



# HOPE-PV 2019

1<sup>st</sup> International School on Hybrid,  
Organic and Perovskite  
Photovoltaics

**BOOK OF ABSTRACTS**

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Perovskite solar cells;

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# **Tutorial and Invited Lectures**

## **Dye Sensitized and Perovskite Photovoltaics: from cells to modules**

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Photovoltaic (PV) technologies are facing an exciting and stimulating development due to the use of organic and hybrid organic-inorganic solution process materials. In this so called III-Generation PV, the electrochemical cell named Dye Sensitized Solar Cells (DSSCs) laid the foundation for the development of the Perovskite Solar Cells (PSCs) that permit to achieve certified efficiency exceeding 24%.

DSSCs have revealed important features in terms of cost, lightning conditions and lifetime, with respect to other photovoltaic (PV) technologies. Processing of DSSC enables a full customization of the photo-active area of the devices that allows for achieving aesthetical requirements partially disabled by traditional photovoltaic technologies. In the first part of this talk, I will focus on this technology and its application in Building Integrated PV (BIPV). The second part of the talk is devoted to Organometal Lead Halide Perovskites, such as  $\text{CH}_3\text{NH}_3\text{PbI}_3$  (MAPI), which have opened up new directions to fabricate cost effective and high efficient PV devices. I will focus in particular in the recent developments in the use of Graphene and related 2D materials in conjunction with PSCs. Many factors can influence the efficiency and stability characteristics of PSCs. In this perspective, 2D nanomaterials, such as graphene and related materials can play a primary role owing to their 2D nature and the large variety of 2D crystals, whose complementary opto/electronic properties, can be on-demand tuned by chemical functionalization and edge modification. Here, we show the use of graphene and 2D materials as an effective way to control the morphology [1] and to stabilize the device's interfaces. Several strategies have been used to master interface properties both at the anode and cathode parts of the cell. By dispersing graphene flakes into the mesoporous  $\text{TiO}_2$  layer and by inserting graphene oxide (GO) [2] or  $\text{MoS}_2$  as interlayer between perovskite and Spiro-OMeTAD layers, we show that PCE exceeding 20% with a two-step MAPI deposition can be achieved also for process in air. This approach can be exploited for the fabrication of state-of-the-art large area perovskite modules with a PCE > 15% on an active area exceeding 80 cm<sup>2</sup>. The use of 2D materials permitted to increase the PCE by more than 10% with respect to "conventional" modules.[3]. A discussion on the relation between 2D interface engineering and stability of the PSC will be presented.

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

[2] A. Agresti et al. ChemSusChem 2016, 9, 2609

[3] L. Najafi et al. ACS nano, 2018, 12, 10736-10754

[4] A. Agresti et al. ACS Energy Lett. 2017, 2, 279–287

## **Iodobismuthates, polyiodides, and polyiodobismuthates: any prospects for modern lead-free photovoltaics?**

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Toxicity and bio-availability compromise lead perovskites, which have shown themselves as wonderful materials for modern photovoltaics. Despite high efficiency of light-to-current conversion and low cost, ecological and environmental issues hinder widespread uses of lead perovskites as light-harvesting materials. In response to this issue, other compounds, first of all, iodometallates and polyiodometallates have become increasingly attractive.

In this paper, we present and discuss our recent discoveries in the field of chemistry of inorganic and hybrid iodobismuthates and polyiodobismuthates. These compounds are non-toxic and provide no harm to the environment but their photovoltaic prospects have not yet been studied in detail.

We consider complex bismuth iodides and polyiodides formed with different cations ranging from those of alkali and rare-earth metals to various singly or doubly charged organic ammonium cations. We discuss their structural features paying utmost attention to dimensionality of iodobismuthate substructures and their assembling into supramolecular structures by using various weaker interactions, including hydrogen and halogen bonds. We also observe their electronic structures; in particular, we will show that the fine structure near the Fermi level is less sensitive to the nature of a cation and that the optical absorption is primarily associated with the charge transfer from the I 5p orbitals at the top of the valence band to the Bi 6p orbitals at the bottom of the conduction band. Moreover, we will show that a number of non-covalent interactions influence the electronic structure and hence optical absorption properties allowing their fine tuning. Finally, we discuss synthetic methods and pay attention to polyiodides as intermediate products, which can be used as media for the synthesis.

