independent OFET parameters such as mobility, threshold voltage and subthreshold slope,⁴ the general principle suitable for any target gas has to be developed. Changes in the active layer structure and addition of the receptor layer induces semi-selective response to different analytes due to different kinetics of their sorption. For example, TiO-containing receptor layer improve selectivity towards NH₃ while suppress response to H₂S. In this work we have compared gas sensor properties of TF-OFETs with different metal-porphyrins receptor layers and combined them into sensor array. Our system comprised of 5 sensors has limit of detection to NH₃, H₂S, EtSH and NO₂ down to 100 ppb and keep working at humid air with RH up to 60%. Multidimensional analysis of the array response and machine learning methods resulted in efficient distinguishing of this gases and ability to compare complex gas mixtures and training set. Considered system is very flexible and can be easily tuned to required target gases by choice of receptor layer. It can further be used in the medical breath analysis, fabrication automation problems and environmental monitoring.

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Stimuli Responsive Aggregation-Induced Emission of Bis(4-((9H-fluorene-9-ylidene)methyl)phenyl)thiophene Single Crystals

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Highly emissive organic materials with external stimuli response e.g. mechanical stress, optical impulse or thermal annealing are of great interest for functional applications in light-emitting devices, sensors or security papers.¹⁻³ A design of organic materials with specific optical response is still a challenge because both inter- and intramolecular factors should be considered. One of the approaches to the molecular design of multi-stimuli responsive materials based on the combination of rigid conjugated fragments with twist-elasticity and forbidden planarity functionalities. In this work we synthesized and studied diphenylthiophene capped with fluorene-9-ylidene groups - 2,5-bis(4-((9H-fluorene-9-ylidene)methyl)phenyl)thiophene (BFMPT, Fig. 1) as a novel stimuli-responsive Aggregation Induced Emission material.

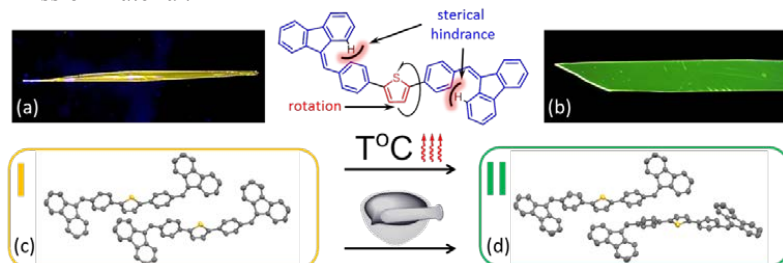


Fig. 1. The chemical structure of BFMPT and fluorescence micrographs of it's single crystals: polymorph I (a) and II (b); X-ray structure of dimers in polymorph I (c) and II (d).

BFMPT was synthesized by a combination of Knövenagel condensation and Stille cross-coupling reaction. The crystals of BFMPT have been grown by solvent-antisolvent crystallization. The crystals of two conformational polymorphs with different emission colors can be obtained simultaneously - triclinic orange needles (form I, Fig. 1a, c) or monoclinic green-yellow plates (form II, Fig. 1b, d). BFMPT demonstrated aggregation-induced emission effect: the photoluminescence quantum yield (PLQY) for it's solution was lower than 1% whereas both polymorphs are highly emissive with PLQY up to 40%. Polymorph I undergo mechano- and thermo-responsive transformation to more thermodynamically stable polymorph II. The twisting and conformational changes are considered as the main contributors to the PL change of the polymorphs. Despite the thermal-induced cracks these defects was demonstrated to not affect the photoluminescence efficiency in BFMPT single crystals.

Due to high intrinsic conformational elasticity BFMPT-related compounds could serve as a basis for further molecular design of novel high performance AIE materials.

This work was supported by RSF (project № 18-73-00081).

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Simple Model for Efficient Screening of High-Mobility Organic Semiconductors

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Efficient operation of organic electronic devices requires organic semiconductors (OSs) with high charge mobilities. Accordingly, screening of the plethora of synthesizable OS to reveal the high-mobility ones is of paramount importance for organic electronics. However, a rigorous model that could reliably predict the charge mobility in OSs of various kinds is still lacking. Moreover, state-of-the-art charge transport models are cumbersome and thus hardly applicable to rapid assessment of charge mobility in various OSs. In this context, screening of the materials is usually performed by means of Marcus model¹ that however was recently shown to overlook the high-mobility OSs possessing small conjugated cores,² e.g. HM-TTF and F₂-TCNQ, mainly because of the neglect of intermolecular charge delocalization. Thus, a simple model for charge mobility assessment that reasonably considers an interplay between charge localization and delocalization is highly desired.

In this study, a novel analytical model for screening the high-mobility crystalline OSs is suggested. Following our recent findings,² we modify Marcus formula for the charge transfer rate to account for intermolecular charge delocalization, static and dynamic disorder – the key factors governing the charge transport in high-mobility OSs. The basis of the suggested model constitutes the proposed analytical expression for the charge delocalization degree in dependence of the material properties and temperature. We tested our approach on 20 crystalline OSs and found that it reliably predicts charge mobility for OSs possessing various chemical structures and sizes, in contrast to the Marcus model (see Fig. 1). Thus, we anticipate that the suggested model is an efficient tool for the search of the high-mobility organic semiconductors. Its possible combination with crystal structure prediction opens the way towards assessment of the charge mobility in crystalline OSs just from their molecular structure – the fascinating opportunity that can boost the development of the organic electronics.

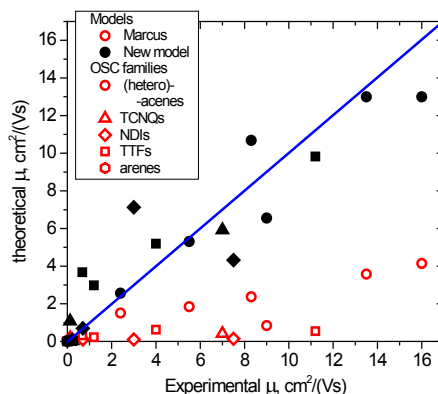


Fig. 1. Comparison of the charge mobility, μ , obtained using Marcus model (red) and the suggested one (black) with the experimental data.

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Generic Model for Describing Lamellar Order in Conjugated Polymers: Studying Mesoscopic Morphology and Charge-Transport

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We consider soluble conjugated polymers and develop¹ a generic coarse-grained model to study their self-assembly into lamellar mesophases (see Fig. 1). In actual materials, lamellae are formed by layers of co-facially stacked conjugated backbones alternating with layers of side chains. We describe the polymer architecture by a hindered-rotation model where each interaction center represents an entire repeat unit of the actual polymer, including its cyclic moieties and side chains. Soft anisotropic non-bonded potentials capturing coplanarity in chain orientation and stacking are a novel methodological feature of our approach.^{1,2} The potentials are developed using generic symmetry arguments. The model provides a framework for efficient Monte Carlo simulations and can generate nematic and lamellar mesophases; the latter belong to the class of smectic smectics.³

Poly(3-hexyl)thiophene (P3HT) is considered as a test system. We demonstrate that our lamellar mesophases match morphologies that have been experimentally reported⁴ for P3HT at elevated temperatures. We characterize lamellar order using various quantifiers, including scattering patterns which can be compared with experimental GIWAXS. We investigate the influence of conformational properties and mesoscale organization of polymer on charge-carrier mobility introducing a qualitative charge-transport model. Modeling large systems with long chains allows us to observe charge-transport between lamellar layers. This direction of charge transport is enabled by molecular pathways which are provided by rare, but thermodynamically allowed, backbone bridges between adjacent lamellar layers.

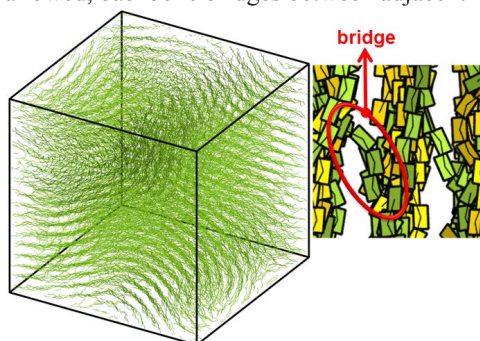


Fig. 1. Left: large morphology of P3HT with multiple lamellar domains. Right: enlarged view of a bridge connecting two layers. Empty space are layers of alkyl side-chains, implicitly described in our model.

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On the Description of Hopping Transport by the Multiple Trapping Model

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Charge transport in disordered organic semiconductors is one of the key physical processes, responsible for the operation of organic electronic devices. The transport level concept^{1,2} is a useful tool for analytic modeling, because it can greatly simplify the description of hopping transport by its reduction to the formalism of multiple trapping (MT) model. Both analytic and numerical modelling of a transport level has been based in general on the Miller-Abraham's model for the hopping rates. Meanwhile, other models of hopping rates are in use, in particular – the Marcus model, which accounts for the polaron effect. In this work, we show how the MT- description of hopping transport can be expanded beyond the Miller-Abraham's model and even beyond the transport level concept.

Results of our analytic and Monte-Carlo simulations, see Fig.1, show that the escape time of a carrier from the rather deep state of energy E follows the exponential law, $\exp((E_C - E)/kT)$, for the rather broad and relevant energy interval, where E_C is the effective transport level, providing Marcus hopping rates. This result confirms an applicability of the effective transport level concept for the case of Marcus hopping rates.

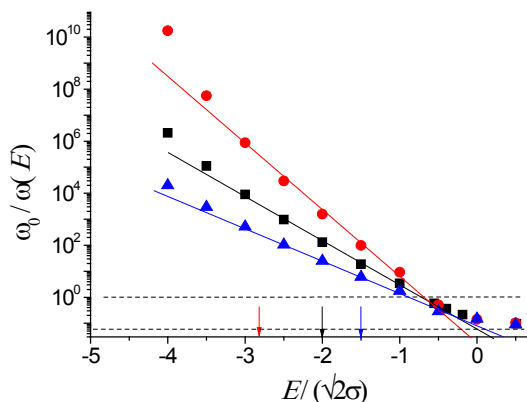


Fig. 1. The dependence of the reciprocal escape rate on initial energy, parametric in disorder, $\sigma/kT=4$ (circles), 2.83 (squares), 2.13 (triangles), $E_t=4kT=0.1$ eV.

Moreover, we develop the MT-formalism, which is not including the transport level explicitly. The master equation of hopping transport reduced to the balance equation of MT model, irrespective to the use of a concrete model for the hopping rates between localized states. One can apply this formalism for the non-stationary and spatially non-uniform problems. One can consider the well-known methods of effective transport level² and mean hopping parameter³ as simplified and special versions of this formalism.

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

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Novel Donor Small Molecules for Organic Photovoltaics

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During the past two decades, organic solar cells (OSCs) have attracted considerable scientific and technological interest compared to conventional PV technologies based on traditional inorganic semiconductors, since printed, inexpensive, and mechanically flexible OSC modules can be fabricated on plastic substrates such as PET and PEN at low temperatures using less capital intensive, high throughput roll-to-roll solution-process methodologies such as slot-dye, bar coating, and gravure/flexo printing. In this work, we report on the design and synthesis of novel donor small molecules for OSCs based on electron rich either triphenylamine¹⁻⁴ or benzodithiophene cores and end capped with alkyldicyanovinyl or alkyl cyanoacetate electron withdrawing groups. The properties of the molecules were studied by a complex of techniques such as optical absorption spectroscopy, differential scanning calorimetry, thermal gravimetric analysis and cyclic voltammetry. The photovoltaic performance of the molecules were studied both in fullerene and non-fullerene-based OSCs. The effect of different donor cores, length of conjugated p-bridge and nature of acceptor groups on properties of the molecules and their photovoltaic performance in OSCs were elucidated.

This work in the part of triphenylamine-containing oligomers was supported by Russian Science Foundation (RSF) (19-73-30028), whereas the work in the part of linear and other oligomers was supported by RSF (19-73-10198). The work was performed in the framework of leading science school NSh-5698.2018.3.

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Ultra-Thin and Ultra-Conformable Tattoo-Like Organic Photovoltaics

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Organic Photovoltaics (OPVs) attracted increasing attention thanks to the compatibility to fabricate large area OPV modules with low-cost scalable process. Solution process OPVs has in fact been proved using many different printing and coating technologies, such as ink-jet printing, screen-printing, roll-to-roll, bar coating and spin-coating. Despite the encouraging results, and the promising future perspective, at present OPV is not yet competitive with inorganic photovoltaic technologies. However, OPV devices already possess appealing performances for low-power electronics and portable ubiquitous devices, where the Si-photovoltaic stiffness is a limit and/or high performances are not required. The possibility to fabricate ultrathin and lightweight devices that are flexible and conformable, offer the basic features to enable a new generation of portable rechargers and power supply systems for low power portable and ubiquitous devices. The tuning of both material properties and the devices layers thicknesses permit to optimize OPV devices for specific illumination conditions^{1,2}, such as outdoor as well as indoor applications. Indoor illumination condition is of interest in the envision of the internet of things (IoT), with many portable wireless devices requiring local continuous power supply or secondary batteries recharging. OPV under indoor low-light illumination have been investigated by several groups^{1,2}, showing that specifically tuned materials and optimized device architectures can be adopted to fabricate OPV devices able to operate under multiple illumination conditions with sufficiently high performance for low-power applications. The development of ubiquitous low-cost and ready to use ultraflexible and ultraconformable solar cells would be of great impact ubiquitous devices supply and more specifically for epidermal electronics. In this envision, an interesting tool is provided by tattoo substrate that allow to fabricate the devices and easily transfer it, as already demonstrated by several work in literature that adopted it for skin-contact applications^{1,3,4}. In this work, commercial temporary tattoo paper was adopted as substrate for the fabrication of transferrable tattoo-like organic solar cells operating under both indoor and 1-sun illumination conditions, achieving 4.5% of power conversion efficiency and 55% of fill factor at 300 lux and 2.7% of power conversion efficiency and 61% of fill factor at 1-sun. The device did not have any encapsulation and could be easily transferred simply using normal water.

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Comparing Charge Generation and Extraction in ITIC and PCBM[70] Devices

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Recently, non-fullerene acceptors (NFAs) are becoming more attractive compared with fullerene based electron acceptors in organic solar cells (OSCs) due to numerous advantages such as large absorption coefficient and ease of tuning of the optical and electronic properties via molecular design¹. On the other hand, most OSCs often suffer from a modest fill factor (FF)². Reduced FF is the manifestation of voltage dependent charge photogeneration and inefficient free charge extraction. To elucidate the reasons behind this phenomena, we present a comparative study between a fullerene and a non-fullerene acceptor, namely PCBM[70] and ITIC when blended with naphthothiadiazole-based polymer (NT812) as the electron donor. Our results show that the non-fullerene system demonstrates balanced carrier mobilities with a high open circuit voltage (V_{OC}) and short circuit current (J_{SC}) while exhibiting a lower FF. We employed time-delayed collection field (TDCF) measurements to probe the nature of these mechanisms by studying charge generation and recombination in both systems. Our data indicate that although both systems exhibit field-independent charge generation, the NT812:ITIC device exhibits fast time-dependent non-geminate recombination which is correlated with a lower FF³.

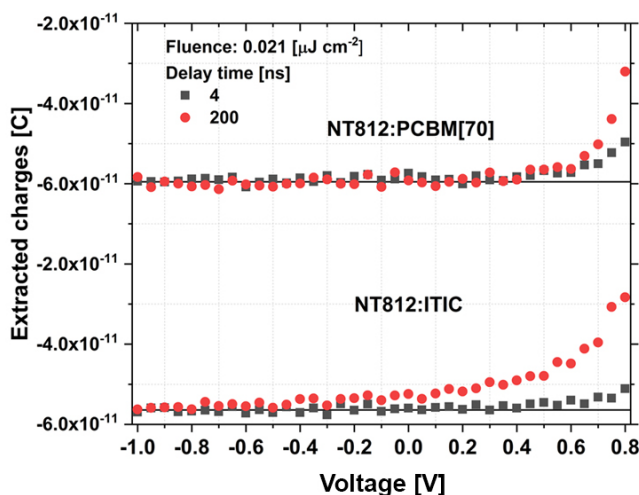


Fig. 1. Extracted charges versus voltage obtained from TDCF measurement.

This work was supported by Alexander von Humboldt Foundation (Sofja Kovalevskaja award).

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Role of Triplet Excitons in Non-fullerene Based Organic Solar Cells

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In the past, most organic solar cells (OSCs) employed fullerenes as electron acceptors. Recently, the synthesis of novel non-fullerene acceptors (NFAs) resulted in a power conversion efficiencies (PCE) of 15.7 %¹, which is higher than fullerene-based OSCs. It has been shown, that in fullerene-based OSCs the formation of triplet excitons (TE) may open up an additional recombination pathway² and also cause enhanced degradation. These TEs are localized on donor or acceptor molecules and can be formed either via intersystem crossing (ISC) or electron back transfer (EBT) (fig. 1). In this work, the formation of TEs in NFA-based OSCs is investigated. We studied the polymer donor (D) PBDB-T and the NFA acceptor (A) ITIC in pristine films, in blend films and OSC devices based on the blend. Energies of singlet excited states and triplet states of D, A and charge transfer (CT) states were obtained using optical measurements and DFT calculations. Results are shown in the Jablonski diagram (fig. 1). $T_{1,2}$ energy levels in D and A are lower compared to CT state and singlet excited states, thus population of TE states via EBT or ISC should be energetically possible. Low temperature spin-sensitive photoluminescence measurements reveal the formation of TEs in pristine films of D and A, as well as in the blend films. However, no TE signals were observed by electrically detected magnetic resonance measurements in OSCs under working conditions, thus ISC and EBT are suppressed by more efficient charge separation. The lack of TEs matches well with the high PCE of NFA-based OSCs and their stability.

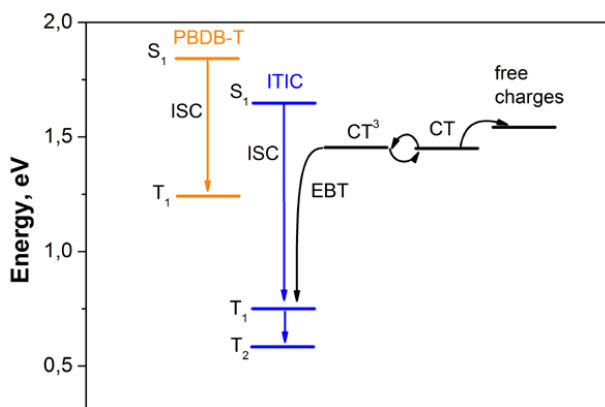


Fig. 1. Top: Jablonski diagram depicting the relevant electronic states in the PBDB-T:ITIC blend, ground state S_0 , singlet excited states S_1 , triplet excited states T_i , singlet and triplet charge transfer states S_{CT} , T_{CT} and free charge carriers. Bottom: PLDMR spectra

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

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Enhanced Performance of Bulk Heterojunction Solar Cells by Ultrathin Metal-Organic Framework Nanosheets

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We present the first example of a ternary bulk heterojunction solar cell incorporating metal-organic nanosheets (MONs) - an emerging class of two-dimensional materials which allow the creation of diverse, well-defined architectures with tailored properties. Metal-organic framework nanosheets (MONs) are the two-dimensional analogues of MOFs, consist of self-supporting, sheet-like materials approaching monolayer thickness and can be readily processed as suspensions and spin-coated to form thin films.¹

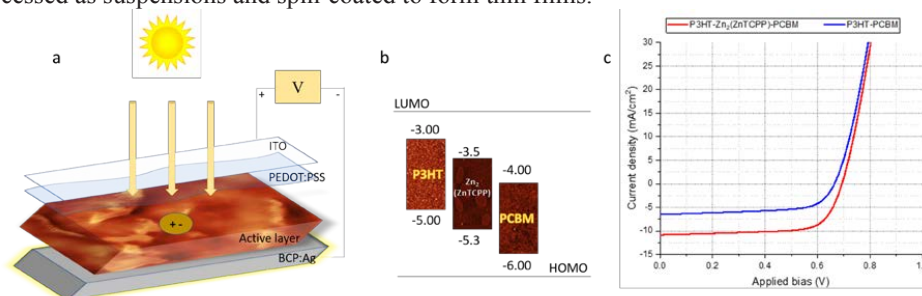


Figure 1. a. Schematic representation of the P3HT-Zn₂(ZnTCPP)-PCBM ternary blend bulk heterojunction solar cell in this study; b. The HOMO-LUMO levels of the components in the ternary blend; c. I-V curve showing the enhancement in performance of the device observed upon incorporation of the MONs in the active layer

In this work, we synthesised ultrathin zinc porphyrin based MONs which were found to have an intermediate band gap with respect to the components within the archetypal bulk heterojunction P3HT-PCBM.² Optimization of the active layer composition, thickness and thermal treatment resulted in the creation of devices with power conversion efficiency (PCE) of 5.2%; twice that for reference devices without nanosheets at 2.67%.