## **Periodic Table elements' chemical platform for advanced functional materials with perovskite structures**

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A perovskite type lattice represents a natural platform for chemical design of advanced functional materials. An interplay between chemical bonding, defects and chemical features make the perovskite structure a suitable basis for practical application of chemical elements and shaping preparation routes of modern materials. In this report, crystal chemistry and bonding features, physical and functional properties, preparation methods and tuning the properties with periodicity "tools" of the Periodic Table of Elements will be exemplified for famous families of high temperature superconductive cuprates, colossal magnetoresistive manganites and hybrid lead halides of a new generation of solar cells.

## Science via Mirage and Investigation of Passive and Dynamic Defects in Perovskites

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My talk would be based around on one of the most sensitive absorption measurement techniques called – *Photothermal Deflection Spectroscopy* (PDS). PDS possesses a capability of measuring absorption with 4-5 orders of magnitude dynamic range of sensitivity as compared to 1-2 orders of magnitude demonstrated by traditional absorption spectrometers. I will talk about how PDS works and how is it useful in undertaking some in-depth analysis of material quality, defects, new kind of states known as charge transfer states and doping, etc. I will showcase the utility of this tool in various fields of research including solar cells, light emitting diodes (LEDs), etc. based on thin-film semiconductors (not limited to polymers and perovskites). I will also present my latest results on the dual nature of defects in perovskites – passive and dynamic. I will also talk about the opportunities available to get rid of these or exploit them for innovative optoelectronic applications (including solar cells and LEDs).

[1] Venkateshvaran, D. *et al.* Approaching disorder-free transport in high-mobility conjugated polymers. *Nature* **515**, 384–388 (2014).

[2] Kronemeijer, A. J. *et al.* Two-Dimensional Carrier Distribution in Top-Gate Polymer Field-Effect Transistors: Correlation between Width of Density of Localized States and Urbach Energy. *Adv. Mater.* **26**, 728–733 (2014).

[3] Sadhanala, A. *et al.* Blue-Green Color Tunable Solution Processable Organolead Chloride–Bromide Mixed Halide Perovskites for Optoelectronic Applications. *Nano Lett.* **15**, 6095–6101 (2015).

[4] Zhao, B. *et al.* High Open-Circuit Voltages in Tin-Rich Low-Bandgap Perovskite-Based Planar Heterojunction Photovoltaics. *Adv. Mater.* **29**, 1604744 (2017).

[5] Barker, A., Sadhanala, A., *et al.* Defect-assisted photoinduced vertical halide segregation in mixed-halide perovskite thin films. *ACS Energy Lett.*, **2**, 1416-1424 (2017).

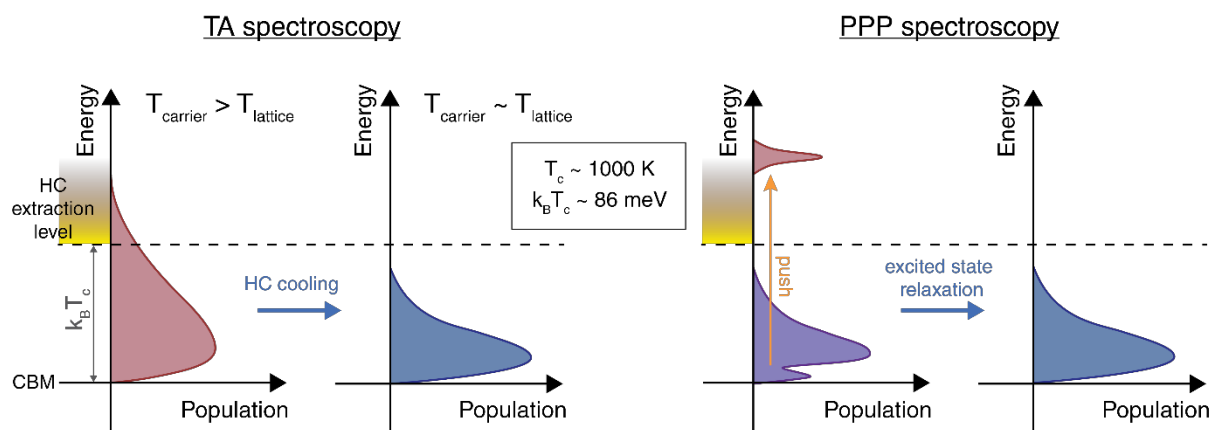
[6] Luo, D. *et al.* Enhanced photovoltage for inverted planar heterojunction perovskite solar cells: Enhanced photovoltage for inverted planar heterojunction perovskite solar cells. *Science*, **360**, 1442-1446 (2018)