This work introduces for the first time the concept of including metal-organic framework as nanosheets into bulk heterojunctions in order to control the morphology of the active layer and improve absorption and charge mobility in order to enhance the performance of BHJ solar cells. We anticipate that our approach and the insights gained through this study will enable new generations of high efficiency organic solar cells and other electronic devices.

KS thanks the University of Sheffield Doctoral academy scholarship for funding this project. DGL thanks the UK EPSRC for partly funding this research via grants EP/M025020/1 'High resolution mapping of performance and degradation mechanisms in printable photovoltaic devices' and EP/J017361/1 'Supersolar Solar Energy Hub.'

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Single Component Solution-Processed Organic Solar Cells Based on Conjugated Star-Shaped Small Molecules

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High-performance organic solar cells (OSC) are based on a bulk heterojunction (BHJ), which provides extended interfaces between the donor and acceptor components, resulting in efficient exciton dissociation and high OSC efficiency. However, the BHJ morphology strongly depends on fabrication conditions, methods and postprocessing. It can easily change during the device operation due to thermodynamic instability.¹ The precise control of phase separation in the BHJ films is very difficult. Therefore, single component organic solar cells (SCOSC) based on donor-acceptor molecules are of great interest. Although the efficiency of SCOSC is still low compared to the heterojunction devices, they have attracted high attention in the organic photovoltaic community for the recent years.² It was recently shown that efficient exciton-to-charge conversion occurs in pristine films based on conjugated donor-acceptor molecules N(Ph-nT-DCV-R)₃,³ which is very beneficial for SCOSC. In this work, we demonstrate a high potential of conjugated donor-acceptor molecules with general structure: N(Ph-nT-DCV-R)₃ for SCOSC. Photovoltaic properties were investigated in solution-processed SCOSC with the structure: glass/ITO/PEDOT:PSS/N(Ph-nT-DCV-R)₃/Ca/Al. For SCOSC based on N(Ph-2T-DCV-Et)₃, which showed the highest PCE of 1.2% and EQE up to 24%. Charge generation, recombination and transport properties were explored in detail.

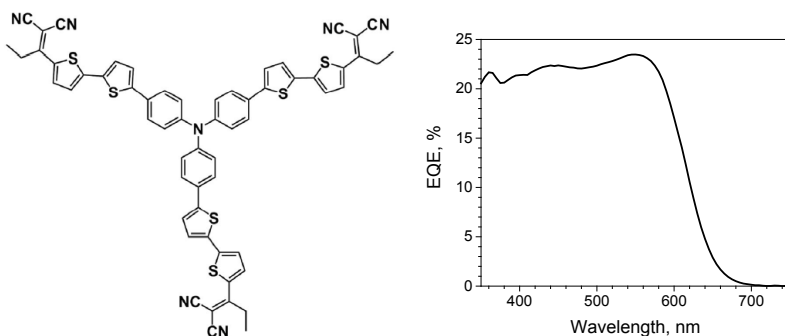


Fig. 1. Structural formula of N(Ph-2T-DCV-Et)₃ and EQE spectra for N(Ph-2T-DCV-Et)₃ solar cell.

This work was performed in the framework of leading science school NSh-5698.2018.3. EQE and charge generation investigations were supported by Russian Science Foundation (grant 19-73-30028).

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Electron Spectroscopy Studies of Surface Deposited Conjugated Molecular Layers

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In this presentation some backgrounds on investigation of electronic properties of thin films of conjugated organic molecules on solid surfaces will be discussed. Mechanisms of the energy level alignment and the density of the electronic states at organic film interfaces with metal and semiconductor surfaces studied by core-level and ultraviolet photoelectron spectroscopy are considered. The electronic properties of the surface organic layers can be tuned by means of the influence of the substrate material and by introducing polar substituents into the molecules. Those changes may be readily monitored by the analysis of the density of valence states and of unoccupied electronic states (DOS and DOUS, respectively). Particular attention is paid to the techniques, which use the low-energy electron beam as a probe of the materials under study, such as total current spectroscopy (TCS) technique which can be operated in Partial electron yield or Total electron yield mode. Experimental results on 5-10 nm thick organic layers prepared from phenylene-vinylene oligomers, bisimide substituted perylene based molecules and on thiophene/phenylene co-oligomers (TPCO) (Fig. 1) are presented^{1,2}. Changes of the DOUS peak structures in the energy range of the π^* - and the low-lying σ^* - orbitals occurred when the substituted and the unsubstituted molecules were used for forming the organic film are discussed.

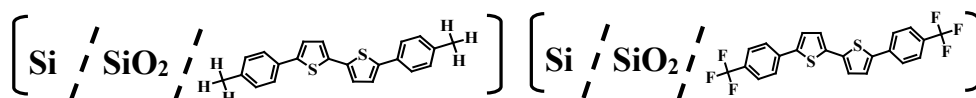


Fig.1. The schematics of the interfaces formed by the of the dimethyl-TPCO and of the bis-trifluoromethyl-TPCO films.

The work was supported by RFBR grants 18-03-00020 and 18-03-00179. Synthesis of TPCO was made in the framework of Leading Science School (grant NSh-5698.2018.3). The TCS investigation of the phthalide films was supported by the Russian Science Foundation (project № 19-13-00021). The XPS and UPS measurements were performed at the Centre “Physical methods of surface investigation” of the Research park of St. Petersburg State University.

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Voltage Dependence of Light-Emitting Area Position in Channel of Oligothiophene-Phenylene Based Organic Light-Emitting Field-Effect Transistors

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Organic light emitting transistors (OLETs) are perspective optoelectronic devices that combine the switching ability of organic field-effect transistors (OFETs) with the light-generation capability. OLETs have a potential application in lighting, displays and injection lasers technologies. Light generation in the OLET channel occurs at the electron-hole recombination zone with a typical width of 15 – 200 nm¹. The spatial position of this zone is controlled by the gate voltage V_G . Both for practical applications and theoretical studies it is important to know the exact form of dependence of the spatial position of light emission zone on V_G .

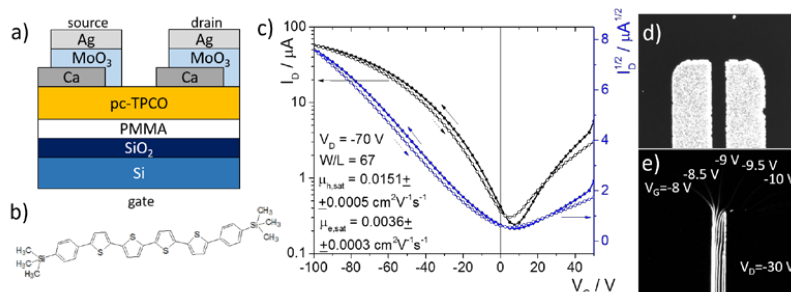


Fig. 1. (a) OLET structure. (b) Structural formula of the studied TPCO. (c) OLET transfer characteristics. (d) OLET image: the dark area corresponds to the active layer, and the light areas correspond to source/drain electrodes. (e) Light emission from channel at different V_G .

In this work, we study the V_G dependence of light-emitting area position for OLETs based on single layer of polycrystalline (pc) or single crystalline (sc) oligothiophene-phenylene co-oligomers (TPCO) which have a band gap near 2.7 eV and high luminescence quantum yield up to 44%². OLETs are prepared on silicon substrates with electron and hole-injecting electrodes (Fig. 1). The transfer characteristics (Fig. 1c) demonstrate ambipolar behavior with rather low hysteresis and high hole and electron mobilities even in pc film. Fig. 1d shows an image of part of OLET sample, where the. Fig. 1e depicts an image of the same area captured without external light with a long exposure time during which nine different values of V_G from –12 V to –8 V with a step of 0.5 V were successively applied. For OLETs with different channel length, width and thickness we extract dependences of light emission area spatial position on V_G and compare them with results of modeling with the use of a simple drift-diffusion model. The obtained results are expected to contribute to better understanding of processes of charge injection, transport and recombination in organic semiconductors.

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

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Poster presentations

Investigation of N-Heteropolycyclic Molecules on Metal Surface by High Resolution Electron Energy Loss Spectroscopy

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Small molecule organic semiconductors based on N-heteropolycyclic aromatic compounds are promising candidates for a variety of (opto) electronic applications. In these molecules, introduction of nitrogen in their aromatic backbone in its pyridine form decreases the energy of both HOMO and LUMO, resulting in an improved stability due to an increased ionization potential and electron affinity of organic semiconductor.^{1,2}

Understanding the adsorption and electronic properties of these molecules on inorganic substrates provides important insights into the charge transfer properties at organic/inorganic interface. High-resolution electron energy loss spectroscopy (HREELS) is a powerful tool for investigating both the adsorption geometry via vibrational excitations and electronic properties of the molecules by utilizing electrons with sufficient energy to excite electronic transitions. In this study, HREELS is used to determine the adsorption and electronic properties of new classes of N-heteropolycyclic molecules including diazapentacene and its derivative as a function of coverage on Au(111).

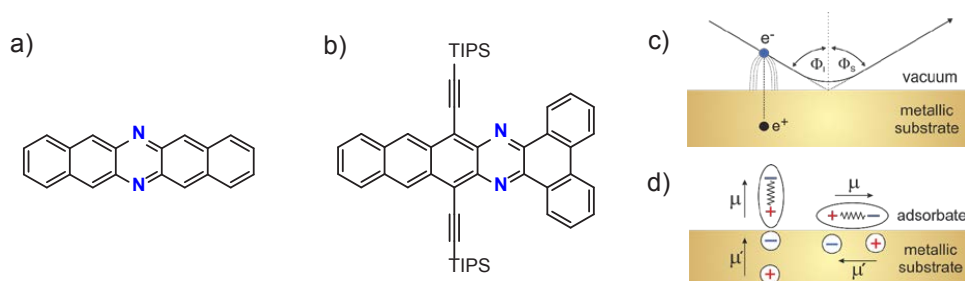


Fig. 1. a) Schematic of diazapentacene molecule; b) diazapentacene derivative; c) basic principle of HREELS measurement; d) surface selection rule.

This work was supported by SFB 1249.

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Lanthanide Aromatic Carboxylates as Red, Green and Blue Emitters for Solution-Processed OLEDs

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Nowadays OLED technology is developing very rapidly, as evidenced by the large variety of commercially available devices based on OLED. To achieve high OLED efficiency, it is necessary that the triplet level be involved in the luminescence process, due to 75% of the excitons under electric excitation have a triplet nature according to spin statistics. Therefore, lanthanide coordination compounds (Ln CCs) are very prospective electroluminescent materials, in which luminescence occurs due to energy transfer from the triplet level of the ligand to the lanthanide ion. In addition, due to the 4f electron features, lanthanide ionic luminescence bands are narrow, which is important for ensuring a high purity of light in OLED. The OLED technology requires three red, green and blue emitters. Among lanthanide ions, europium ion possesses red luminescence, terbium ion possesses green luminescence, but there is no lanthanide ion, which effectively emits blue light. To obtain blue luminescence, gadolinium CCs can be used with the ligand-centered luminescence, and the gadolinium ion, due to strong spin-orbit interaction, facilitates phosphorescence forbidden by the Laport rules, thereby providing radiative relaxation of triplet excitons. Among all classes of lanthanide complexes, aromatic carboxylates are particularly promising, since they are stable and have high luminescence quantum yields.

The **Eu(mfb)₃(BPhen)**, **Tb(pobz)₃(PO₄)** and **Gd(ker)₃(H₂O)₃** complexes (where mfb⁻ is 2-fluorobenzoate, BPhen is bathofenanthroline, pobz⁻ is phenoxybenzoate, PO₄ is bis(diphenylphosphine oxide)-4,4'-biphenyl, ker⁻ - 5-(thiophen-2-yl)-7-(trifluoromethyl)pyrazolo[1,5-a]pyrimidine-2-carboxylate) were synthesized, were purified by recrystallization and their photophysical characteristics were measured. The Ligand→Ln³⁺sensitization efficiency reached 100% for **Eu(mfb)₃(BPhen)** and **Tb(pobz)₃(PO₄)**, while **Gd(ker)₃(H₂O)₃** possessed ligand phosphorescence at room temperature.

The spin-coated thin films of **Eu(mfb)₃(BPhen)**, **Tb(pobz)₃(PO₄)** and **Gd(ker)₃(H₂O)₃** complexes were tested in OLEDs, and obtaining diodes demonstrated pure ionic europium, terbium and ligand-centered ker⁻ electroluminescence, respectively. The maximum luminance reached 300 Cd/m².

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

Novel Benzodithiophene-Based Donor Oligomers for Non-fullerene Organic Solar Cells

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The novel non-fullerene acceptors molecules (NFAs) development has made it possible to achieve previously inaccessible power conversion efficiency (PCE) values for both single and tandem organic solar cells (OSC) devices. One of the most studied classes of donor compounds used in NFAs OSC are conjugated donor-acceptor arylene and heteroarylene polymers with a linear structure. However, polymers have a number of known and significant drawbacks. Oligomers are deprived of these shortcomings, since they are monodisperse compounds, and their synthesis is distinguished by relative simplicity and high reproducibility. Thus, the search of novel donor oligomers for the NFAs OSC application is still an actual task to date. In this work, we report on an efficient synthesis and complex properties studies of novel benzodithiophene-based p-type organic semiconductor molecules for NFAs OSC application. These molecules, which contain dicyanovinyl or alkyl cyanoacetate electron-withdrawing groups, linked through bithiophene or terthiophene π -spacer with electron-donating benzodithiophene core were synthesized in high yields. The electrochemical, thermal and optical properties of these compounds were investigated by cyclic voltammetry, differential scanning calorimetry, thermogravimetric analysis and UV-Vis spectroscopy with interesting optical and thermal properties exhibition. In addition, NFAs-based OSC prototypes based on these oligomers were designed and demonstrated promising results.

The work was performed in the framework of leading science school NSh-5698.2018.3.

3,9-Disubstituted *anti-anti*-Bis[1]benzothieno[1,4]thiazines: Diversity Oriented Synthesis and Structure-Property Relationships of Potentially Antiaromatic Heterocyclic Donors

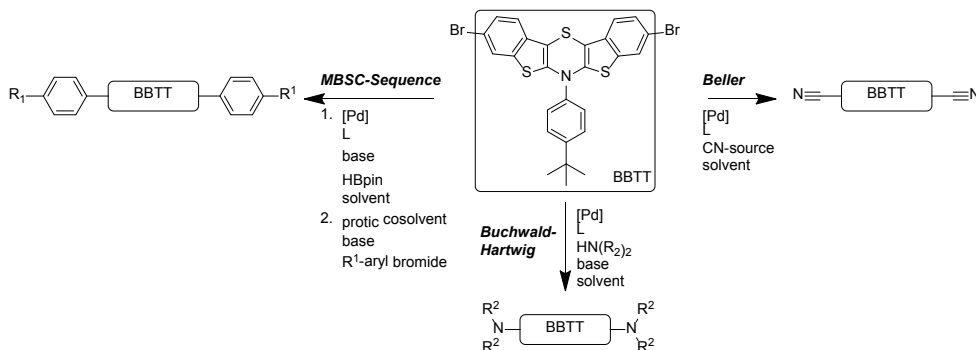
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Bis[1]benzothieno[1,4]thiazines (BBTTs) have first been reported by *Schneeweis* in early 2019. As a compound family related to and as an evolutionary derivative of phenothiazines, most members show a folding angle along the *S-N*-axis resulting in a butterfly-like folded structure.^[1, 2] The *anti-anti*-bis[1]benzothieno[3,2-*b*:2',3'-*e*][1,4]thiazines, however, partially show planarity of the pentacyclic \square system in solid state, making these derivatives examples of rarely known benchtop stable antiaromatic heterocyclic compounds. Furthermore, these redox active compounds luminesce intensively. Further examination of substituted derivatives of these regioisomers and determination of structure-property relationships in analogy to our earlier works is therefore necessary to evaluate potential applications in OLED and OPV devices.^[3]

For synthesizing a diverse range of disubstituted *anti-anti* bis[1]benzothieno[1,4]thiazines, 3,9-dibromo-6-(4-*tert*-butylphenyl)-bis[1]benzothieno[1,4]thiazine was selected as pivotal starting material, which can be prepared from benzo[*b*]thiophene in 5 steps with an overall yield of approx. 40%. Due to poor solubility, low-temperature reactions were not manageable. However, using various cross-coupling methodologies, such as *Masuda-Borylation-Suzuki-Coupling-Sequence* (MBSC)^[4] or *Buchwald-Hartwig-Amination*,^[5] versatile substitution patterns are accessible. Strong fluorescence in solution of both unsubstituted BBTTs and the dibrominated starting material can thus be intensified and a fine-tuning of the absorption bands is feasible.



Scheme 1: Modular syntheses of variably disubstituted BBTTs.

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New Derivatives of Benzothienobenzothiophenes (BTBT) and Tetrathienoacenes (TTA) for Organic Electronics

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

This work was supported by Russian Science Foundation (grants № 18-73-10182) and performed in the framework of leading science school NSh-5698.2018.3.

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New Organic Luminophores for Manufacturing Scintillation and Wavelength Shifting Polymer Fibers

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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 – convertors 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 supported by RFBR (№18-29-17006MK).

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Novel tetrathienoacene and benzothienobenzothiophene derivatives: investigation of self-assembly and thin films electrical properties.

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In our laboratory novel semiconducting materials based on organosilicon derivatives of [1]benzothieno[3,2-b][1]-benzothiophene (BTBT) and [3,2-b]thieno[2',3':4,5]thieno[2,3-d]thiophene (TTA) were synthesized in the framework of searching new materials with higher charge carrier mobility.

The processes of self-assembly were investigated for all synthesized oligomers in Langmuir layers on the water surface and in Langmuir-Schaefer (LS) layers on silicon substrates as well as in self-organized layers fabricated by spin-coating (SC) and Dr. Blade (DB) techniques. Optimal fabrication conditions such as solution concentrations, rotational speed, blade movement speed, substrate temperature were tried to select.

Unfortunately, neither SC nor DB methods allow to get a uniform thin film on the substrate surface, most likely, due to high tendency of the investigated materials to crystallize and the absence of any specific interactions between the synthesized oligomers with the silicon substrate.

It was decided to use LS technique and it turned out that all materials are able to form homogeneous films on the substrate surface. The structure and morphology of the formed films were studied by atomic force (AFM) and polarization-optical microscopies (POM). The thickness of TTA LS-films was 1,7-1,9 nm and BTBT LS films was 7-8 nm that should correlate with mono- or bilayer films. It was noticed that chemical structure of semiconducting core strongly affects to further behavior of LS-monolayers. TTA derivatives are tend to devetting with time due to high hydrophobicity and crystallinity of semiconducting core. Thus, electrical characteristics for these materials were obtained only from freshly prepared films and max hole mobility was $10^{-5} \text{ cm}^2/\text{Vs}$. BTBT derivatives have better hydrophilic-hydrophobic balance that allow to save film morphology for more long time and max hole mobility for such compounds were $10^{-3} \text{ cm}^2/\text{Vs}$.