## Hot Carrier Extraction in Halide Perovskites

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Halide perovskites recently emerged as a promising material for development in hot carrier solar cells, where the excess energy of above-bandgap photons is harvested before being wasted to heat to enhance device efficiency. Presently, hot carrier separation and transfer processes at higher energy states remain poorly understood. Here we discuss the excited-state dynamics in the ubiquitous  $\text{CH}_3\text{NH}_3\text{PbI}_3$  using ultrafast pump-push-probe spectroscopy [1,2], which has its intrinsic advantages for studying these dynamics over the conventional transient spectroscopy, albeit complementary to one another. By exploiting the broad excited state absorption characteristics, our findings reveal the transfer of hot carriers from these higher energy states into bathophenanthroline (bphen), an energy selective organic acceptor far above perovskite's bandedges. The insights gained from this study are essential for the development of a new class of optoelectronics.



**Figure. Schematic comparison of the carrier population under probe in transient absorption (TA) and pump-push-probe (PPP) spectroscopy.** In TA spectroscopy, at thermalized carrier temperatures of  $T_c \sim 1000 \text{ K}$ , i.e.  $\sim 86 \text{ meV}$  above the bandedge, only a fraction (37%) exists. This contrasts with PPP spectroscopy, where a fraction of the excited carrier population is re-excited above the LUMO level of the hot-carrier acceptor, and the excited state lifetime is directly probed.

[1] Artem A. Bakulin, Akshay Rao, Vlad G. Pavelyev, Paul H.M. van Loosdrecht, Maxim S. Pshenichnikov, Dorota Niedzialek, Jérôme Cornil, David Beljonne, and Richard H. Friend "The Role of Driving Energy and Delocalized States for Charge Separation in Organic Semiconductors", **Science** **335**, 1340-44 (2012)

[2] Swee Sien Lim, David Giovanni, Qiannan Zhang, Ankur Solanki, Nur Fadilah Jamaludin, Jia Wei Melvin Lim, Nripan Mathews, Subodh Mhaisalkar, Maxim S. Pshenichnikov, and Tze Chien Sum, "Hot Carrier Extraction in  $\text{CH}_3\text{NH}_3\text{PbI}_3$  Unveiled by Pump-Push-Probe Spectroscopy", **Science Advances**, to be published (2019)



## Unravelling Intrinsic Bulk and Interfacial Degradation Mechanisms in Lead Halide Perovskite Solar Cells

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The emerging perovskite solar cells demonstrated impressive power conversion efficiencies exceeding 24%, while their practical application is restricted mainly by poor operation stability. We have reported recently that hybrid MAPbX<sub>3</sub> perovskites undergo facile thermal and photochemical degradation even under anoxic conditions without exposure to oxygen and moisture, while their all-inorganic counterparts CsPbX<sub>3</sub> proved to be significantly more stable.

Here we will discuss our the most recent results coming from a systematic study of the intrinsic stability of a broad range of materials represented by various lead-based perovskites and compare them with some lead-free complex halides of tin, germanium, bismuth and antimony. The revealed pathways of thermal, photochemical and electrochemical degradation processes will be presented and a conclusion on the potential of different groups of materials for practical application in PV technology will be drawn. We will particularly focus on analyzing the interface degradation effects occurring between the electrodes, charge transport layer materials and the photoactive layer induced by electric field, elevated temperatures, solar light or a combination of these stress factors. Finally, it will be shown that reaching any commercially interesting operation lifetimes for perovskite solar cells requires a considerable shift from the currently used device design paradigms as well as a comprehensive multiparametric optimization of all used materials and functional components.

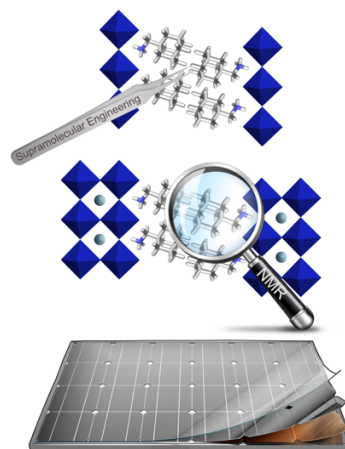
# Supramolecular Engineering for Hybrid Perovskite Photovoltaics and Beyond

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Hybrid perovskite solar cells exhibit remarkable solar-to-electric power conversion efficiencies, however, their limited stability and molecular-level engineering remain challenging [1-5]. In contrast to three-dimensional perovskites, their layered low-dimensional analogs have demonstrated superior stabilities, though at the expense of the corresponding efficiencies [1,4-5]. We demonstrate a strategy to provide stabilization without compromising the performance by employing multifunctional molecular modulators that are designed by fine-tuning noncovalent interactions complemented by structural

adaptability [2-5]. These systems are devised to interact with the hybrid perovskites in a manner uniquely assessed at the atomic level by solid-state NMR spectroscopy [2-3]. As a result, we obtain perovskite solar cells with superior properties and high power conversion efficiencies, accompanied by enhanced operational stabilities [3]. Moreover, extending the design into low-dimensional architectures provides further stability enhancements [4-5]. This approach has been investigated using a combination of techniques complemented by solid-state NMR to unravel the design principles and exemplify the role of supramolecular engineering in advancing perovskite research.



*Schematic representation of a layered perovskite prototype structure*

- [1] J. V. Milić, D. J. Kubicki, L. Emsley, M. Graetzel, *Chimia* (2019) 73, 317.
- [2] M. M. Tavakoli, W. Tress, J. V. Milić, D. J. Kubicki, L. Emsley, M. Graetzel, *Energy Environ. Sci.* (2018), 11, 3310.
- [3] D. Bi, X. Li, J. V. Milić\*, N. Pellet, J. Luo, T. LaGrange, P. Mettraux, L. Emsley, S. M. Zakeeruddin, M. Graetzel, *Nature Commun.* (2018) 9, 4482.
- [4] Y. Li, J. V. Milić\*, A. Ummadisingu, J.-Y. Seo, J.-H. Im, H.-S. Kim, Y. Liu, M. I. Dar, S. M. Zakeeruddin, P. Wang, A. Hagfeldt, M. Graetzel, *Nano Lett.* (2019) 19, 150.
- [5] J. V. Milić, J.-H. Im, D. J. Kubicki, A. Ummadisingu, J.-Y. Seo, Y. Li, M. A. R. Preciado, I. Dar, S. M. Zakeeruddin, L. Emsley, M. Graetzel, *Adv. Energy Mater.* (2019) 1900284.

## **The interfaces might play a critical role in improving performance and stability of organic-inorganic and all-inorganic perovskite solar cells**

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Organo-lead halide perovskites have emerged as an amazing photovoltaic material by raising the power conversion efficiency to above 25% in mere 10 years of development since the pioneering work by Miyasaka et al.[1] In 2009. However, the two current pressing challenges with perovskite solar cells are poor stability and high toxicity of Pb. While intrinsic material instability of organo-halide perovskites has been a great concern and extensive compositional engineering has resulted in compositions with high structural stability, device performance instability is rather seeming to come majorly from the chemical exchanges occurring across the interfaces. For instance, in a study on thermal stability of MAPbI<sub>3</sub> solar cells, we found that spiro-OMeTAD (used as hole transporting material) plays a notorious role in performance deterioration of the cells at elevated temperatures. It seems that not the degradation of perovskite (MAPbI<sub>3</sub>) but some physical/chemical alteration at the perovskite/spiro-OMeTAD interface is the main reason for performance degradation in the MAPbI<sub>3</sub> cells. [2] Inserting suitable interlayer between the perovskite and spiro-OMeTAD or surface treatment of perovskite with suitable molecules can reduce such exchange at the interface and thus, improve stability of the device. Recovery of performance after recycling the degraded device by replacing with a fresh HTM layer depends on the composition of perovskite, indicating loss of organic cation being involved in the process.

As the organic part of hybrid perovskites is believed to be responsible for poor thermal stability of these materials, all-inorganic CsPbX<sub>3</sub> perovskites are gaining much interest these days. However, the challenge in CsPbI<sub>3</sub> perovskites is the stabilization of its photoactive black phase under ambient conditions (at room temperature) because the black phase is formed only at a temperature above 300 °C. In an earlier study, we have found that Eu (Eu<sup>2+</sup> or Eu<sup>3+</sup>) inclusion into CsPbI<sub>3</sub> precursor solution can form the black phase at ambient conditions (85 °C). [3] The devices made from such Eu-stabilized photoactive CsPbI<sub>3</sub> (CsPbI<sub>3</sub>:xEu) perovskites demonstrate a power conversion efficiency of around 7% at best conditions. All-inorganic CsPbI<sub>2</sub>Br with more suitable polymer HTMs (not spiro-OMeTAD) can also perform at an efficiency above 15%. Based on several other results, we believe that surface properties of perovskite and interface matching with the HTMs are more sensitive to performance and stability of perovskite solar cells. The present talk will cover all our experiences with effect of surface treatment of perovskite and perovskite/HTM interface on cell performance and stability.