However, none of the studied films showed sufficient reproducible semiconducting properties. We suggest that this is due to the low uniformity of the film in the transistor channel. Thus, it was concluded that these materials are potentially capable to form semiconducting films with high electrical characteristics, but due to its low solubility in common organic solvents the most promising techniques for semiconducting films fabrication are vacuum deposition or single crystal growth.

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A Study of Charge Transfer at the Interfaces of Organic Semiconductors

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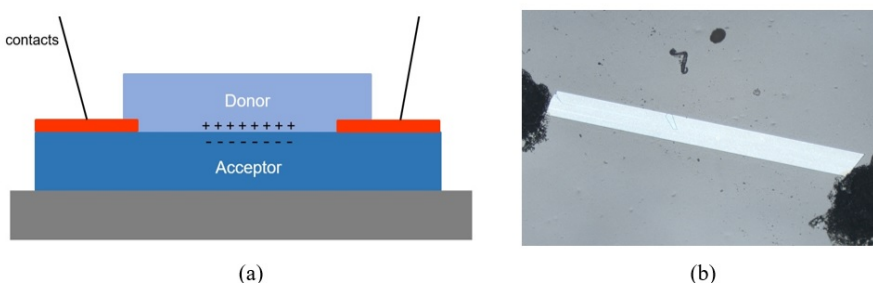


Fig. 1. (a) Schematic of charge transfer interface and (b) Rubrene single-crystal and F6-TCNNQ charge transfer interface

With the recent progress in organic electronics, charge transfer interfaces become significant research interest to study and understand the fundamental properties of organic semiconductors. To understand the mechanism of charge transfer, single-crystal based charge transfer interface devices are proved to be a very promising tool.¹⁻³ In recent studies¹⁻³, it has been observed that the electrical properties at the interfaces of two organic semiconductor materials can differ noticeably from those of the individual materials, which are initially insulators. In this work, we investigate single-crystal based charge transfer interfaces (see Fig. 1) where Rubrene, in form of single crystals, is used as a donor material. As acceptors, we use new striking acceptor materials such as, F₆-TCNNQ, Hexacyano-[3]-radialene anion-radical family materials, and Fullerenes through thermal evaporation or solution process. We observe strongly enhanced electrical conductivity and perform temperature dependent as well as Hall-effect measurements to investigate the charge transfer effects.

This work is financially supported by DFG (KR 4364/4-1)

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Impact of Fluorination on Crystal Packing of Di-phenyl naphthalene Diimide

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Organic field effect transistors (OFETs) are key elements for various emergent organic electronic devices such as integrated circuits, displays, sensors, storage devices, photodetectors and light-emitting devices, which are essential parts of lightweight, flexible and transparent high-tech devices. The progress in n-channel OFETs is not so impressive as compared to that of p-channel ones. This is partially related to difficulties with creation of organic semiconductor materials with low energy values of LUMO (lowest unoccupied molecular orbital) energy, which typically should be lower than -4.0 eV. Such LUMO energy values ensure stability of an organic semiconductor to air oxidation and facilitate electron injection¹.

Owing to combination of chemical and thermal stability², stacked molecular packing³ and efficient electron transport, naphthalene diimides derivatives (NDIs) are promising materials for n-channel OFETs. In this study, we investigate the effect of fluorine atom in p- position of the phenyl rings of *N,N'*-diphenyl-1,4,5,8-naphthalene-tetracarboxylic diimide (Ph-NDI) on physicochemical properties, crystal packing and charge mobility in the crystalline NDI derivatives.

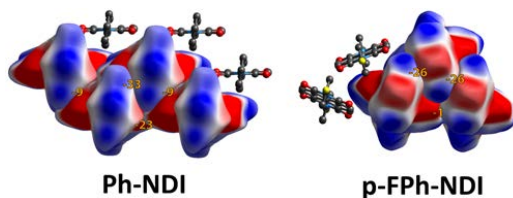


Fig. 1. ESP mapped on Hirshfeld surfaces for Ph-NDI and p-FPh-NDI crystals.

Our research shows that the minor change in electrostatic potential (ESP) distribution after the fluorination results in altering the molecular packing from planar one to herringbone one (Fig.1). As a result, changes in the crystal packing results in a slight increase of calculated charge-carrier mobility (by $\sim 20\%$). This increase results from the increase of the distance between the molecular centers along the main charge transport direction, while the corresponding charge transfer integral do not change significantly. We anticipate that the obtained results are important for rational design of organic semiconductors with improved electron transport.

This work was partially supported by RFBR (projects № 19-32-50003 and № 18-52-45024).

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Switching Between p- and n-type Transport in Organic Field-effect Transistors by Terminal Substitution of Thiophene-phenylene Co-oligomers

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Thiophene-phenylene co-oligomers (TPCO) are promising optoelectronic materials for light-emitting devices and lasers as they combine efficient charge carrier transport and high luminescence^{1,2}. These organic materials exhibit mostly p-type charge transport; whereas the n-type transport is not easy to realize. Fluorination is a well-known approach to alter the electronic properties of p-type semiconductors. For example, common p-conductive organic semiconductors such as pentacene, copper phthalocyanine, diethynyl naphthalene and oligophenylenevinyls can be converted to the n-conductive ones via fluoro-substituents^{3,4}. Here, we study the impact of fluorination of the methyl terminal group on the structural and electronic properties of single- and polycrystals of TPCO with the phenylene-thiophene-thiophene-phenylene (PTTP) conjugated core using x-ray diffraction, DFT and dipole moment calculations, total current spectroscopy (TCS) and field-effect transistor (FET) measurements.

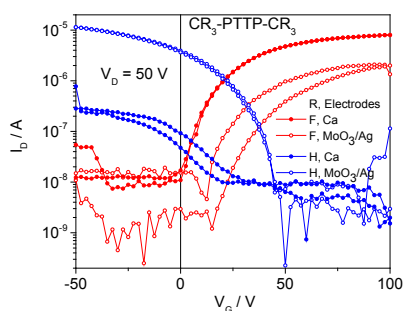


Fig. 1. Transfer characteristics of single-crystal TPCO based OFET devices with Ca and MoO₃/Ag top electrodes at $|V_d|=50$ V.

Our experimental data show that fluorination of the methyl terminal group in CH₃-TPCO results in an insignificant impact on the crystal habit and on the molecular orientation vs their basal plane but switches the conductivity from the p-type to the n-type (Fig. 1). We suggest that the terminal groups control the charge injection type into the FET active layer.

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Solution-processed High Performance 2D Field-effect Transistors Based on Luminescent BTBT Derivative

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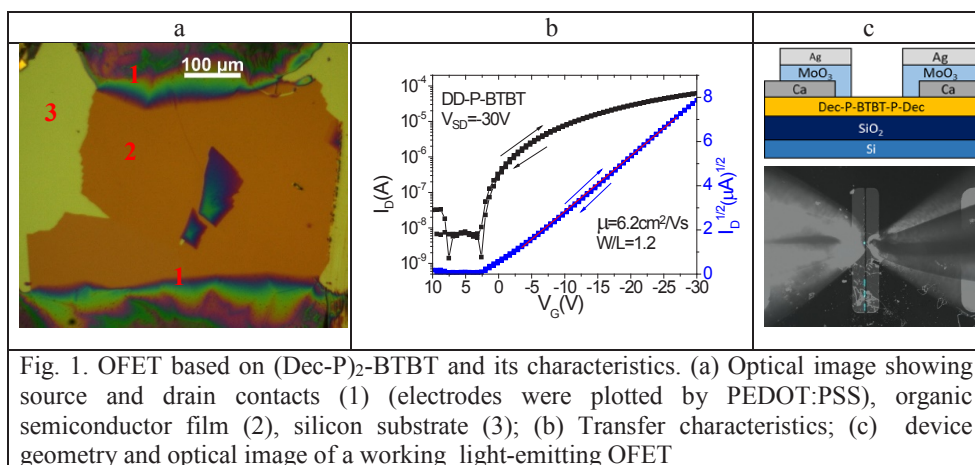
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Recent progress in organic field-effect transistors (OFET) based on ultrathin (mono- or a few layer) single crystals stimulates the interest to ultrathin organic light-emitting transistors (OLET). BTBT-based small molecules show high carrier mobilities in OFET,¹ but they are weakly luminescent. Therefore, it is highly desirable to combine good electrical performance of BTBT-based semiconductors with efficient luminescence, which could be achieved via appropriate functionalization of the BTBT conjugated core.

In this work, we use BTBT-based molecules (2,7-bis(4-decylphenyl)[1]benzothieno[3,2-b][1]benzothiophene) (Dec-P)₂-BTBT (P stands for phenylene), which show the photoluminescence quantum yield more than 40% in solution, obtained ultrathin films and investigated their performance as active layers of OFET and OLET. Ultrathin films with lateral dimensions in the range of 300–600 μm were grown on silicon substrates. Figure 1 (a,b) shows an image of a typical OFET fabricated on a silicon substrate and its transfer characteristic. The hole mobility in OFETs based on few-layer films was in the range 5.5–7.5 cm^2/Vs in the saturation regime. The device geometry and optical image of a working light-emitting OFET are shown in Figure 1c. Our study shows that 2D solution-processed FETs have a high mobility and electroluminescence, and we conclude that this oligomer can be a promising platform for light-emitting transistors.



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

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Diversity-oriented Pd-Catalyzed Synthesis of Donor-Acceptor-Substituted Psoralens with Photosensitizing Properties for DNA-Intercalation

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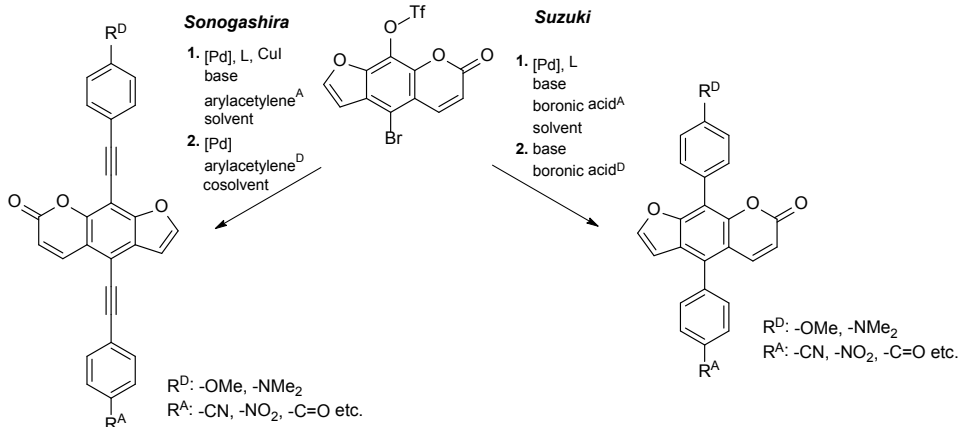
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Psoralens are DNA intercalators and undergo photoreactions causing hampered DNA replication and transcription. With this respect the PUVA (psoralen + UV-A-light) therapy offers advantages in treatment of cancer and several skin diseases.^{1,2} To study the crosslinking photocycloadditions with DNA the electronic structure of the psoralens has to be controlled and optimized.

A diversity-oriented approach leads to a new generation of 8-donor-5-acceptor substituted psoralens. Simultaneously, structure-property relationships of the photoreactivity of psoralens with DNA are investigated. Starting from commercially available pyrogallol, an efficient route to 8-(5-bromo)psoralen trifluoromethanesulfonate as the pivotal coupling partner was generated.^{3,4}

Hence, 5-acceptor-8-donor substituted psoralens can be synthesized by site-selective cross-coupling methodologies, such as *Suzuki* and *Sonogashira* reactions. Introduction of donor groups at the 8-position cause a bathochromic shift of the absorption bands. Furthermore, substituted psoralenes fluoresce in solution and in the solid state.



Scheme 1: Conceptual synthetic route to 5-acceptor-8-donor substituted psoralens.

This work was supported by Deutsche Forschungsgemeinschaft e. V. (Mu 1088/14-1).

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Linear Spirocyclic Conjugated Systems as New Materials for Optoelectronics

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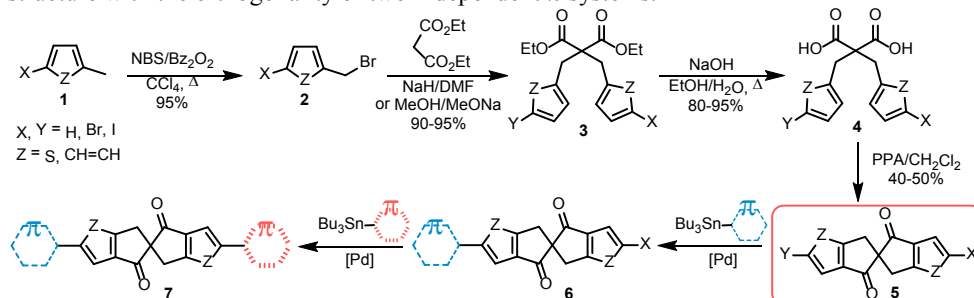
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High-performance organic semiconducting devices such as organic light-emitting diodes (OLEDs) and organic light-emitting transistors (OLETs) require materials combining efficient electroluminescence and high semiconducting properties. However, synthesis of such compounds is a non-trivial task since the dense packing that is crucial for improved semiconducting properties causes quenching of luminescence due to the aggregation effects.

Thermally activated delayed fluorescence (TADF) is a promising way to increase electroluminescence efficiency of OLEDs. This phenomenon is observed for molecules in which donor and acceptor parts are orthogonal to each other and the energy difference between the first singlet (S_1) and triplet (T_1) excited electronic states is $\sim kT$. It facilitates reverse intersystem crossing (RISC) and allows harvesting all triplet excitons achieving almost 100% of the internal quantum efficiency of electroluminescence.

Herein we develop synthesis and study properties of linear spirocyclic compounds – 2,2'-spiro[indene]s and 5,5'-spirobi[cyclopenta[*b*]thiophene]s – which combines rod-like structure with the orthogonality of two independent π -systems.



The synthetic route to spiro unit **5** includes the sequential alkylation of malonic ester with the corresponding halogenides **2**, hydrolysis of the obtained ester **3**, and the intramolecular cyclization of the resulting acid **4** in the presence of polyphosphoric acid (PPA).

Quantum chemical calculations were used for theoretical study of ground and excited states geometries, frontier orbitals electronic densities, singlet and triplet states energy. As a result, it was shown that spiroconjugation could be effectively used for design materials with specific optical and electronic properties.

This work was supported by Russian Science Foundation (project № 19-13-00327).

Organic Infrared Photodetectors Based on Photoinduced Vibronic Phenomena

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Low cost infrared sensing is receiving a lot of interest due to broad applications including free-space communication, surveillance, spectroscopy, chemical sensing, and non-invasive biomedical imaging.¹ Important characteristics of such photodetectors include high detectivity, fast response and ease of fabrication.² While there have been great advances made in the field driven by graphene and quantum dot photodetectors, it is still problematic to achieve optimal performance on all fronts in one device, especially extending the photosensitivity into the mid- and far-IR.^{3,4} Using both continuous wave and ultrashort, ultrafast laser pulses, a well-established polymer electron donor PBDB-T (PCE12) was studied to understand light absorption, charge separation and transport dynamics in organic polymer devices. Optical sensing with near IR light using the pump-push-photocurrent technique was performed on these single component devices.⁵ Visible ‘pump’ light was used as optical gating, while the IR light was utilised as a ‘push’ to give rise to IR-induced photocurrent as CT states become free charges. In these organic polymer devices, the effect of electrode thickness was also investigated down to the semi-transparent electrode. Future work will focus on using IR vibronic charge activation on quantum dot photodetector devices sensing in the 5-10 μm region and beyond.

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Intraband Cooling Dynamics in Lead Halide Nanocrystals

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Lead-halide perovskites (LHP) are emerging as a promising candidate for the future generation of solar cells. They are solution-processable, defect tolerant and have achieved power conversion efficiency (PCE) of over 20% to date. Currently, the major limitation of PCE in conventional solar cells arises from the rapid relaxation of hot carriers to the band edge. In order to harvest these above-bandgap carriers, the cooling mechanisms require careful analysis. Previous studies have shown that the cooling in LHPs is slower at higher hot carrier density and dependent on the material composition,¹ but the role of cold carriers is less understood. Here, we investigate the intraband cooling dynamics in nanocrystal lead halide perovskites using a sequence of ultrafast pulses; visible pump – IR push – IR probe. By independently controlling the pump and push fluences, we can scrutinise the effect of the cold and hot carrier density on the intraband cooling dynamics. We demonstrate that the intraband relaxation time is dependent on both hot and cold carrier density, conveying two competing pathways of hot-carrier cooling (see Fig. 1).

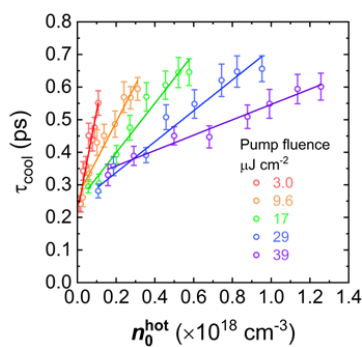


Fig. 1.

Based on the experimental result, we propose that the intraband relaxation occurs via carrier-carrier interaction and the carrier-phonon interaction. The carrier-phonon interaction is the loss of excess energy of hot carriers in forms of lattice vibration, which slows down as the density of hot carriers increases.¹ The carrier-carrier interaction is the rapid redistribution of heat in carriers via Auger-type interactions, which becomes faster as the density of cold carriers increases. We derived a kinetic model based on our understandings to fit the experimental data, which could be used to extract the information on polaron size, phonon density and the coupling range of carrier-carrier and carrier-phonon interactions.

This work was supported by RSC (project № 00-00-00000).

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Synthesis and Properties of Novel Liquid Benzothiadiazole-based Luminophores

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The liquid organic luminophores have a number of unique properties.^{1,2} For example, such substances having decreased aggregation do not require the use of organic solvents and provide the possibility of obtaining functional layers by modern printing methods, thus, the liquid luminophores can act as a solvent with a high quantum yield of luminescence for other organic and inorganic components. All these properties result in significantly improving the manufacturability and environmental friendliness of production processes.

Benzothiadiazole-based oligomers are known for their high quantum yield of luminescence, good temperature resistance and unique optical and electrical properties.^{3,4}

In the course of this work, a series of novel liquid benzothiadiazole -based luminophores containing two conjugated thiophene units with terminal trihexylsiloxane groups on each side of the central core were synthesized. All precursors and the target compounds were characterized by ¹H NMR spectroscopy and size exclusion chromatography in an individual state. Optical, thermal and electrochemical properties of novel molecules were studied and compared. The obtained luminophores are promising candidates for organic photonics.

This work was supported by the Russian Foundation for Basic Research (grant № 18-33-20224) and performed in the framework of Leading Science Schools (grant №NSH-5698.2018.3).

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Polymer Muscles on the Base of Silicones

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A search for materials for soft artificial muscles has attracted significant attention due to high demand from engineering department.

Silicones have characteristics that suite almost all the requirements for the soft actuators - elasticity, strain, biocompatibility, environmentally-friendliness. In the paper Miriyev et al. 2017 the new promising material for soft actuators - elastic polymer matrix with dispersed ethanol bubbles as an active agent - were introduced. Due to high strain of polymer used for matrix and liquid-vapor transition triggered by Joule heating of NiCr wire inside the material the actuator could lift more than 1700 times their weight having an energy efficiency around 0,3%. High stress, low density, simplicity of fabrication and low cost makes this design overcome problems of more traditional technologies like the high voltages needed for electroactive polymers (> 1KV), low strain (< 10%) of shape memory alloys and use for external compressors and pressure-regulating components for hydraulic or pneumatic fluidicelastomer actuators.