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[2] Ajay Kumar Jena, Youhei Numata, Mashashi Ikegami, Tsutomu Miyasaka, *J. Mater. Chem. A*, 2018, **6**, 2219-2230

[3] AK Jena, A Kulkarni, Y Sanehira, M Ikegami, T Miyasaka, Chemistry of Materials 30 (19), 6668-6674

## Bi-dimensional materials for new generation photovoltaics

**Antonio Agresti<sup>1,2</sup>, Sara Pescetelli<sup>1</sup>, Danila Saranin<sup>2</sup>,  
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Recently the exploitation of the sun energy by efficient and cost effective photovoltaic technologies has been proposed as an easy way to address the increasing global energy demand. In this context, new generation photovoltaics aims to conjugate the high efficiency typical for the silicon-based first generation photovoltaics with the low production costs of thin-film second generation. However, organic technologies based on polymer or small-molecule heterojunction as active material demonstrated power conversion efficiency (PCE) still lower than 15.6% hardly comparable with the already commercialized technologies. On the contrary, perovskite solar cells (PSCs) have recently attracted the scientific community interests due to the demonstrated record PCE overcoming 25% and their promising coupling with the already exiting inorganic PV technologies in tandem devices.[1] The still opened issues limiting their commercialization mainly regard the device dimension scalability (record PCE are certified only on lab-scale cells) and stability under real working conditions. With this aim, bi-dimensional materials can be easily integrated in the PSC structure as inter or intra-layer by exploiting their exceptional physical and opto-electronic properties to tune energy level alignment, [2] efficiently extract and collect charge at the electrode, [3,4] enhance interface stability [5] and help the device scalability by controlling the perovskite morphology over the 2D-materials modified charge transporting layer.[4,6] In this work, the use of graphene and related materials (GRMs),[3] transition metal dichalcogenides (TMDs)[7] and 2D transition metal carbides, nitrides and carbonitrides (MXenes) [2] in PSCs will be demonstrated to design efficient [7] and stable perovskite [8,9] devices on both small and large-scale dimensions.[10,11]

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[2] A. Agresti et al., *Nature Materials* **2019**, DOI: 10.1038/s41563-019-0478-1.

[3] A. Agresti et al., *Adv. Funct. Mater.* **2016**, 26, 2686–2694.

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[7] L. Najafi, et al., *ACS Nano* **2018**, 12 (11), 10736–10754.

[8] Y. Busby et al., *Mater. Today Energy* **2018**, 9, 1-10.

[9] P. O’Keeffe et al., *Nano Lett.* **2019**, 19, 684–691

[10] A. Agresti et al., *ACS Energy Lett.* **2019**, 4, 1862–1871.

[11] Taheri B. et al., *2D Materials* **2018**, 5, 045034.

## How to assess operational stability of perovskite solar cells?

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The talk will review consensus procedures for planning, conducting, and reporting stability testing of perovskite solar cells (PSC) recently formulated by a broad perovskite research community [1]. In particular, the suggested protocols highlight the importance of testing for: (1) Redistribution of charged species upon application of electric fields [2]; (2) distinguishing between degradation induced by various stress factors, (3) reversible degradation with qualitatively different recovery dynamics [3,4]. The recommended protocols are not meant to replace existing qualification standards (i.g., IEC 61730 and IEC 61215), but rather to contribute to developing an understanding of PSC degradation mechanisms. Acceptance of these protocols and sharing the suggested datasets will facilitate inter-laboratory coordination and assist in the accumulation of PSC stability data acquired under well-defined and comparable conditions. This would allow the application of advanced approaches to analyzing large data sets, such as machine learning methods, and accelerate the development of stable PSC devices.

[1] M. V. Khenkin, E. A. Katz, A. Abate, G. Bardizza, J. J. Berry, C. J. Brabec, F. Brunetti, V. Bulović, Q. Burlingame, A. Di Carlo, R. Cheacharoen, Y.-B. Cheng, A. Colmann, S. Cros, K. Domanski, M. Dusza, C. J. Fell, S. R. Forrest, Y. Galagan, D. Di Girolamo, M. Grätzel, A. Hagfeldt, E. von Hauff, H. Hoppe, J. Kettle, H. Köbler, M. S. Leite, S. (Frank) Liu, Y.-Lin Loo, J. M. Luther, C.-Q. Ma, M. Madsen, M. Manceau, M. Matheron, M. McGehee, R. Meitzner, M. K. Nazeeruddin, A. F. Nogueira, Ç. Odabaşı, A. Osherov, N.-G. Park, M. O. Reese, F. De Rossi, M. Saliba, U. S. Schubert, H. J. Snaith, S. D. Stranks, W. Tress, P. A. Troshin, V. Turkovic, S. Veenstra, I. Visoly-Fisher, A. Walsh, T. Watson, H. Xie, R. Yıldırım, S. M. Zakeeruddin, K. Zhu and M. Lira-Cantu. Consensus on ISOS Protocols for Stability Assessment and Reporting for Perovskite Photovoltaics. *Submitted*.

[2] M. V. Khenkin, K.M. Anoop, E. A. Katz and I. Visoly-Fisher. Bias Dependent Degradation of Various Solar Cells: Lessons for Stability of Perovskite Photovoltaics. *Energy & Environmental Science*, v. 12, No. 2, p. 550-558 (2019).

[3] M. V. Khenkin, K.M. Anoop, I. Visoly-Fisher, S. Kolusheva, Y. Galagan, F. Di Giacomo, O. Vukovic, B. R. Patil, G. Sherafatipour, V. Turkovic, H.-G. Rubahn, M. Madsen, A. Mazanik and E. A. Katz. Dynamics of photoinduced degradation of perovskite photovoltaics: from reversible to irreversible processes. *ACS Applied Energy Materials*, 1, 799-806 (2018).

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## Accurate evaluation of the solar cell efficiency

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During the last decades, intensive research in photovoltaics has led to appearance and substantial development of novel solar cell families. The power conversion efficiency (PCE) of a solar cell is the main driver of the field; therefore, an accurate and proper estimation of PCE is crucial for scientific and technological progress in the field. Furthermore, an accuracy estimation is necessary to compare various cells measured in various laboratories. However, there are rising concerns about correctness of PCE values presented in literature [1-3]. To tackle this issue, Nature group released a checklist for PV publications[4].

We start with analysis of the main pitfalls in laboratory characterization of the various type of emerging solar cells. The main difficulty is correct determination of the solar cell current. We discuss how masking of the solar cell active area and the transient behavior (because of an intrinsic slow process or/and degradation) impact the measured solar cell current and its hysteretic behavior. Meanwhile, the most complicated issue leading to under/overestimation of the solar cell current is a practically unavoidable mismatch between the solar spectrum and the solar simulator spectrum. Usually, this mismatch is taken into account with the use of a reference solar cell, whose normalized spectral response, ideally, should be equal to that of the solar cell under test. A reference cell-based PCE measurement method is widespread across the community: in this approach, the solar simulator intensity is adjusted to the current of the reference cell. This technique has been adopted from the silicon photovoltaics and implies a good spectral correspondence between the photocurrents of the reference and test cells. Unfortunately, this correspondence is not easy to achieve for novel materials (organic, hybrid, perovskites), whose absorption spectra strongly differ from that of the test cell (usually a silicon cell with an appropriate color filter).

In the original part of this tutorial talk, we present a laboratory measurement technique for PCE evaluation—the spectral technique—and demonstrate its applicability for advanced solar cells [5]. In contrast to commonly used methods, the spectral technique provides estimation of accuracy in PCE. Using as examples, organic and perovskite solar cells, we show that the reference cell-based technique either over- or underestimates PCE. Nevertheless, the spectral technique delivers the PCE values with a guaranteed accuracy (4% in our realization), independent from the type and spectral properties of the test cell. The spectral technique allows reliable evaluation of PCE and its measurement inaccuracy, which are independent from the spectral properties of a studied cell type or a solar simulator used. We anticipate that the spectral technique will facilitate easier comparison of the results across the community and between various solar cell technologies contributing to credibility of photovoltaic research and development.

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[2] *Nature Photonics* **2014**, 8, 665

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## Spatially Resolved Measurements of Semiconductor Interfaces

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The development of advanced materials and technologies to efficiently convert sunlight directly into electricity is of urgent importance due to increasing energy demands of an ever growing world population and the growing need to diversify to renewable energy alternatives. However, tremendous scientific challenges remain before successful implementation of any number of competing solar cell technologies can be adopted. The materials, interfaces and device architectures currently being explored are very challenging to interrogate by ensemble-averaging, bulk experimental methods since they do not exhibit long-range order or homogeneity, contain unique nano-morphological features and possess non-uniform chemical compositions and defect chemistry. Additionally, these materials and interfaces are dynamically “reactive” and their performance degrades significantly during use which limits their cycle life and their ultimate commercialization prospects. This presentation will highlight the development of high resolution spatially resolved tools [1-4] for studying photo(electro)chemical processes at semiconductor interfaces. Information obtained from these new tools enables the elucidation of complex charge transfer mechanisms and degradation processes in existing and emerging materials considered for advanced energy conversion (solar cell) applications.