However, two main limitations also arise from this design. A long response time of the material due to low heat conductivity of the silicon and fast expiration date because of the diffusion of ethanol make this concept less acceptable for engineering applications.

The aim of this work is to eliminate these shortcomings via a replacement of the active agent, a modification of silicon matrix and a search for a suitable actuator design.

The report will present the results of replacing ethanol as an active agent with hexafluoroisopropanol and its mixture with ethanol to reduce the liquid-vapor transition temperature, use a mixture of glycerol and ethanol to reduce the response time and diffusion of ethanol, use highly filled smiloxane compositions as a shell of the material to lower the rate of ethanol diffusion, as well as various options for heating the soft actuator, eliminating the presence of microheating, leading to degradation of the silicone matrix and the more uniform heating.

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

Low Phonon Frequency Expansion for Charge Transport in Organic Crystals: Transient Localization in the Quantum Regime

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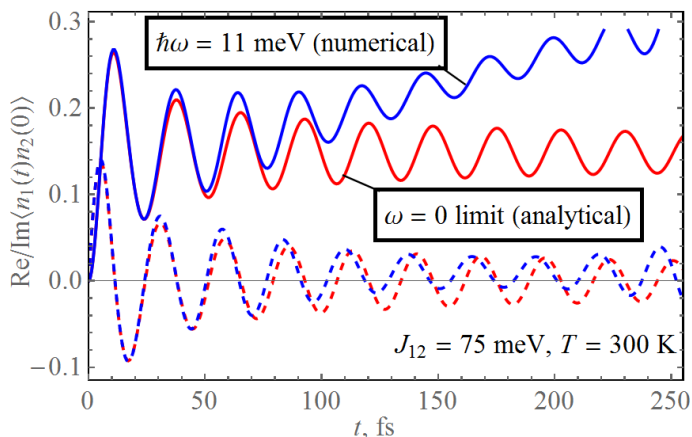


Fig. 1. Electron number correlator in a two-site Holstein–Peierls model and its LF asymptotic

Being typically excited at room temperature, low-frequency (LF) intermolecular vibrational modes in crystalline organic semiconductors are known to have a considerable impact on the charge carrier mobility in such materials, representing a kind of dynamic disorder.¹ Although the issue has been addressed within a number of frameworks,^{2,3} LF intermolecular vibrations are typically considered classically within them. To shed light onto the effect of phonon correlations in the LF regime, we make an LF expansion in a Holstein–Peierls model for a two-site cluster and a 1D chain of molecular sites in a fully quantum way. It turns out that such an expansion leads to intermediate-time plateaus signaling the phenomenon of transient localization, which gives way to further delocalization due to higher-order terms. We analyze the agreement of this behavior with the predictions of the semiclassical frameworkⁱⁱ, and discuss the drivers of charge-carrier mobility in light of LF phonon modes.

The research was supported by the Russian Science Foundation (project № 18-72-10165).

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Synthesis of Poly(vinylidene fluoride-co-chlorotrifluoroethylene)-grafted-poly(acrylonitrile) Polymers for Ferroelectric Organic Field-effect Transistors

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Ferroelectric polymers have been the subject of intensive research during past fifty years.¹⁻⁶ It has been shown that the most perspective ferroelectric polymer applied for wide range of applications was poly(vinylidene fluoride) (PVDF).³⁻⁶ Besides PVDF based polymers are very attractive materials to be combined with organic field-effect transistors and to be used as sensors that convert the response generated by the material to an voltage signal. In fact, PVDF is typically crystalline polymer having five crystal polymorphs named α , β , γ , δ , ϵ , where the β phase is more significant due to it's piezo-, ferro- and ferroelectric properties.² It is well known that the technique of obtaining PVDF films from solution or melt leads to producing a polymer with α phase. The polar crystalline phase β can be obtained by post treatment of the films using straining, stretching or quenching techniques, which is quite complicated. In order to reverse the difficulties of phase β production copolymers based on PVDF can be applied. In this work, polyacrylonitrile (PAN) was grafted onto the side chain of vinylidene fluoride-co-chlorotrifluoroethylene copolymers through atom transfer radical polymerization (ATRP). The content of PAN was determined by the method of NMR spectroscopy. The influence of various synthetic parameters on properties of obtained polymers such as solubility and content of incorporated PAN segments was studied.

This work was supported by Russian Science Foundation (RSF) (19-73-30028). The work was performed in the framework of leading science school NSh-5698.2018.3

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Performance of Novel Organic Semiconductors 2,2'-[2,2'-(arene-1,4-diyl)bis(anthra[2,3-b]thiophene-5,10-diylidene)]tetrapropanedinitriles as Non-fullerene Acceptors in Photovoltaics

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Organic composite materials for solar cells are now attracting more and more interest due to low cost of converting solar energy into electricity. Most photoelectric composites are a combination of a donor organic compound with fullerene as an acceptor. For the development of organic photovoltaics, it would be nice to replace the fullerene with a cheaper acceptor.

In the present work photoelectric cells were made using novel acceptor compound 2,2'-[2,2'-(arene-1,4-diyl)bis(anthra[2,3-b]thiophene-5,10-diylidene)]tetrapropanedinitriles (A1). Polymer PCDTBT was used as a donor molecule.

The composite of polymer donor PCDTBT with A1 demonstrates good solubility in organic solvents and bulk heterojunction morphology with characteristic donor and acceptor domain size of several tens of nanometers, favourable for photoelectric conversion.

This composite exhibits prominent light-induced EPR signal indicating efficient photoinduced free charge generation. OPV devices based on this composite were fabricated by vacuum-free method.

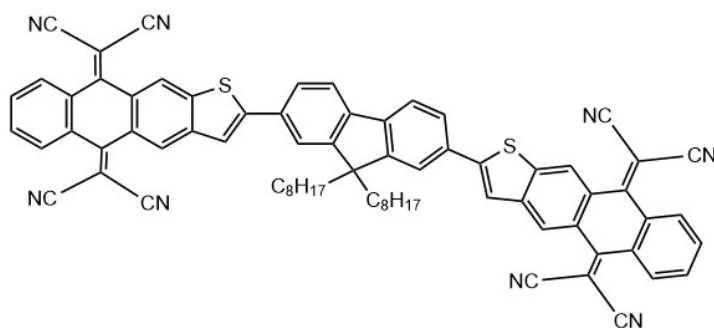


Fig. 1. Chemical structure of 2,2'-[2,2'-(arene-1,4-diyl)bis(anthra[2,3-b]thiophene-5,10-diylidene)]tetrapropanedinitriles (A1)

OPV device was manufactured using standard architecture: ITO/PEDOT:PSS/Active layer/FM (Field's metal alloy, eutectic mixture of Bi, In and Sn). $V_{oc} = 0.785$ V, $J_{sc} = 3.15$ mA/cm², FF = 28.3%, PCE = 0.71% were obtained.

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Computer Simulations of Nanocomposites Based on Conjugated Polymers and Fullerenes

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The using of polymeric materials as the basis of photovoltaic cells provides high manufacturability and low cost of production of flexible polymer solar cells (PSC) of a large area. The recent increase in a parameter of the solar energy conversion efficiency (up to 10 %) for materials based on conjugated polymers and fullerenes makes commercialization of plastic solar cell gainful. The peculiarity of the manufacture of PSC leads to the fact that the photoactive layer of photovoltaic cells is formed as a thermodynamically unstable system (with a kinetically frozen state). As a result of constant heating/cooling cycles, a gradual phase separation of the initial components occurs. Thus, searching for key factors helping to increase the long-term stability of organic solar cells is the main challenge for their widespread adoption in everyday practice.

Because of the lack of fundamental understanding of the phase behavior of donor-acceptor mixtures in the active layers of organic photovoltaic cells, we are carrying out a systematic study of the structural changes that occur after the phase separation of different systems based on a mixture of conjugated polymers with fullerenes. In the report, we discuss our first results on computer simulations of polymer nanocomposites based on conjugated polymers and fullerenes. Specifically, we are interested in the effect of the chemical structure of donor-acceptor copolymers on the morphology of nanocomposites and their thermal stability. Representative systems, that we have chosen to study, are polythiophenes such as poly(3-hexylthiophene-2,5-diyl) (P3HT), poly(3-2-methylbutylthiophene) (P3MBT), poly(3-2-metilpentilthiophene) (P3MPT), and fullerene [6,6]-phenyl C₆₁ butyric acid methyl ester (PC₆₁BM).

We have constructed and parameterized a coarse-grained model of a photoactive layer based on selected polymers and PC₆₁BM. This model is used to study the structure of the photoactive layer. In addition, within the framework of the atomic molecular dynamics method, we carried out a study of the miscibility of selected conjugated polymers with PC₆₁BM. The obtained results make it possible to predict the relationship of the chemical structure of conjugated polymer chains to the morphology of conjugated polymers/fullerenes nanocomposites, their thermophysical properties, the stability of the interface, and to perform the comparison of these data with the optoelectronic properties and functioning of the photocells. The forthcoming experimental studies will allow us to calibrate the design of PSC better.

The research is carried out using the equipment of the shared research facilities of HPC computing resources at Lomonosov Moscow State University and the resources of the federal collective usage center Complex for Simulation and Data Processing for Megascience Facilities at NRC "Kurchatov Institute" (ministry subvention under agreement RFMEFI62117X0016), <http://ckp.nrcki.ru/>. The financial support of the Russian Foundation for Basic Research (project № 19-53-52004) and the Ministry of Science and Technology of Taiwan (Project MOST 108-2923-E-002-001-MY3) are highly appreciated.

Mesoscale Simulations of Active Layer of Hybrid Polymer/Semiconducting Nanoparticles Solar Cell

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At the present time polymer based solar cells (PSC) have attracted great attention as a perspective replacement for inorganic solar cells due to their lightweight, low-cost and easy manufacturing. Single layered PSC are manufactured by sandwiching of a layer of organic optoelectronic material between two conductors. The mixtures of conjugated copolymers (CP) and inorganic nanoparticles (NPs) are considered as promising materials for a photoactive layer (PAL), which can be prepared by spin casting of a solvent-based dispersion of CP and NPs. The forming morphology of the PAL is critical for performance of PSC. Therefore, it is important to carry out a pilot study of such materials for the subsequent design of the PAL with improving energy conversion efficiency. It is thought that a bicontinuous, interconnected, well phase-separated morphology of electron donor and acceptor phases can be optimal for transport of holes and electrons respectively.

All results presented in this report anticipate our experimental studies on design of the PAL in the bulk heterojunction polymer solar cell based on conjugated polymer/semiconducting nanoparticles mixtures. We discuss our current working concept of how to obtain well-organized current-conducting paths within the PAL. To achieve this goal, we implement an idea of using the fact that depending on the chemical structure of AB diblock copolymer, the thermodynamically stable domains with cubic symmetry of the double gyroid type, having three-dimensional periodicity in space, may be formed during microphase separation of A and B blocks. Therefore, the solar cell devices, in which these structures are formed, will have well-organized separate paths for transport of electrons and holes and, as a result, the high power conversion efficiency.

We have checked this idea in the framework of the mesoscale simulations with using dissipative particle dynamics methods. We demonstrate that by the proper choice of the type of surface modifier of NPs (which controls the compatibility of NPs with the polymer matrix), of the chemical structure of the conjugated copolymer blocks and of their length, we can control the morphology of the photoactive layer of SC devices. The region of parameters at which the domains with cubic symmetry and percolation for all components are formed, can serve as a reference points for the experimental synthesis of CP to obtain PAL with the optimal mesh of electrically conductive paths needed to create highly efficient PSC device.

This work was supported by the Russian Foundation for Basic Research (Project No. 17-53-52009) and the Ministry of Science and Technology of Taiwan (Project MOST 106-2923-E007-001-MY3). The research is carried out using the equipment of the shared research facilities of HPC computing resources at Lomonosov Moscow State University and the resources of the federal collective usage center Complex for Simulation and Data Processing for Megascience Facilities at NRC "Kurchatov Institute" (ministry subvention under agreement RFMEFI62117X0016), <http://ckp.nrcki.ru/>.

Charge Transport Properties of C₈-BTBT Field-effect Transistors

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The use of organic materials in terms of electronic applications has evolved in the last decades. Nevertheless there are still obstacles to overcome in terms of performance of organic electronic devices. The organic semiconductor community is eager to improve the performance of these devices and find new materials with high charge carrier mobility to utilize them. The family of [1]Benzothieno[3,2-b]benzothiophene (BTBT) is a new type of high hole mobility organic semiconductor. In this family, C₈-BTBT is investigated the most in the past years. Using shear coating as an up scalable solution based process one can produce large-area thin film transistors. In 2018 new record mobility values of such devices containing highly ordered thin films of C₈-BTBT were published.¹ Beside that there are still open questions concerning the intrinsic charge carrier mobility of this material. For further improvement one has to understand the transport mechanisms in these organic semiconductor devices. Here we present our results of temperature dependent field-effect transport and Hall-effect measurements. These measurements allow for a closer look into the transport behaviours of solution processed C₈-BTBT films.

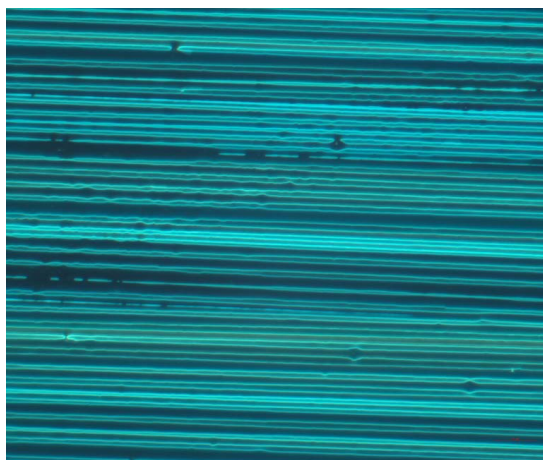


Fig. 1. Surface structure of highly ordered C₈-BTBT film produced by shear coating

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Efficient and Stable Organic Solar Cells Based on Small Molecule Donor and Polymer Acceptor

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Organic solar cells (OSCs) have received widespread attentions because of their potential as cheap and flexible photovoltaic technology. Besides the efficiency, the stability and cost should be considered for the future practical application. Nowadays the mainstream of OSCs use the combination of polymer donor and small molecule acceptor as the active layer, which has raised the power conversion efficiency (PCE) to 14%. On the contrary, OSCs based on the combination of small molecule donor and polymer acceptor (M_D/P_A) suffer from the low device performance, and only show PCE of lower than 6%. Herein, we demonstrate efficient and stable M_D/P_A -type OSCs. This OSC exhibits initial PCE over 9%. Moreover, the OSC maintains ca. 90% of the initial PCE after annealing the active layer at 180 °C for 7 days, and retains 68% of the initial PCE after illumination under 100 mW cm⁻² AM 1.5G simulated solar light for 7 days.

Typical small molecule donors do not match polymer acceptors because of their large difference in the tendency toward aggregation and crystallinity, which leads to large-size phase separation in the active layer and consequently results in low efficiency of the M_D/P_A -type OSCs. I will present our recent developments in morphology manipulation of M_D/P_A blend and their influence on the performance of M_D/P_A -type OSCs.^{1,2} The design of small molecule donor with suppressed aggregation property, and how to match polymer acceptors with this weak-aggregated small molecule donor will be proposed.³ The aggregation and crystallinity effect on the blend film nanostructure and the charge generation and transport behaviors of M_D/P_A -type OSCs will be discussed. I will also show you the origin of the high thermal and light stability of our M_D/P_A -type OSCs. The relationship between the morphology stability and the thermal properties of small molecule donor and polymer acceptor materials will be discussed.

This work was supported by the National Natural Science Foundation of China (No. 21625403, 51873204, 21875244), the Strategic Priority Research Program of the Chinese Academy of Sciences (No. XDB12010200).

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Towards Understanding the Interfacial Degradation Effects in p-i-n Perovskite Solar Cells

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Perovskite solar cells (PSCs) have demonstrated impressive power conversion efficiencies going beyond 23% for the best laboratory samples, while their operation stability still requires substantial improvements before this technology can be successfully commercialized. Many publications provided evidences that stability of PSCs is strongly dependent on the interface chemistry between the absorber and charge transport materials. In particular, we have shown recently that perovskite solar cells incorporating fullerene-based electron transport layers (ETLs), e.g. based on [60]PCBM or [70]PCBM, undergo rapid degradation under illumination. The revealed mechanism is featuring the initial dissociation of MAPbI₃ to PbI₂ and MAI followed by accumulation of the latter component in the fullerene-based ETL.

In the present work, we explored the impact of the hole-transport materials (HTLs) on the operation stability of p-i-n perovskite solar cells under continuous light soaking. In addition, we investigated the degradation effects induced at the interfaces formed by MAPbI₃ with such HTLs as PEDOT:PSS, PTAA, NiO_x, and NiO_x/PTAA blend using UV-vis optical spectroscopy, X-ray diffraction, steady-state photoluminescence (PL) and TOF-SIMS analysis. The revealed degradation pathways open new opportunities for rational design of new HTL materials for efficient and stable perovskite solar cells.

¹ A. F. Akbulatov et al. *Adv. Energ. Mater.* 2017, **7**, 1700476.

Spectral Shapes of Cyanine Dyes Mediated by Counterion Positioning in Non-/Polar Media: a Computational Study

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Cyanine dyes constitute an important class of positively charged chromophores with intense, sharp absorbance due to small bond length alternation (BLA), arising from symmetrical resonance structures. Interestingly, the absorption properties in solution can be controlled by tuning the solvent polarity: in polar solvents (e.g. dichloromethane), with fully dissociated ion pairs, the well-known absorption (i.e. a sharp, intense band) is observed, while in apolar solvents (e.g. toluene), the absorption is strongly broadened. This was attributed to close contact of the dye-anion pair in the apolar medium, which is thought to break the symmetry of the cyanine chain¹. Despite the experimental evidence however, a proof of this counterion effect is missing by now.

Here, we prove this concept by unbiased TD-DFT calculations of the vibronic spectra in polar and apolar media using the polarizable continuum model (PCM), which reproduce the experimental finding in a reasonable manner.² Explicit inclusion of solvent effects by molecular dynamics (MD) simulations give the same result as PCM for the anion positions in polar and apolar media, which proves that this is driven by polarizability. In the apolar media, the close, asymmetric positioning of the anion breaks the symmetry of the cyanine, increasing dramatically the BLA, and thus causing the observed spectral broadening. Our work should have important consequences in the understanding and prediction of cyanines' spectral properties, for instance in heterogeneous (bio-)environments.

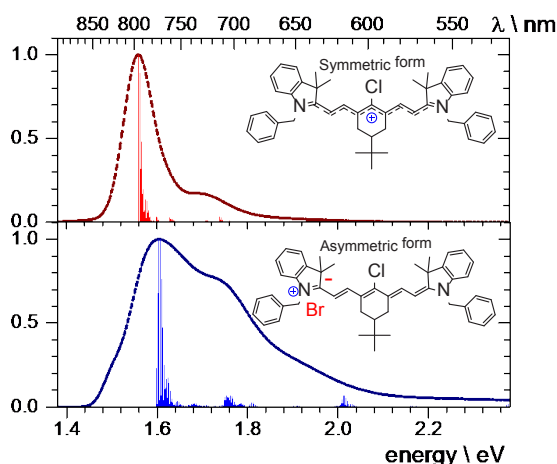


Fig. 1. Computed stick and experimentally spectra for both symmetrical and asymmetrical cyanine dyes. Normalized intensities are presented.

¹ Bouit P.A., et al *J. Am. Chem. Soc.* 2010, **132**, 4328.

² Eskandari, M., et al, **to be submitted**.