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## Ex-situ and in-situ evaluation of perovskite solar cell degradation using atomic force microscopy

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Hybrid organic-inorganic and fully inorganic halide perovskites are promising materials for next generation solar cells. Power conversion efficiency (PCE) of the best research devices— starting from 3.8% in 2009 [1]— already exceeds 25% for hybrid [2] and 17% for fully inorganic perovskite solar cells [3]. Despite their sufficient PCE and cheap production cost, they are not commercialized due to fast degradation under operation conditions such as light illumination, electric field, and elevated temperature[3,4]. Hence, understanding and resolving the degradation problem seems to be the key element for successful commercialization. In this talk we will focus on implementation of Atomic Force Microscopy (AFM) for investigation of fresh and degraded perovskites. Both topography and functional properties such as local surface potential and photocurrent can be measured simultaneously. Ex-situ and in-situ implementations will be demonstrated.

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## Conjugated donor-acceptor oligomers for organic and hybrid photovoltaics

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Organic semiconductors are very important type of functional materials, which find their application in various devices of organic and hybrid electronics, including organic photovoltaics (OPV), dye-sensitized solar cells (Graetzel cells) and perovskite solar cells. They are small molecules, oligomers and polymers, which consists of  $\pi$ -conjugated aromatic and/or heteroaromatic fragments, with efficient light absorption in the visible and/or IR spectral range. In this lecture historical overview of the development of several generations of organic semiconductors used in different photovoltaic devices will be considered. The last generation consists of donor-acceptor conjugated organic molecules and polymers, which allowed to achieve record high efficiency and stability for OPV and perovskite solar cells. Recent advances in organic and hybrid photovoltaics accelerated by the appearance of novel highly efficient organic semiconducting materials will be highlighted. Examples of novel linear and star-shaped donor-acceptor oligomers developed in ISPM RAS, as well as their application in OPV [1-4] and perovskite optoelectronic devices will be discussed [5].

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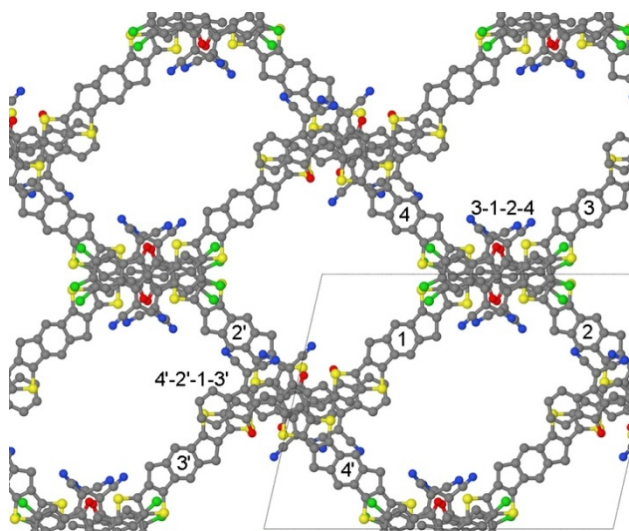
## Computational studies of organic semiconductors

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This presentation consists of two parts. The first part provides a tutorial overview of state of the art in first principle modeling of organic semiconductors: from purely computational studies to concerted theory-experiment investigations. In the second part, original results of studies of charge transport in molecular crystals are presented, emphasizing advance towards achieving three dimensional electronic connectivity, demonstrated recently for novel non-fullerene acceptors with acceptor-donor-acceptor (ADA) molecular architecture in high-efficiency solar cells [1]. Crystals of these molecules show distinctive intermolecular packing where neighbor molecules are connected to each other via terminal groups. Globally this often creates a "wire mesh" topology of electronic connectivity as illustrated in the figure below for a representative system [2]:



Importantly, the connectivity is three dimensional, providing a robust framework for charge carrier transport in contrast to low-dimensional pathways typically observed in solids of extended  $\pi$ -conjugated oligomers. Calculations of electronic properties of these systems confirm that they can have superior charge transport properties if intermolecular couplings are strong enough and site electronic levels are aligned.