Impact of the Molecular Structure of Conjugated Block-copolymers on Their Thin Film Morphology and Photovoltaic Performance

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Block-copolymers have found wide application as functional coatings, nanoporous membranes, materials for stretchable/flexible electronics and sensors due to their ability to form different supramolecular structures (e.g. spherical, cylindrical, lamellar, etc.). Efficient self-assembling of block copolymers might be used in organic photovoltaics to create an optimal morphology of photoactive layer. Despite the fact that the concept of single-material solar cells based on block-copolymers was proposed long time ago, maximum efficiency of such devices did not exceed 3% so far. A limited progress in that field might be explained by poorly defined correlations between the structure and properties of block-copolymers, their ordering in thin films and performance in solar cells. The formation of ordered structures for block copolymers can be predicted using segment–segment interaction parameter (SSIP). In particular, if the energies of self-association of donor or acceptor parts exceed the energy of interactions between donor and acceptor units, some phase segregation and the formation of distinct domains can be observed in thin films. The SSIP strongly depends on the lipophilic-lipophobic interactions between the side chains in donor and acceptor blocks.

In the present work, we investigated a set of six model block-copolymers (Fig. 1). Donor and acceptor blocks were loaded with the solubilizing chains of fundamentally different nature, e.g. alkyl vs. fluoroalkyl or polyether units, in order to facilitate their demixing and phase segregation in thin films.

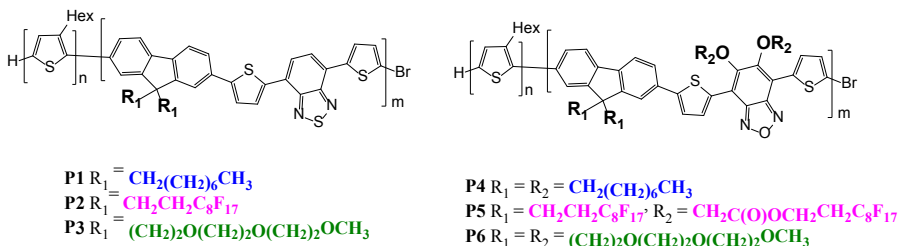


Fig. 1. Chemical structures of designed conjugated block-copolymers

Probe microscopy revealed the nanoscale morphology of block copolymers in thin films and confirmed the formation of separate donor and acceptor domains. A clear relationship has been established between the structure and film morphology of the block-copolymers and their photovoltaic performance. In particular, it was confirmed that crystallization of donor P3HT block represents the main driving force for phase separation. At the same time, materials with amorphous acceptor blocks demonstrated better supramolecular ordering and enhanced photovoltaic performance since there was no competitive crystallization of donor and acceptor parts. These findings highlight a promising strategy for future design of new photoactive block copolymers with improved characteristics to enable efficient and stable organic solar cells.

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Optical and Luminescent Properties of Cesium-copper Iodides Thin-films

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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. But it was demonstrated that this type of materials also has electroluminescent properties. However, a significant drawback of a large amount of compositions is the tendency to degradation during oxidation, exposure to ultraviolet radiation and other factors. The use of inorganic iodides with more stability than organic-inorganic compounds looks promising. For this purpose, the cesium iodocuprate CsCu_2I_3 was chosen as the object of study, which, according to the data obtained earlier, has the ability to photoluminescence in the visible region.

The aim of the work was to obtain films of cesium ioduprate and the study of their optical and transport properties. Within its framework, problems were dissolved on the synthesis of continuous films, the analysis of their morphology, the determination of the phase composition and the subsequent analysis of their transport characteristics.

To obtain films, the solution method was used, with the varying solvents and their mixtures for deposition, as well as the procedure for applying the reagents — one-step and two-step. The one-step method involved co-precipitating copper iodides with cesium and subsequent thermal removal of the solvent. The two-step method consisted in obtaining a film of copper iodide, which subsequently immersed for some time into cesium iodide solutions. The analysis of the properties of the films obtained was carried out with the help of X-ray phase analysis and optical microscopy.

As a result, CsCu_2I_3 films were synthesized under various conditions. It was found that with an increase in the concentration of dissolved substances, the degree of continuity of the resulting film increased. As a result of the two-step synthesis, according to X-ray phase analysis, a significant amount of the impurity phase $\text{Cs}_3\text{Cu}_2\text{I}_5$ was formed. Copper iodide films obtained by this method in the first step of two-stage synthesis demonstrate texture and are oriented along the $\langle 111 \rangle$ direction.

In one-step synthesis DMSO, acetonitrile, dimethylformamide, ethyl alcohol and other substances were tested as solvents. In the synthesis, temperatures from 110 to 190 °C were used, and it was found that at temperatures up to 150 °C some DMSO remained in the film, which acted as the main component of the solvent mixture.

The amount of the impurity phase $\text{Cs}_3\text{Cu}_2\text{I}_5$ in this method of synthesis was significantly smaller, which follows from the diffraction data of the products. The best results in terms of the uniformity of the coating showed films obtained from dimethyl sulfoxide and a mixture of dimethyl sulfoxide with acetonitrile. In all cases, the growth of rod-like CsCu_2I_3 particles was observed. According to X-ray diffraction data, the presence of orientation of the films along the $\langle 110 \rangle$ direction was revealed, which was observed for films obtained at temperatures higher than 110 °C.

Further work will be aimed at studying the transport characteristics of films and individual CsCu_2I_3 whisker crystals by the two-contact method.

¹ Shan Q. et al. High Performance Metal Halide Perovskite Light-Emitting Diode: From Material Design to Device Optimization. *Small*. 2017, **13** (45), 1–25.

J-aggregate Monolayers Resulting from Non-classical Multistage Crystallization

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Due to π -stacking, many dyes with extended conjugated π -electron systems self-assemble into the so called J-aggregates with a monolayer or fibrillar structure and unusual photophysical and electron-transport properties (a strong fluorescence and the intense red-shifted absorption peak).¹ Crystallographic analysis of two-dimensional monolayer shapes of monomethine cyanine dye 3,3'-di(γ -sulfopropyl)-5,5-dichlorotiamonomethinecyanine (thiacyanine, TC) has been recently conducted and the inclined imperfect one-dimensional substructure with a characteristic width ~ 7 -10 nm has been unexpectedly observed by high-resolution AFM (Fig. 1a).^{2,3} Similar imperfectness at the nanometer scale has been found in monolayers of other cyanine and carbocyanine dyes.⁴

In this work we propose the explanation of the observed imperfectness of J-aggregate monolayers by invoking the general idea of the “non-classical” multistep crystallization mechanism developed over the past two decades in considering the crystallization of various inorganic and organic compounds and proteins.⁵ The general scheme illustrating the proposed three-step (i-iii) mechanism of the formation of the intrinsic roughness of J-aggregate monolayers is shown Figure 1b. (i) Dye molecules rapidly self-assemble in stacked molecular rows at the stage I driven by the strong intermolecular π -stacking interaction. (ii) As soon as the row length reaches the critical value ~ 7 nm (~ 20 stacked molecules), the side-by-side aggregation of rows is started which results in the formation of linear nanostrips (stage II). At the last stage (III), the nanostrips aggregate (again in a side-by-side manner) forming the well-defined crystallographically two-dimensional monolayer crystal shapes. In the proposed scheme, J-aggregate monolayers should be considered as imperfect two-dimensional mesocrystals inheriting the one-dimensional structure of nanostrips as building units. The observed characteristic spatial inhomogeneity imposes the upper limit on the exciton coherence length which is expected to be about ~ 10 nm. Thus it can strongly influence the exciton transport in J-aggregate monolayers.

This work was supported by Russian Fund for Basic Research (project No 17-03-01179 A).

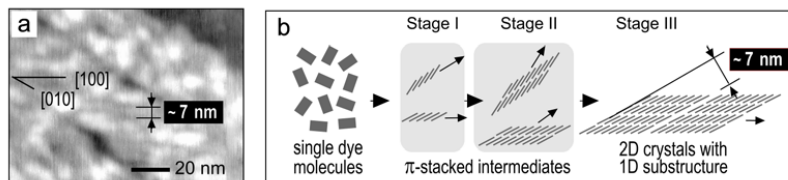


Fig. 1. High-resolution AFM image of the one-dimensional irregularity of the TC dye two-dimensional J-aggregate monolayer (a) and the proposed model of its formation via the multistage crystallization.

¹ Saikin S. K., Eisfeld A. et al. *Nanophotonics* 2013, **2**, 21.

² Prokhorov V.V., Perelygina O.M. et al. *J. Phys. Chem. B*, 2015, **119**, 15046.

³ Prokhorov V.V., Pozin S.I. et al. *Langmuir*, 2018, **34**, 4803.

⁴ Prokhorov V.V., Pozin S.I. et al. *Mendelev Communications*, **in press**.

⁵ Yoreo J. J. De et al., *Science*, 2015, **349**, aaa6760.

Effect of J-aggregate Nanocrystals on OLED Stability

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J-aggregates of cyanine dyes still attract attention as active nano-sized components in organic optoelectronic devices. For the first time, J-aggregates/ polymer composites were used as dopants in light-emitting layers of OLEDs structures about 20 years ago.¹ It was shown that the disadvantage of such devices is the rapid degradation of J-aggregates as light-emitting centers. The possibility of using J-aggregates/polymer composites as charge-transport layers was not previously considered.

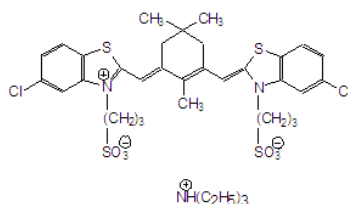


Fig.1. Chemical structure of CD-1 (triethylammonium salt of 3,3'-di(γ -sulfopropyl)-5,5'-dichloro-9,11-(β,β' -dimethyltimethylene)-10-methyl-thiadicarbocyaninebetaine)

We investigated the composite J-aggregates/polymer as hole-transport layers (HTL) in OLEDs. The dye CD-1 was used (Fig. 1), since it significantly exceeds similar dyes in photostability due to the inclusion of a portion of the polymethine chain in the cycle.² The matrix was a water-soluble polyaniline complex (PAN). The presence of J-aggregates in the layer was monitored by absorption spectra. The polymer Super Yellow (SY) was used as a light-emitting layer, the HOMO level of which corresponds to the HOMO level of J-aggregates. A series of OLED structures (ITO/HTL(50nm)/SY(80nm)/LiF/Al) with different contents of J-aggregates in the HTL was manufactured. EL characteristics of the samples weakly depended on the concentration of J-aggregates in the range of 0-10% by weight. The maximum brightness and efficiency reached 2×10^4 cd/m² and 4 lm/W, respectively. It was found that the operating time of the OLED-structure increases by 5-10 times in the presence of 5% J-units in the HTL. We assume that the nanophase of J-aggregates prevents the degradation of the charge-transport polymer matrix.

This work was supported by Russian Fund for Basic Research (project No 17-03-01179 A).

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Confocal Photoluminescence Microscopy of Organic Semiconducting Ultrathin Films

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In recent years, ultrathin (2D) organic electronics – an area of research and applied development aimed at creating ultraflexible, superlightweight, transparent and inexpensive electronic devices based on organic semiconductor films with a thickness of one or more molecular layers – has been rapidly developing. However, 2D optoelectronics is still in its infancy¹, and luminescent properties of 2D semiconductor single crystals, which could be very beneficial because of their high structural order, are unknown. Thiophene-phenylene materials are promising for organic optoelectronics because of lucky combination of decent charge-carrier mobility and high luminescence. Linear conjugated thiophene-phenylene molecules with long alkyl terminal substituents easily form large-area 2D single-crystal monolayers².

In this work, we study photoluminescence (PL) of 2D samples based on DH-TTPPT and (Dec-P)₂-BTBT molecules (Fig.1, top), which show pronounced semiconducting and PL properties. The 2D samples were prepared by drop- or spin-castingⁱⁱ and studied with the use of confocal laser scanning microscopy. We compare PL from monolayer and a-few-layer domains of the ultrathin films. In addition, we have found a considerable PL signal coming from the sample area between the film domains as illustrated in Fig.1b, c. This PL signal is assigned to sub-monolayers. The spectra and intensities of PL from monolayers, a-few-layer films, and sub-monolayers are presented and discussed.

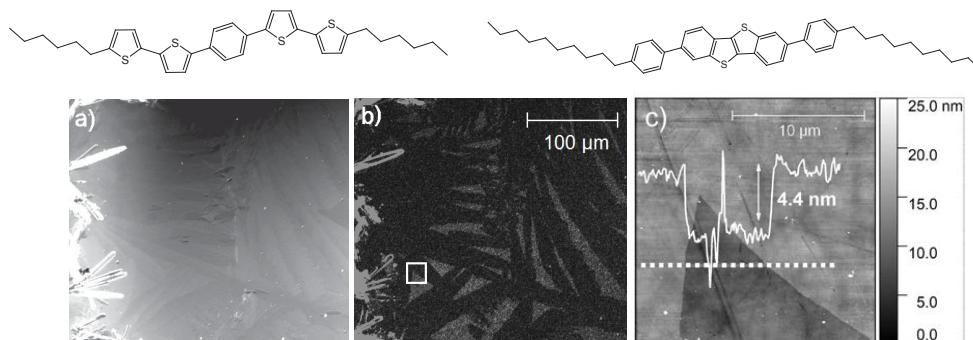


Fig 1. Top: chemical structures of DH-TTPPT (left) and (Dec-P)₂-BTBT (right) molecules.

Bottom: optical (a), PL (b), and atomic-force (c) microscopy images of a 2D DH-TTPPT sample. The area outlined by the square in panel (b) corresponds to the atomic-force microscopy image in panel (c); inset in panel (c) shows height profile along the dashed line.

This work was supported by RSF (project № 18-12-00499). We thank A.A. Ezhov for his help in PL measurements.

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The Design of Lanthanide Heteroaromatic Carboxylates for Thermometry and OLED

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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 as well as bioimaging materials should demonstrate solubility, high absorption and stability in solution. We suggested that heteroaromatic carboxylates possessing nitrogen in α -position relative to carboxylic group as well as high conjugation length of the ligand may increase solubility due to the decrease of polymerization degree, increase stability in solution due to better coordination and increase absorption. Therefore as anionic ligands the anions of heteroaromatic ligands presented in Figure 1 were selected, their lanthanide complexes obtained, tested in OLED as emitting layer, in luminescence thermometry and in bioimaging

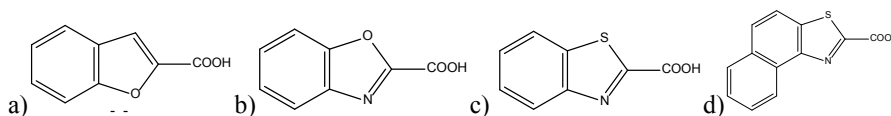


Figure 1. Structure formula of a) H(bfc) b) H(boz) c) H(btz) d) H(ntz)

Syntheses of carboxylic acids were optimized and their lanthanide complexes obtained. All the europium complexes demonstrated intensive 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, the terbium complexes including two-ring conjugate systems demonstrate low ionic luminescence intensity due to effective back energy transfer, which is explained by high excited state energy of Tb^{3+} . That allowed to obtain luminescent thermometers based on $\text{Eu}_x\text{Tb}_{1-x}(\text{L})_3 \cdot 3\text{H}_2\text{O}$ ($x=1, 2, 5$ and 5% ; $\text{L}=\text{boz}$ and btz) compositions which shows sensitivity up to $2.8\ \%/K$. All the complexes demonstrate solubility in several solvents up to $16\ \text{g/ml}$ in chloroform, though complexes with three-ring ligand were less soluble than with two-ring ligands. All the complexes were tested in solution processed OLEDs in the form of mixed ligand complexes where phenantroline and bato-phenantroline were used as neutral ligands. These mixed ligand complexes were synthesized and demonstrated high europium electroluminescence intensity.

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 (projects №№ 18-33-00250, 16-53-76018).

Computational Study of a Novel AIE Luminogen bis(4-((9H-fluoren-9-ylidene)methyl)phenyl)thiophene

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Highly-emissive solid-state materials are of a great interest for organic optoelectronics as active layers in organic light-emitting devices, lasers and sensors.¹ However, design of materials with specific optical response is still a challenge since several inter- and intramolecular factors should be taken into account. Recently, a novel AIE luminogen based on bis(4-((9H-fluoren-9-ylidene)methyl)phenyl)thiophene (BFMPT) showing two-colour polymorphism-dependent AIE was synthesized and studied. In this work, we present a computational study of BFMPT intrinsic properties and both intra- and intermolecular interactions in polymorphs.

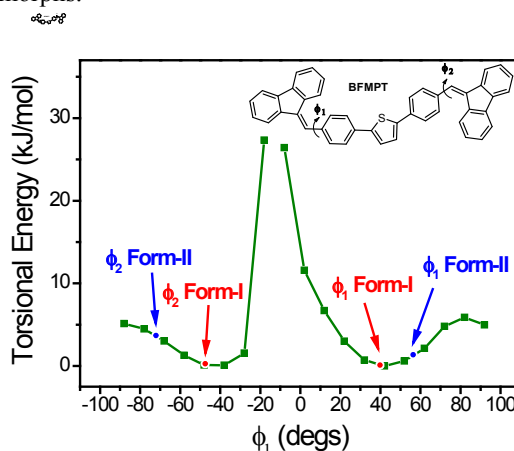


Fig. 1. Potential energy surface of BFMPT as a function of ϕ_1 dihedral angle. Red and blue dots and arrows show the values of ϕ_1 and ϕ_2 dihedral angles of Form-I and Form-II, respectively.

The analysis of the potential energy surface profile as a function of ϕ_1 dihedral angle (Fig. 1) revealed the values of dihedral angles in the Form-I are almost coincident to the computed value corresponding to the minima, whereas those of Form-II are farther. These difference in conformers' torsional energy should be considered as one of the factors determining Form-I kinetic stability. Computational study of BFMPT revealed that positive solvatochromism is caused by the change of quadrupole moment upon solvation. The optical difference of BFMPT polymorphs was demonstrated to be mainly related to the change of BFMPT conformation, whereas intermolecular interactions are very similar in both forms. All in all, due to high intrinsic conformational elasticity BFMPT-related compounds could serve as a basis for further molecular design of novel high performance aggregation induced emissive materials.

This work was supported by RSF (project 18-73-00081).

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A Microscopic View on Spectral Inhomogeneity in Molecular Nanotubes

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The success of natural photosynthetic complexes served as inspiration for self-assembled molecular aggregates that have garnered considerable interest as artificial light-harvesting systems in recent years. Specifically, in aqueous solution a family of functionalized cyanine dye molecules autonomously assembles into highly uniform nanotubes of ~15 nm diameter and several 100s of nanometers lengths.¹ The strong coupling of many thousands of molecules gives rise to remarkable exciton diffusion lengths along the nanotubes,² which are believed to be only limited by the nanotubes inhomogeneity. A quantitative investigation of the latter requires single nanotube spectroscopy in order to overcome the limitation of ensemble averaging.

In this contribution we present results from combined spectroscopy/microscopy investigations of the spectral inhomogeneity at the level of *individual nanotubes*. Here, we focus on the fluorescence signature of single nanotubes at room as well as to cryogenic temperatures. Comparison of the fluorescence emission spectra of bulk nanotube solution and single nanotubes reveals an even narrower fluorescence linewidth of the latter of only 54 cm⁻¹ at room temperature. This remarkably low degree of structural/dynamic disorder of the nanotubes facilitates high exciton mobilities as well as large exciton delocalization.

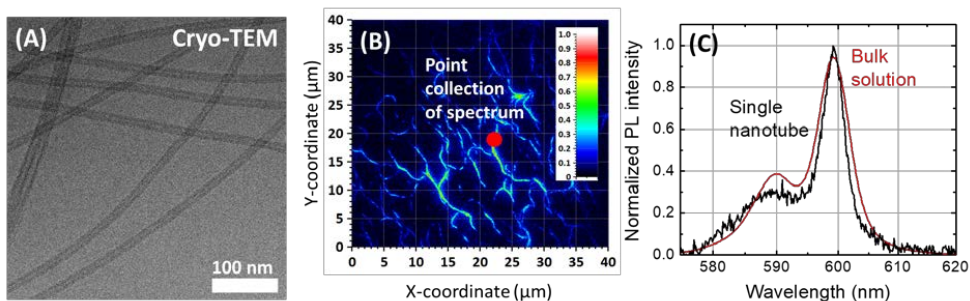


Fig. 1. (A) Cryo-TEM micrograph of double-walled C8S3-Cl nanotubes. (B) Fluorescence microscopy image showing a dense network of nanotubes. Intensity is depicted on a color scale normalized to the maximum intensity. (C) Comparison of PL emission spectra of bulk nanotube solution and a single nanotube revealing a narrower emission linewidth for the latter.

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Doping of Furan/Phenylene Co-oligomer Single Crystals as an Efficient Way to Control Their Optoelectronic Performance

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Nowadays a number of extremely valuable organic crystalline materials combining good photoluminescence (PL) and semiconducting properties have been found. One of the most promising materials are furan-phenylene co-oligomers¹ due to their higher solubility, molecular rigidity and planarity leading to efficient charge and exciton transport.² Moreover, solution processing allows obtaining materials with a small amount of dopant appearing as a by-product of the synthesis³ or added artificially.⁴ In this work we have studied the doping of promising highly-luminescent organic semiconductor 1,4-bis(5-phenylfuran-2-yl)benzene (FP5) by its synthetic by product 5,5'-bis(4-(5-phenylfuran-2-yl)phenyl)-2,2'-bifuran (FP8).

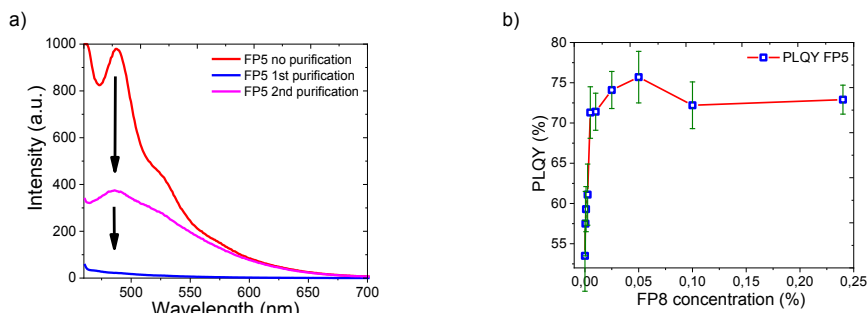


Figure 1. a) PL spectra of FP5 of different purity: raw material (red), purified by PVT (violet), twice purified by PVT (blue); b) PLQY for FP5 crystals doped by different amount of FP8.

By using a combination of separate synthesis of potential by-product FP8 and a PL spectroscopy of FP5 solution we demonstrated that a raw FP5 material contains ~0.2% of FP8. Two stage re-crystallization by a physical vapor transport (PVT) method allowed purification, the residual amount of FP8 being <0.002%. Furthermore the intentional doping of solution-grown FP5 crystals was performed to elucidate the optimal doping level. Remarkably, the 0.05% of dopant was demonstrated to be enough for maximizing the PL efficiency of FP5 crystals. Single crystal field-effect transistors fabricated on doped FP5 crystals revealed the decrease of hole mobility and increase of threshold voltage upon doping, what is assigned to the generation of shallow and deep traps in the crystals.

The work was supported by the Ministry of Education and Science of the Russian Federation (grant number 4.7154.2017/8.9) and Novosibirsk State University program “5-100”.

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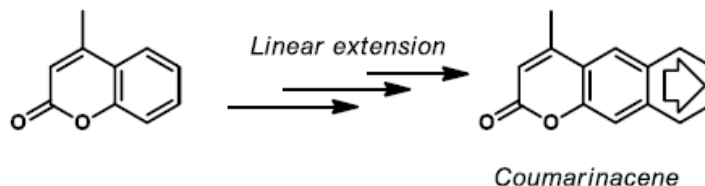
Coumarinacenes: Linearly π -Extended Coumarins

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Linearly π -extended (1D) acenes, like tetracene and pentacene,¹ are excellent organic semiconducting materials and have been used in organic field-effect transistor devices due to their excellent charge carrier mobilities.² Herein, we report the synthesis of a coumarin-based tetracene derivative, i.e., coumarinacene, starting from cheap starting materials. These compounds are relatively photostable when compared to tetracene or pentacene.³ Besides, they can be conveniently vacuum-sublimed quantitatively without any decomposition to achieve high-purity materials of electronic grade. The UV-vis absorption, photoluminescence, cyclic voltammetry, and thermal stability studies were conducted on coumarinacenes. Our preliminary studies on coumarinacenes, that promise their potential utilization in organic electronic devices in near future, will be discussed in this presentation.



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Structural Features and Polymorphism in New Organic Metals Based on BDH-TTP Donor and $[\text{ReF}_6]^{2-}$ Anion

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The design and synthesis of new polyfunctional compounds are one of the top priorities in the chemistry of modern materials. In particular, compounds with electrical conductivity and magnetism in the same crystal lattice are objects of intensive study, which is associated with the search of the synergism of these properties and the appearance in them of new phenomenon. Recently, the first conductive single molecule magnet (SMM), $(\text{BEDO})_4[\text{ReF}_6] \cdot 6\text{H}_2\text{O}$, (BEDO = bis(ethylenedioxo)tetrathiafulvalene)¹ was synthesized and structurally characterized, in which high conductivity (up to 4.2 K) and monomolecular magnetism coexist in the same temperature range. This result opens the way to the creation of conducting at helium temperatures SMMs based on cation-radical salts. As a π -donor, 2,5-bis(1,3-dithiolan-2-ylidene)-1,3,4,6-tetrapiapentalene (BDH-TTP) was used by us due to its ability to form radical cation salts with metallic conductivity down to 4.2 K.²

The $(\text{Ph}_4\text{P})_2\text{ReF}_6$ electrolyte, possessing the properties of SMM, was used as a source of counterion $[\text{ReF}_6]^{2-}$. Here we report obtaining three new organic metals $(\text{BDH-TTP})_3(\text{ReO}_4)_2$ (**I**) and $(\text{BDH-TTP})_4\text{ReF}_6$ (**II** and **III**). The salts **II** and **III** are polymorphs. They have the same composition but different crystallographic cell. The crystal structures and conductivity the compounds were studies. Compound **I** crystallizes in a triclinic cell with the parameters $a = 8.0214(4) \text{ \AA}$, $b = 9.3521(4) \text{ \AA}$, $c = 17.4018(7) \text{ \AA}$, $\alpha = 97.018(4)^\circ$, $\beta = 98.064(4)^\circ$, $\gamma = 110.032(4)^\circ$, $V = 1193.82(9) \text{ \AA}^3$, space group $P(-1)$, $Z=1$, $R_1=0.0485$. The main crystallographic parameters for polymorphic salts are: **II**- triclinic cell, $a = 13.5224(4) \text{ \AA}$, $b = 18.4114(6) \text{ \AA}$, $c=19.3598 \text{ \AA}$, $\alpha = 84.489(2)^\circ$, $\beta = 87.940(2)^\circ$, $\gamma = 75.510(2)^\circ$, $V = 4644.7(2) \text{ \AA}^3$, space group $P(-1)$, $Z=3$, $R_1=0.1125$; **III** - monoclinic cell, $a = 20.0098(11) \text{ \AA}$, $b = 8.05668(4) \text{ \AA}$, $c = 10.8367(5) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 92.795(3)^\circ$, $\gamma = 90^\circ$, $V = 1744.96(16) \text{ \AA}^3$, space group $P21/c$, $Z = 1$, $R_1 = 0.0927$. All synthesized salts have a layered structure, which is characterized by alternation of conducting κ -type cation-radical layers and insulating anion layers formed octahedrons $[\text{ReO}_4]^-$ (in **I**) or $[\text{ReF}_6]^{2-}$ in polymorphs. A distinctive feature of **I-III** compounds is the partial population of rhenium atoms positions, respectively, 1/2 for **I** and **II** and 1/4 for **III**. Incomplete occupancy of Re positions leads to disorder in the anion layer. Cation radicals in the conductive layers of **I** are bonded by short contacts $\text{S} \dots \text{S}$ and $\text{S} \dots \text{C}$ and in **II-III** by short contacts $\text{S} \dots \text{S}$, $\text{S} \dots \text{C}$ and hydrogen bonds $\text{S} \dots \text{HC}$. Between the cationic and anionic layers there are also shortened contacts of the type $\text{S} \dots \text{O}$, $\text{C} \dots \text{O}$ and hydrogen bonds $\text{CH} \dots \text{O}$ in **I** and $\text{CH} \dots \text{F}$ in **II-III**. The radical cation salts **I** and **II** are metals up to 4 K. Compound **III** exhibits a metallic behaviour of resistance to $\sim 50 \text{ K}$. Below this temperature, a slight increase in resistance is observed.

This work was supported by RFBR (projects № 17-03-00167, 18-02-00280).

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The Effect of Hydrostatic Pressure on Interlayer Charge Transport and the Electronic Structure of Metal Layers in a Two-layer in a Quasi-two-dimensional Organic Metal (BETS)₄CoBr₄(C₆H₄Cl₂)

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The behavior of the resistance and magnetoresistance in a two-dimensional two-layered organic metal (BETS)₄CoBr₄(C₆H₄Cl₂) under normal pressure and under the action of hydrostatic pressure up to 10 kbar was investigated. In this material, unlike traditional quasi-two-dimensional organic metals, the electronic and molecular structure of neighboring cationic layers differs from each other.¹ In the studied conductor, metal cationic layers alternate with cationic layers having a dielectric electronic structure. Such configuration leads to incoherent interlayer electron transport. Interlayer resistance at normal pressure increases with decreasing temperature to $T \sim 25\text{K}$ and then falls to low temperatures. An analysis of the behavior of the angular and field dependences of the magnetoresistance showed that the incoherent transfer mode exists over the entire temperature range. In this case, the low-temperature metallic behavior is associated with the inclusion of a transfer mechanism through resonant impurities. The application of external pressure strongly weakens non-metallic growth of resistance, but the transfer remains incoherent. The Fourier spectrum of Shubnikov-de Haas oscillations in (BETS)₄CoBr₄(C₆H₄Cl₂) under normal pressure is consistent with theoretical calculations and contains two fundamental frequencies $F_\alpha \approx 870\text{T}$ and $F_\beta \approx 4500\text{T}$ in a field perpendicular to the conducting layers, corresponding to α and β orbits. The cyclotron masses associated with these frequencies are: $m_\alpha \approx 1.0m_0$ and $m_\beta \approx 2.0m_0$, where m_0 is the mass of a free electron. In addition to the fundamental frequencies, the spectrum contains the combination frequencies $F_{\beta-\alpha}$ and $F_{\beta-2\alpha}$, which do not have allowed closed orbits and are associated with the effect of quantum interference. The applied pressure increases the fundamental frequencies by several percent. Most likely, this is due to a decrease in the size of the unit cell. Cyclotron masses under pressure practically do not change.

This work was performed in accordance with the state task, state registration no. 0089-2019-0011 (synthesis of samples) and under support of RFBR no. 18-02-00308 (physical measurements).

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Amino-selective Gas Sensor Based on Organic Field-effect Transistor Using Porphyrin Receptor Monolayer at the Semiconductor/Dielectric Interface

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Using organic field-effect transistors (OFET) as gas sensors have attracted much attention recently due to their impressive characteristics reported by several research groups. These devices usually demonstrate high sensitivity, while achieving any decent sensor selectivity still represents a big challenge. Selectivity of sensors to certain analytes can be induced through modification of the device with certain receptor molecules capable of specific or at least selective recognition of an analyte. In view of the fact that the vast majority of charge carriers in operating OFET are flowing within a few molecular layers of organic semiconductor adjacent to dielectric, the receptor molecules should be placed at the semiconductor/dielectric interface to induce maximal effect on the device performance.

We have applied this approach for designing chemosensitive OFETs with a high selectivity to amines. 4,4',4''-(Porphine-5,10,15,20-tetrayl)tetrakis(benzoic acid)) (TCPP) was utilized as amine-selective receptor, while C₁₂-PDI was serving as organic semiconductor. The designed devices demonstrated comparatively strong and reversible increase in the source-drain current I_{ds} upon exposure to 1 ppm of amine-type analytes such as ammonia, trimethylamine, diethylamine, etc. We show that such selectivity is related to the introduction of the TCPP receptor layer, which boosted sensor response by >200 % with respect to amines and suppressed the responses to some non-amine type analytes such as alcohols, ketones, aromatic compounds, etc.

In conclusion, we have shown that using TCPP monolayer as a receptor component placed at the interface between the gate dielectric and organic semiconductor strongly affects the selectivity profile of the OFET-based gas sensors. In a more general case, the selectivity of the sensors can be tailored via easy variation of self-assembled receptor monolayers in the same OFET structure including even usage of cocktails of sensing molecules. Moreover, one can also employ different semiconductor materials, which can additionally tune the sensitivity and selectivity profiles of chem-OFETs. Thus, the proposed concept paves a way to the development of electronic nose, which can be considered as a versatile platform for multiple applications ranging from product quality control to medical diagnostics.

This work was supported by the Russian Foundation for Basic Research (grant 18-33-20222 mol_a_ved).

Changes of Graphene Transistors Electronic Properties by Organic Deposition

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Graphene based technology becomes more and more demand in modern electronics. Depending on scope of use graphene structures should be modified in different ways. Promising way to functionalize graphene is molecular doping.¹ It can be used for photodetectors, transistors and biosensors production.²

One method of functionalization in such way uses direct deposition of organic molecules on graphene transistors from solution by ink-jet printing. For ink-jet printing technology, inks must be viscos enough, substrate wettability and has low melting point for stable drop formation and uniform ink deposition on substrate surface. With such limits organic molecules was dispersed in solution with solvent and thickener.³

CVD grown graphene was transferred on silicon substrate and transistor structured was formed with Cr/Au contacts. In this work, we used polyaniline (PANI), quatrotiophene (HEX) and perylene dicarboximide (PDI). Ink with this dyes consisted n-methylpyrrolidone (NMP), toluene, chlorobenzene as solvents and isopropanol as thickener. Prepared inks were printed with ink-jet printer Dimatix 3000.

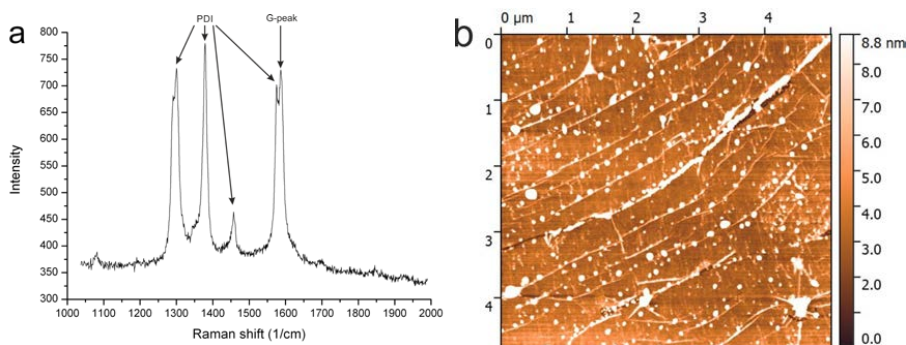


Fig. 1. a – Raman spectroscopy of PDI, b – AFM of PDI surface on graphene

Drops on substrate formed non-uniform structures, but on graphene it is thin layer of molecules was observed. Also it can be seen cluster formation on wrinkles. Transfer current-voltage characteristics (CVC) show changes in electronic structure of graphene and Dirac point is shifted. With such results, we can assume that organic molecules interact with graphene even after simple deposition on its surface.

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³ Ng L. W. T. et al. *Springer International Publishing*, 2019.

Influence of Light Soaking on Charge Injection Properties at Hybrid Metal Oxide/Organic Interfaces

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The establishment of ohmic contact for hole and electron is crucial for efficient organic opto-electronic devices. Despite its sensitivity to UV-light, ZnO is frequently used as an electrode material in organic and hybrid organic/inorganic optoelectronic devices.^{1,2} Surface modification of metal oxides with self-assembled monolayers (SAMs) allows engineering of the work function (WF) to align with the charge transport levels of organic semiconductors and, thus, optimizing the charge injection capabilities.³ In fact, it has been reported that ZnO is able to inject either electrons or holes into organic semiconductors, depending on the specific energetics at the hybrid interface.⁴

Here, we have systematically investigated the combined effect of UV radiation and surface modification on its work function of ZnO substrate and on the efficiency of hole injection into the prototypical conjugated polymer P3HT. We manipulate the work function of ZnO films by treatment with SAMs and controlled UV exposure. This allows us to correlate the hole injection current from ZnO into P3HT in unipolar devices with the change in injection barrier height. Our results confirm that the ohmic hole injection from the ZnO into the organic is possible by SAM treatment but may be disabled by UV-exposure. Additionally, the carrier injection is not merely determined by the ZnO-work function but significantly improves upon introduction of a SAM. Evidently, the work function and with that the injection efficiency depends strongly on the history of light exposure. Valid conclusions about the contact energetics are only possible, if the sample history is precisely known and controlled.

This work is funded by Deutsche Forschungsgemeinschaft, (SFB 951, B7), Hybrid Inorganic/Organic Systems for Opto-Electronics (HIOS).

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An Analytic Model of J-V Characteristics of Quantum Dot Based and Hybrid Photovoltaic Cells

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Quantum dot (QD) solids are promising materials for optoelectronic applications due to their unique optical properties and high photostability¹. One of the remaining problems of the QD-based photovoltaics is increasing the power conversion efficiency (PCE) of the cell. The application of hybrid QD-organic materials seems to be a reasonable solution, since it provides better separation of electrons and holes. The well-known Shockley-Queisser model² gives the limiting value of the PCE, however, it does not provide the understanding of how transport characteristics of charge carriers and excitons affect the performance of the photovoltaic cell. The latter is the subject of this work.

We propose the analytic model of J-V characteristics of QD-based and hybrid solar cells, which includes drift and diffusion of electrons and holes, and diffusion of excitons. The equations of this model are solved analytically and the analytical expression for the PCE is obtained in the case of neglected recombination. The model considers charge mobilities and the exciton diffusion length as the effective parameters. The effect of these parameters on the PCE, short-circuit current and open-circuit voltage is discussed.

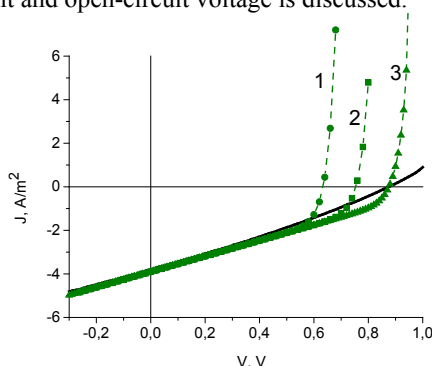


Fig. 1. Experimental (solid line) and calculated according to the presented model (dashed line + symbols) J-V characteristics of a QD-based solar cell, parametric in charge mobilities μ , m²/Vs: 1 – $8.2 \cdot 10^{-8}$, 2 – $8.2 \cdot 10^{-10}$, 3 – $8.2 \cdot 10^{-12}$.

Fig. 1 illustrates the experimental and calculated J-V characteristics for photovoltaic cell based on 2.9 nm PbS QDs and the effect of the charge mobility. The parameters are chosen in order to fit the experimental values of the open-circuit voltage and short-circuit current.

This work was supported by the Russian Foundation for Basic Research, Grant No. 16-29-09623 (OFI_M).

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² Shockley W., Queisser H.J., *J. Appl. Phys.* 1961, **32**, 510.

Organic Photodetectors Based on Donor-acceptor Star-shaped Oligomers: Towards Artificial Eye

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The concept of the electronic eye is an opto-electronic means of sensing. It should involve the use of organic semiconductor molecules as a photoreceptor in order to be biocompatible. There are two approaches: either the creation of an artificial eye (matrix of organic photodetectors with different spectral sensitivity) or the creation of photoactive "prostheses" for the eye, which is devoid of sensitivity to light due to certain diseases. For this application, conjugated oligomers and polymers can be used, which were primarily developed for organic solar cells, because they are capable of forming water-soluble columnar nanostructures close in shape to cones and rods. This is vital, because in the second case the molecules are inserted directly into the eye.

The molecules are tested as an active layer of photodetectors to gain their properties such as responsivity, EQE and dark/light current. The goal of this work is to find molecules that fit absorbance spectra of cones and rods to test them both as "prostheses" for the eye and as a photodetector.

Achieving the correct absorbance spectra is possible by multilateral adjustment and modification of molecular design varying the values of their energy levels, and hence the width of the optical band gap i.e. the absorption spectrum. Also in photodetectors, it is possible to tweak the thickness of charge transport and active layer to create a system favoring wavelengths, close to those in eye receptors (peaks at 488, 534, 564 nm).

As a result, the molecules: N(Ph-T-CNO-EtHex)₃, N(Ph-3T-DCV-Hex)₃, N(Ph-2T-DCV-Et)₃ have peaks in responsivity (the electrical output per optical input) at 510 nm (0.133 A/W), 550 nm (0.206 A/W), 560 nm (0.135 A/W), accordingly. In case of use as "prostheses", all of the molecules have clear maximum points close to targeted ones. EQE measurements show peaks at 475 nm (33.4 %), 480 nm (47.9%) and 530 nm (30.3 %) for the same molecule order. The dark current values of -9.8E-11, -1.0E-10 and -2.3E-10 Amperes were measured without any reverse bias. Further work on spectral narrowing and positioning by molecule design and active layer thickness tweaking is on the way.

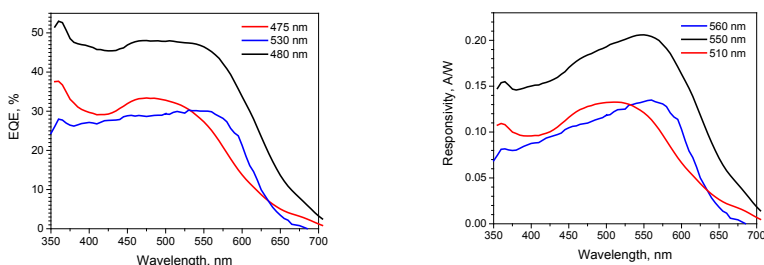


Fig.1 Wavelength dependent EQE and photoresponsivity for N(Ph-T-CNO-EtHex)₃, N(Ph-3T-DCV-Hex)₃, N(Ph-2T-DCV-Et)₃

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Electronic States of Pentacene Derivatives

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Pentacene is an interesting semiconducting material for optoelectronic applications. However, its electronic properties may be optimized to improve the performance of organic molecule-based devices. Furthermore, issues, such as low processability, may be addressed. Hence, N-functionalized pentacene derivatives have been investigated as alternatives.

N-heteropolycyclic aromatic compounds are promising candidates for n-channel semiconductors. The introduction of nitrogen atoms into the π -backbone of the polycyclic aromatic hydrocarbons stabilizes the frontier orbitals and increases the electron affinity, while the size of the HOMO-LUMO (optical) gap is nearly unaffected.¹

Thus, the electronic properties of N-functionalized pentacene derivatives were studied using two-photon photoemission (2PPE). With this powerful technique, the energetic positions of occupied as well as unoccupied states were determined. In addition, the dynamics upon excitation with light were investigated on a femtosecond time scale. Moreover, angle-resolved 2PPE was performed in order to study the dispersion of present states. By evaporating those materials on an electrode material, such as Au(111), hybridization of localized molecular states and delocalized metal bands may occur at the metal/organic interface which has an impact on device performance.

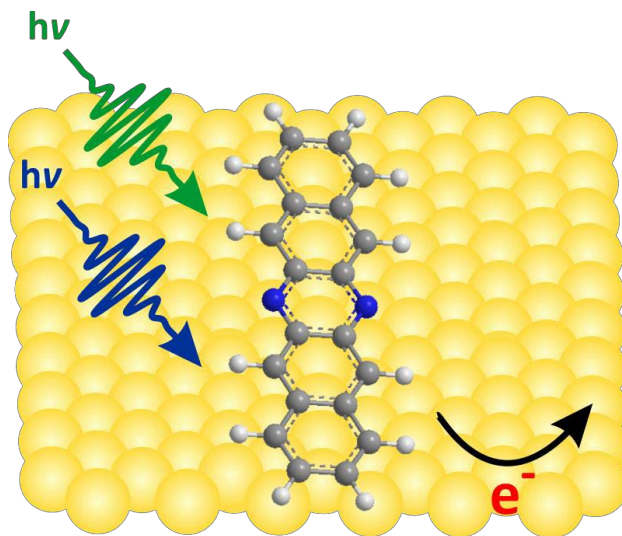


Fig. 1 N-functionalized pentacene derivative on an Au(111) surface studied by 2PPE.

This work was supported by Carl-Zeiss Foundation and the excellence cluster 3DMM2O.

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Bipolar Poly(arylene phosphine oxide) Hosts with Widely-Tunable Triplet Energy Levels for High-Efficiency Blue, Green and Red TADF Polymer Light-Emitting Diodes

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Polymer light-emitting diodes (PLEDs) based on thermally activated delayed fluorescence (TADF) emitters show great potential in developing high-efficiency solution-processed light-emitting devices without use of noble metal complexes. However, a key challenge for the development of TADF PLEDs so far is the lack of polymer hosts with suitable triplet energy levels (E_T) and good carrier transport capability. Here we report the design, synthesis and electroluminescent properties of a novel series of bipolar poly(arylene phosphine oxide) hosts based on electron-transporting arylphosphine oxide and hole-transporting carbazole units, which show widely-tunable E_T s in range of 2.20~3.01 eV by finely tuning the conjugation extent of the polymer backbone. The tunable E_T s make these polymers a universal host family for all the blue, green and red TADF emitters. TADF PLEDs based on these polymer hosts show promising device efficiency with external quantum efficiencies up to 15.8%, 17.1% and 10.1% for blue, green and red emission respectively, which are among the highest efficiencies for TADF PLEDs. These results open an avenue for the development of TADF PLEDs with high efficiency and full-color emission in the future.

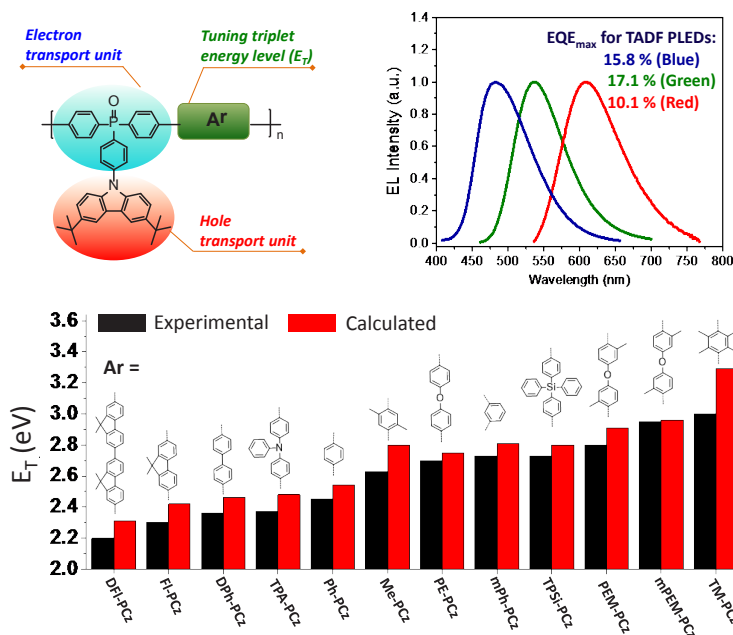


Fig. 1. Bipolar poly(arylene phosphine oxide) hosts with widely-tunable triplet energy.

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Synthesis of New Tetrathienoacene Semiconductors for Organic Field-effect Transistors

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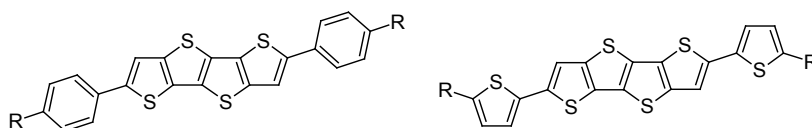
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To date, there are many classes of conjugated molecules that are used in organic electronics devices. Materials based on tetrathienoacene (TTA) derivatives shows their high practical potential due to strong intermolecular interactions, extensive intramolecular π -conjugation, and close intermolecular π - π stacking.^{1,2} However, they are still poorly studied, and synthetic methods for their preparation have a several significant drawbacks: the high cost of the initial reagents, the multi-stage and complexity of purification, low yields.

This work describes a method for preparation of 2,6-dibromo-thieno[3,2-b]thieno[2',3":4,5]thieno[2,3-d]thiophene (TTA) and new semiconductors on their basis. The synthesis route involves the preparation of 3-bromothiopheno[3,2-b]thiophene from 3,4-dibromothiophene, followed by the preparation of the corresponding disulfide and oxidative ring closure to produce TTA. The combination and adaptation of various literature methods^{3,4} allowed to increase the total reaction yields in the case of 3-bromothiopheno[3,2-b]thiophene from 54% to 72% and TTA from 27% to 45%. At the last stage, the Suzuki coupling reaction was used to obtain the final materials (Fig.1).



Also in this paper will discuss the synthetic design of such molecules, fabrication and transfer characteristics of OFET devices based on them.

This work was supported by Russian Science Foundation (grant 18-73-10182) and performed in the framework of leading science school NSh-5698.2018.3.

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Donor-acceptor Triphenylamine-based Oligomers of Different Architecture for Organic Electronics

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Donor-acceptor oligomers based on electron-donating triphenylamine are promising semiconductor materials for organic electronics and photovoltaics.¹⁷ 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 or N-ethylrhodanine groups were synthesized, investigated and compared to each other (Figure 1).

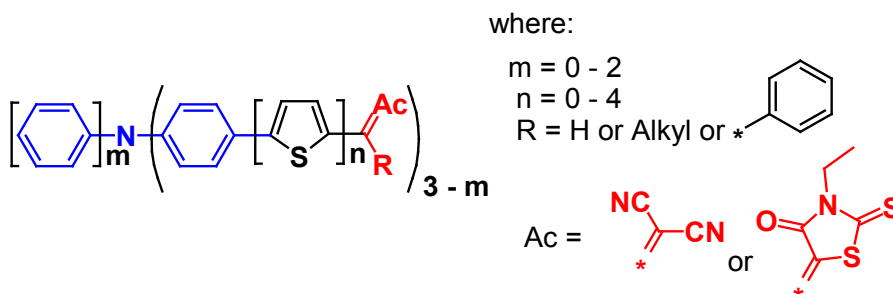


Fig. 1. Schematic representation of donor-acceptor oligomers based on triphenylamine.

Variations of different parameters of their chemical structures such as length and number of oligothiophene blocks and type of electron-withdrawing groups 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.

This work was supported by Russian Science Foundation (№19-73-30028). The work was performed in the framework of leading science school NSH-5698.2018.3.

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Crystal Packing Control of a Trifluoromethyl-substituted Furan/Phenylene Co-oligomer

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Materials combining high luminescence efficiency and efficient charge transport are in strong demand in organic optoelectronics. Furan/phenylene co-oligomers are considered as promising highly-emissive crystalline materials for light-emitting diodes, transistors and organic lasers. Here, the effects of trifluoromethyl substituents on the crystallization, structure and optical properties of furan/phenylene co-oligomer 1,4-bis{5-[4-(trifluoromethyl)phenyl]furan-2-yl}benzene (CF₃-BPFB) are studied systematically (Fig. 1).¹ Crystallization by different methods leads to polymorphs with different nearest neighbors orientations notably differing by slips along molecular long axes. All obtained crystals exhibit high photoluminescence efficiency and have optical properties which strongly depend on the crystal packing. Variable-temperature X-ray powder diffraction analysis shows the thermal transition of two forms into a third one.

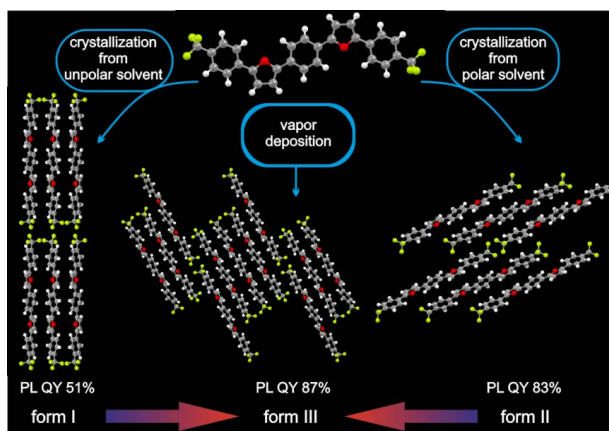


Figure 1. Chemical and crystal structures of polymorphic forms of CF₃-BPFB. Top view – crystallization methods, below view – photoluminescence quantum yields of forms and phase transitions of forms I and II into III.

The introduction of terminal substituents coupled with crystallization by different methods allows a fine tuning of crystal packing being a powerful approach for the morphology and optoelectronic properties control.

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Crystallization and Structures of Dibenzofulvene-based Derivatives

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Aggregation Induced Emission (AIE) materials are in the spotlight of current materials development due to their unique properties and potential applications in light-emitting devices, bio-imaging and sensors. AIE luminophores are usually low-emissive in solution but instead demonstrate high emission in the solid state. Typically, AIE luminogens have conformationally mobile fragments allowing free intramolecular rotations. Mono-substituted dibenzofulvene (DBF) derivatives previously attracted a great interest as potentially AIE active materials.^{1,2}

Here, the crystallization and effect of dibenzofulvene (9H-fluoren-9-ylidene) substituent on the crystal structures of furan/phenylene-, thiophene/phenylene- and thiophene-containing small molecules (Fig. 1) are studied systematically. Ph-Fur and 3Th crystallize in monoclinic space groups ($P2_1/n$ and $P2_1/c$, respectively), 2Th – in orthorhombic ($Pca2_1$) and Ph-Fur – in triclinic ($P-1$). All molecules have different torsion angles between co-oligomer core and dibenzofulvene moieties. The most planar conformation was found for 2Th derivative, due to the absence of intramolecular repulsive interactions. The latter is typical for phenyl derivatives (Fig. 1). In 3Th the twisting of DBF unit is opposite and demonstrates different values of torsional angles. The Ph-Th and Ph-Fur derivatives are highly non-planar. Particularly, due to highly twisted conformation and curved geometry Ph-Fur crystallizes as solvate with hexane, where hexane stabilized structure by C-H $\cdots\pi$ interactions with DBF fragment. All structures except for Ph-Th are controlled by C-H $\cdots\pi$ and π - π interactions, whereas Ph-Th demonstrated only C-H $\cdots\pi$ interactions.

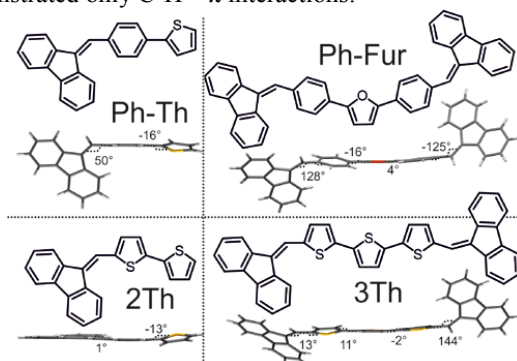


Figure 1. Chemical structures and conformations of studied derivatives.

The introduction of dibenzofulvene to furan/phenylene, thiophene/phenylene and thiophene co-oligomers leads to conformational diversity and could serve as a basis for molecular design of high performance AIE materials with desired intra- and intermolecular interactions.

This work was supported by Russian Science Foundation, project 18-73-00081.

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Two-layer Langmuir-Schaefer OFETs for Real-time Detection of NH₃ and H₂S in Humid Air

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One of perspective ways of highly-sensitive gas sensor creation is based on utilizing of ultrathin organic field effect transistors (OFETs) as sensor devices for detection of different gases in the atmosphere due to strong dependence of the OFET electrical properties on the environment¹. Such devices has several pros such as great amount of inexpensive techniques for device fabrication, low energy consumption as well as the opportunity of easy scale up to the industrial application without losing performance of the devices. The principal drawbacks of such devices are limited selectivity and strong dependence of the OFETs electrical parameters to water vapor that leads to dramatic decreasing of the OFETs electrical performance in the humid air atmosphere.

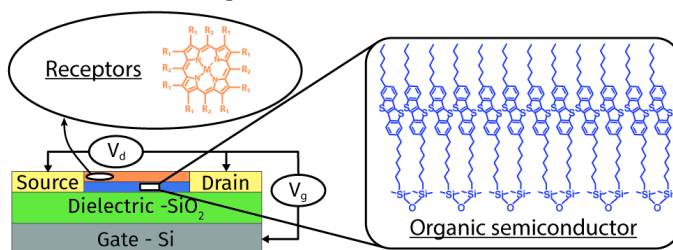


Figure 1. Schematic representation of LS OFET architecture (orange layer above the semiconducting layer (dark blue) corresponds to optional receptor layer)

Here we present a novel simple and fast approach for fabrication of reusable gas sensors based on two-layer Langmuir-Schaefer OFETs with additional receptor layer for NH₃ and H₂S real-time detection. The devices fabricated were found to be highly sensitive to the presence of ammonia and hydrogen sulfide at concentrations lower than 1 ppm and demonstrated the improvement of both limit of detection (down to ca. 40-50 ppb) in dry air and the device response in humid air (humidity up to 60%) as compared with LS monolayers devices without a receptor layer. Addition of metalloporphyrin receptor layer on the top of LS semiconducting monolayer does not influence on its electrical performance while provides the sensor response amplification in humid air as well as allows tuning the sensor selectivity. Impressive combination of the sensor high sensitivity and high-reproducibility with fast response and full recovery after finishing the analyte exposure enables utilizing of the fabricated two-layer OFETs as chemo-sensors in real gas analyzing systems².

This work was supported by RSF (project № 19-73-30028) and performed in the framework of Leading Science School (grant № NSh-5698.2018.3)

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Ground State Geometry and Vibrations of PPV Oligomers

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The poly(p-phenylene vinylene) (PPV) polymer and its oligomers are among the simplest and most thoroughly studied π -conjugated systems. However consistent data on PES features of these molecules are obsolete and reported results on planarity of these systems are ambiguous and incomplete. Our investigation aimed to provide a description of "low-energy" PES regions and benchmark different DFT methods against high quality experiment¹ and CCSD results as well as to investigate how PES changes in condensed state compared to vacuum.

We found that despite the PES of PPV oligomers is shallow with a helical torsion minimum (Fig. 1), the ground state vibrational wave-function is delocalized so that the geometry is *effectively* planar. At the room temperature the molecule is also statistically planar with even broader probability distribution (Fig. 2). Due to extended π -conjugation, increasing the size of oligomer makes system more planar.

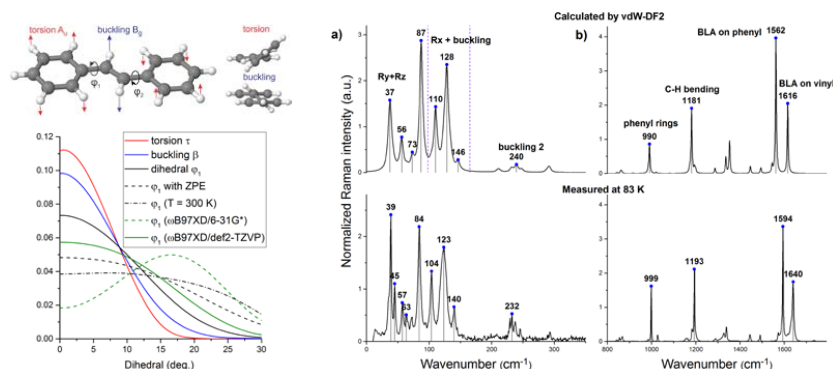


Fig. 1. Structure of trans-stilbene (PPV parent molecule)

Fig. 2. Distribution of the dihedral angles and their symmetric combinations for the ground state vibrational wave functions (default method is CAM-B3LYP/6-31G*)

Fig. 3. Calculated (top) and experimental (bottom) Raman spectra of *trans*-stilbene crystal

For higher energy PES regions rotational motion of the two dihedrals intermix with two bending vibrations of the entire molecule. In a crystalline environment they intermix with translational and rotational motions, with a gap at 15-25 meV separating them from purely intramolecular modes. Four low-frequency modes per molecule representing linear combinations of rotations and buckling motion are Raman-active (Fig 3). Rich spectrum of low-frequency modes in OPV crystals thus formed produces strong dynamic and quasistatic disorder strongly scattering charge carriers which otherwise would form two-dimensional dispersive bands.

This work is supported by Russian Science Foundation (18-72-10165).

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Synthesis of Novel Silicon-containing Oligoarylenevinylenes via Heck Reaction

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Various oligo- and polyarylenevinylenes are successfully applied as organic light-emitting diodes (OLED),¹ organic field-emitting transistors (OFET)² and in other organic electronics devices³ since the moment of discovery of electroluminescence in poly(phenylenevinylene).⁴ It was recently shown that silicon atoms change of optic and electric properties of oligoarylenes.^{5,6} In present work, we studied two alternative strategies to synthesis of symmetric silicon-containing oligoarylenevinylenes via Heck reaction from commercially available dibromoarenes and TMS-substituted styrene (route 1, scheme 1), and from corresponding divinylarenes and TMS-substituted bromobenzene (route 2, scheme 1), using ligand-free catalytic system based on Pd(OAc)₂ as precursor of Pd(0).⁷

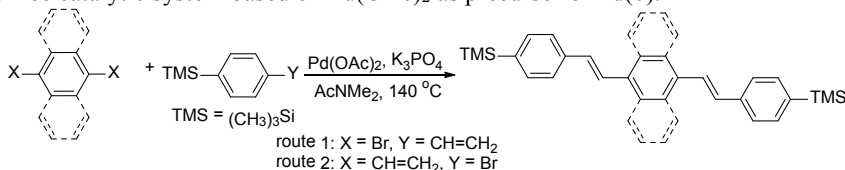


Fig. 1. Reaction routes

It was found, that synthetic schemes depend on nature of substrates: oligoarylenevinylenes with central benzene ring could be successfully obtained through both routes, while oligoarylenevinylenes with anthracene fragment could be synthesized from dibromoanthracene and silicon-containing styrenes since divinylanthracene reacts very poorly with TMS-substituted bromobenzene, and the synthesis is accompanied with desilylation of target oligoarylenevinylene. These data will be applied for synthesis of branched organosilicon oligo- and polyarylenevinylenes. The structures of the synthesized compounds were confirmed by ¹H, ¹³C and ²⁹Si NMR spectroscopic data, and elemental analysis. Thermostability of new oligoarylenevinylenes was studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Optic properties (absorption and emission spectra) were examined in diluted solution, thin films and crystals.

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⁷ Q. Yao, *et al.*, *J. Org. Chem.*, 2003, **68**, 7528

Crystallography of Surface Destruction of Tubular J-aggregates of Cyanine Dye

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J-aggregates of many dyes with extended conjugated π -electron systems display unusual photophysical properties and exist in water solutions in the form of narrow one-dimensional fibrils or two-dimensional crystalline monolayers.¹ Monolayer J-aggregates frequently form giant tubes with submicron and micron diameters and monolayer walls. The universal model of tubes formation by the close-packed helical winding of flexible monolayer strips has been proposed.² We have also found that due to the strong surface adhesion the adsorbed tubular J-aggregates flatten to almost rectangular bilayer rods or exhibit much deeper destruction with the formation of characteristic zigzags.²

In this work, we present crystallographic analysis of zigzags shape observed in ² for thiacyanine J-aggregates on a mica surface and propose the model of zigzags formation. Fig. 1 a-c show three successive video frames of the tube unwinding indicating that zigzags form by fixation of their vertices on the surface and subsequent peeling of the tube wall. The zigzag angles are distributed around $\alpha \approx 25^\circ$ and $\beta \approx 45^\circ$ (Fig. 1 d and e). In accordance with previous crystallographic analysis of (non-destructed) J-aggregate monolayer strips², they are interpreted as angles between unit cell directions with certain Miller indices, i.e. directions [010] and [100] in case of Fig.1d and [010] and [1-10] in case of Fig.1e respectively. The models in Fig.1 d and e predict the orientation of molecular transition dipoles (long molecular axes) in these two zigzag types as shown by double arrowheads. In both cases, the [010] zigzag side (thick line) follows the direction of the original tape which formed the tube by the helical winding mechanism considered in ref.2. Second zigzag side (in the most frequent case of Fig.1d) is parallel to the direction of the inclined one-dimensional substructure observed by high-resolution AFM at the nanometer scale.^{2,3} This direction is inherited from the side-by-side aggregation of constituent nanostrips at the last stage of the proposed non-classical three-stage crystallization of J-aggregate monolayer.⁴

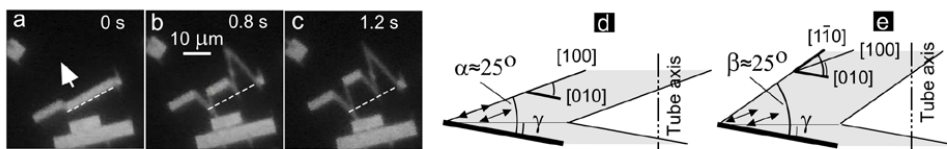


Fig.1. The successive fluorescence optical microscopy images of the J-aggregate tube unwinding by peeling of the tube wall with formation of zigzags (a) and models of two observed zigzag types (double arrowheads are molecular transition dipoles).

This work was supported by Russian Fund for Basic Research (project No 17-03-01179 A).

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Molecular Design of Transport Properties and Energy Levels of Non-fullerene Organic Solar Cells

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One promising method to achieve higher solar cell efficiencies is to replace fullerenes with strongly-absorbing dye molecules, namely, non-fullerene acceptors (NFAs). By combining different building blocks (of donors, acceptors, bridge blocks, etc.) NFAs allow one to obtain electrically active molecules with strong static quadrupole moments. Subsequent tuning of the quadrupole moment can be used to control the photophysical properties of solar cells, such as energy levels and transport properties. However, the systematic design of acceptor molecules with tailored properties has yet to be demonstrated.

The ratio between donor/acceptor material quadrupole moments can be expressed in terms of electrostatic bias potential. By exploring the long-range electrostatic interaction at the interface, we demonstrate that, for a set of recently developed NFAs, the electrostatic bias potential can be directly related to the stabilization (or destabilization) of charge-transfer (CT) states, as well as changes in the photovoltaic gap.

We find that the correlation between quadrupole moment, charge separation efficiency, and CT-state energy, as predicted by our model, is experimentally reproduced for several different donor/acceptor combinations.¹⁻³ In addition, we show that the molecular structure of NFAs can be related to the ambipolar transport in the system. This allows us to predict new NFA structures that incorporate combinations of readily available molecular building blocks that can potentially reach even higher performances than those currently achieved in state-of-the-art NFA devices.

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Highly Sensitive Perovskite-based Gas Sensors

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Development of new medical instruments and technologies gradually improves the quality of the healthcare programs worldwide. In particular, the application of advanced electronic equipment and using artificial intelligence for data processing allow one to detect various diseases in very early stages. Remote and continuous monitoring of human health condition becomes possible while using internet of things technology as a platform. In this context, designing compact and highly sensitive gas sensors for rapid analysis of exhaled air represents a highly promising research direction. As an example, a matrix of sensors based on silicon electronic components was used to to diagnose 17 different diseases with an accuracy of 86%¹. However, conventional silicon electronics has relatively poor intrinsic ability to sense and recognize specific analytes. On the contrary, organic and hybrid semiconductor materials are orders of magnitude more sensitive to the changing environment and, therefore, are commonly considered as a promising platform for development of the most advanced chemical sensors.

In this work, we report a low-cost and easy to produce gas sensors with a diode architecture comprising hybrid semiconductor and gas sensing components based on complex lead halides with the perovskite single crystal structure. The deposited perovskite films were characterized using a set of instrumental techniques such as XRD, SEM and AFM. The designed sensors showed a record response to 1 ppm of ammonia reflected in 700% increase of the nominal device current value at room temperature. Response time of ~1 s and recovery time of 15 s were obtained for the fabricated ammonia sensors. The selectivity of sensors was verified using a panel of 15 different analytes represented by aliphatic amines, sulfides, alcohols and etc. The obtained results confirmed that the designed sensors are orders of magnitude more sensitive to NH₃ as compared to other analytes of a similar chemical nature (e.g. volatile amines or H₂S).

Thus, we demonstrated that complex lead halides with the perovskite structure could be considered as highly promising materials for designing gas sensors operating with excellent sensitivity and selectivity. The ammonia sensors featured in this work can be used for food quality controlling and might also help to diagnose such diseases such as asthma, liver failure, and some bacterial infections in early stages.

This work was supported by RFBR (project № 18-33-20222).

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Highly Responsive Organic Composite Photodetector Based Small Molecules

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We introduce the use of small molecule vanadyl 3,10,17,24-tetra-tert-butyl-1,8,15,22-tetrakis(dimethylamino)-29H,31H-phthalocyanine (VTP), a donor material that has unique absorption properties especially in the lower visible region.¹ A new composite of donor- acceptor blended system is introduced by combining VTP (donor) and PC₇₁BM (acceptor). The combination of these selected materials was mainly chosen based on their electronic, solubility and optical properties. Generally, VTP has relatively good holes transport properties, while PC₇₁BM has good electron transport ability, making them to be donor and acceptor components, respectively. Foremost, both of organic materials, VTP and PC₇₁BM, have good solubility in most organic solvent especially chloroform, which endows to facile solution processable techniques. This soluble property promotes facile fabrication process as it allows the main active layer developed by spin-coating technique. The absorption of both materials that covered different range of light is also plays an important role to capture specific light wavelength in the visible range. By virtue of synergic absorption profile of VTP and PC₇₁BM matrix, the light absorbance towards lower wavelength region is expected to be enhanced in full visible spectrum. The overarching aim of the project is to introduce a novel blended system that may be contribute to the development of highly sensitive photodetectors. In this work, we report the use of VTP in the fabrication of organic photodetector that aimed to be more responsive in the lower region of visible light. The thin active layer of the photodetector has been developed from the VTP:PC₇₁BM blend solution. The combination of VTP and PC₇₁BM has significantly enhanced the absorption of visible light especially below 650 nm for the ITO/PEDOT:PSS/VTP:PC₇₁BM/Al photodetector. The detector showed good photocurrent-illumination linearity, fast response-recovery time and high consistency towards the rapid change of light intensities (Fig. 1). It is found that the detector exhibits a good photoresponsivity of 2.3×10^{-1} A/W and fast response time of 350 ms.

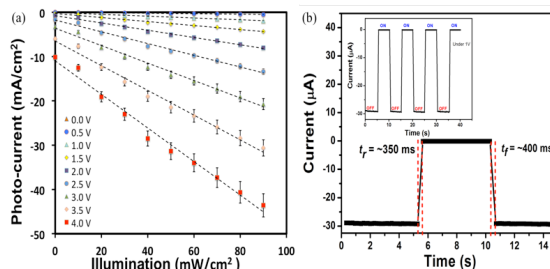


Fig. 1. (a) Photocurrent vs. illumination intensity under various applied voltage, and (b) the change of photocurrent response under light illumination (ON state) and in the dark (OFF state).

This work was supported by UMRG (Project No. RP026C-15AFR) and FRGS (FP046-2015A).

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Lanthanide-based NIR Emitting OLEDs

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Near-infrared (NIR) emitting OLEDs became of wide interest due to their potential use in such fields as telecommunication, medicine and others. Lanthanide-based NIR emitting complexes represent an important class of compounds due to their narrow lines, matching both biological and telecommunication “optical windows”. However, several problems still arise, among which are low luminescence quantum yield and low charge carrier mobility.

In order to solve these problems targeted synthesis of lanthanide-based coordination compounds, aiming on the improvement of both photophysical and electrical properties, as well as solubility and film-forming properties, must be carried out. In the present work lanthanide complexes with specially designed anionic ligands (aromatic carboxylates and Schiff bases), as well as neutral ligands (o-phenanthroline derivatives) was carried out in order to simultaneously improve these properties. It resulted in the obtaining of highly emissive Yb, Nd and Er-based OLEDs, among which those based on Yb complexes demonstrated the highest efficiency to date.

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Through-Space Charge Transfer Polymers for Solution-processed OLEDs

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Charge transfer (CT) is a fundamental and crucial process in π -conjugated systems and π -stacked systems, can be divided into through-bond charge transfer (TBCT) and through-space charge transfer (TSCT) according to the electron interaction pattern. Different from TBCT emitters that feature strong electron coupling through covalent bonds, TSCT ones provide a scaffold for weak electron interaction between donors and acceptors through space. This character provides us a new viewpoint to design novel organic luminescent materials with promising properties.

This presentation will discuss through-space charge transfer non-conjugated polymers and hexaarylbenzene dendrimers with thermally activated delayed fluorescence (TADF) effect and aggregation-induced emission (AIE) effect, for full color and white light emission. Different from through-bond charge transfer polymers with conjugated donor-acceptor architectures, we have developed through-space charge transfer polymers (TSCT-polymers) containing non-conjugated polystyrene skeleton and spatially separated acridan donor and triazine acceptor units, to realize solution-processed OLEDs with full-color from deep blue (455 nm) to red (616 nm) and white emission. The TSCT-polymers show TADF properties with lifetime of 0.36–1.98 μ s for delayed fluorescence, unexpected aggregation-induced emission effect in THF/water mixed solvents with emission intensity enhanced by up to 117 folds from solution to aggregation state, despite that the polymers contain no AIE-active chromophores. Solution-processed OLEDs based on the polymers exhibited promising electroluminescent performance with maximum EQEs of 7.1%, 16.2%, 1.0% and 14.1% for deep blue, green, red and white emission, respectively.

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Photoconductivity of the Interface Between Two Polymer Dielectrics

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The report discusses the processes of transport of charge carriers along the interface between two polymer dielectrics in the case of photoexcitation. In earlier works¹ it was found that the interface between two polymer dielectrics has highly conductive properties, in its characteristics, significantly exceeding the bulk ones. In particular, the mobility of charge carriers by 5–6 orders of magnitude exceeds the mobility of carriers in the bulk of the polymer. In the work, polydiphenylenephthalide (PDP) was chosen as the object of study. Photoexcitation was carried out using lasers of different wavelengths (405 nm, 532 nm and 640 nm.) And a power of 5 mW. Initial measurements were performed in the absence of photoexcitation.

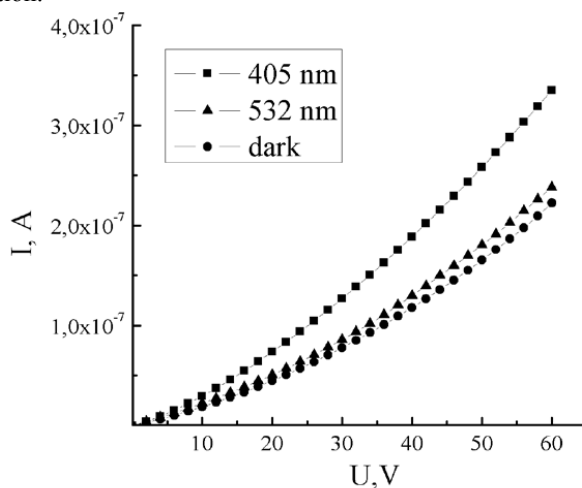


Fig. 1. I-V characteristic of an experimental sample with dark measurement and photoexcitation

It has been determined (Fig. 1) that photoexcitation with a 405 nm light source makes a significant contribution. The weak change is observed at a wavelength of 532 nm. Analysis of the I-V characteristics in the framework of the space-limited current model has shown that the mobility of charge carriers increases from $7 \text{ cm}^2/\text{V}\cdot\text{s}$ to $13.5 \text{ cm}^2/\text{V}\cdot\text{s}$. Apparently, the processes of formation of long-lived traps² in the volume of the polymer film contribute to the final conductivity along the interface. The report discusses the mechanism of the detected delay involving ideas about long-lived electronic states previously found in the study of photoluminescence.

This work was supported by grant from young scientists of the Republic of Bashkortostan..

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Dielectric Properties of Silicone Compositions Containing Metallosiloxanes

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Dielectric elastomers are currently receiving increasing attention due to their potential use in robotics, in particular, for the artificial muscles creation. Silicone elastomers are one of the most preferred as matrix energy converters among these polymers due to a number of properties they have, such as good reproducibility of working cycles, a slight tendency to the Mullins effect and aging, the possibility of working in a wide temperature range, and low toxicity. The main disadvantage of silicones in this aspect is their low dielectric constant, which determines the use of high voltage to energy converter activation and, as a result, does not use the full potential of the silicones mechanical properties (tensile strength). It can be identified the approaches proposed to improve the dielectric constant of silicone transducer layer-energy: chemical modification of silicones with groups having a high dipole moment; introduction of conductive or high-dielectric polymer fillers; introduction of silica or metal oxide particles, obtaining elastomeric interpenetrating networks. Despite the abundance of research in this area, the problem of creating a dielectric electroactive polymer has still not found its solution, that's why research in this area relevant today.

In our study, we obtain silicone material with elastic properties by curing of low molecular weight commercially available polydimethylsiloxanes with organoalkoxymetalosiloxanes through polycondensation processes (Fig. 1). The approach developed allows us not only uniformly introducing a different amount of metal oxide component into the composition, but also varying the type of metal.¹ Iron, aluminum, and zirconium siloxanes were used for research.

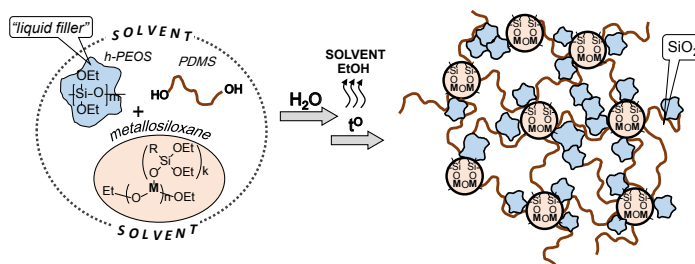


Fig. 1. Scheme of the composition formation.

It is shown that changing the initial ratio of the components can affect the mechanical properties of the final composition. In addition, it is possible to achieve higher values of dielectric constant in comparison with pure polydimethylsiloxane. We believe that this approach is convenient and promising for the production of silicon elastomers with sufficient dielectric properties to create actuators for artificial muscles.

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

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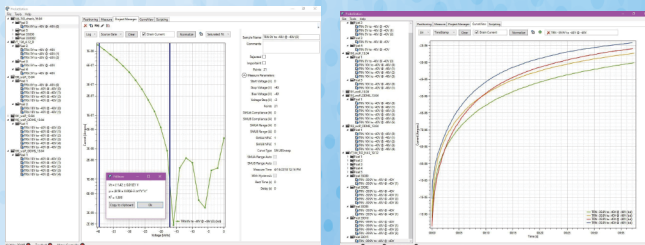
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