From theoretical standpoint modeling of these materials is challenging for two reasons: unit cells contain hundreds of atoms making geometry relaxation highly nontrivial, and also commonly used one-site-per-molecule approximation evidently fails for electrons in ADA molecules requiring sophisticated coarse graining.

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# Oral Talks

## **Inverted perovskite solar cells with inorganic hole transport layer for indoor application**

**Danila Saranin<sup>1</sup>, Yury Karpov<sup>1</sup>, Thai Son Le<sup>1</sup>, Lev Luchnikov<sup>1</sup>, Pavel Gostishchev<sup>1</sup>, Sergey Didenko<sup>1</sup>, and Aldo Di Carlo<sup>1,2</sup>**

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Halide perovskites are a unique class of semiconductors for various optoelectronic applications - solar cells; photodiodes; light-emitting diodes and lasers due to outstanding intrinsic properties such as big diffusion length, tunable bandgap and sharp onset near the edge of the absorption. Among the other features it is worth to highlight differences in operation of perovskite solar cells (PSC) under weak irradiation in comparison to the common wafer or solid-state analogs (Si; A<sub>III</sub>B<sub>V</sub>; CIGS, etc.). Power conversation efficiency (PCE) of PSCs dramatically increases at low intensities of incoming light owing to low rates of bimolecular recombination in thin films of halide perovskites [1]. The values of PCE > 25 % under indoor illumination already achieved and reported in the literature[2], [3]. Therefore, PSCs could be proposed as a promising technology for BIPV, integration to devices of “Internet of Things,” portable sensors that require autonomous low power energy sources with an output level of  $\mu\text{W}$  –  $\text{mW}/\text{cm}^2$ . To date, the record performance of PSC for indoor application was demonstrated with planar n-i-p device architecture that showed hysteresis in JV curves.

In this work, we demonstrated the advantages of p-i-n PSC structures for indoor application with use of two configurations of inorganic HTL based on NiO – compact and nanoparticle films. Device performance was investigated and compared in range of light intensities up to 1000 lux (white LED light) and at standard 1.5 AM G conditions. We observed the absence of hysteresis at all irradiation conditions, but a strong correlation of output performance to interface properties. In the range of 100- 600 lux  $V_{oc}$  values of the PSC with compact and nanoparticles NiO HTL showed different onset with the increase of light intensity, trends of  $J_{sc}$  increment also were obtained with a different slope due to different concentrations of traps and recombination pathways. Analysis of measured dark JV curves for the devices with different HTLs and surface morphology studies for NiO films showed higher current leakages for nanoparticles and changes in diode behavior that result in negative impact at 100 - 400 lux intensities of light.

We found that observed JV output parameters ( $V_{oc}$ ,  $J_{sc}$ , FF and  $P_{max}$ ) under white indoor LED illumination are currently ones of the best reported in the literature for p-i-n structures (16  $\mu\text{W}/\text{cm}^2$  at 200 lux; 40  $\mu\text{W}/\text{cm}^2$  at 400 lux; and 97 $\mu\text{W}/\text{cm}^2$  at 1000 lux) with use of compact NiO HTL configuration and reasonable PCE >16% at standard 1.5 AM G conditions. Nanoparticle NiO configuration showed competitive performance of >15 % of PCE under 1 SUN, but 1.5 -2 times smaller  $P_{max}$  under indoor illumination, caused by enhanced interface recombination. The stabilization of output characteristics was investigated with maximum power point tracking.

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## **Influence of hole transport materials on the electrochemical stability of perovskite solar cells**

**Olga R. Yamilova<sup>1,2</sup>, Yuri S. Fedotov<sup>3</sup>, Andrei V. Danilov<sup>2</sup>, Sergey I. Bredikhin<sup>3</sup>,  
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Recently, lead halide perovskite solar cells have demonstrated impressive efficiencies exceeding 25%, but their practical application is still hampered by stability problems. Besides the intensively investigated photochemical and thermal degradation effects, a particular attention should be paid to the electrochemical stability of absorber materials and completed photovoltaic devices.

Here we report a systematic comparative study of the electrochemical stability of lead halide based perovskite solar cells assembled with different hole-transport materials such as PEDOT:PSS, NiO<sub>x</sub>, PTAA, CuI, Cu<sub>2</sub>O, CuSCN and their combinations. Devices were exposed to a stepwise potentiostatic polarization under anoxic conditions in dark. The evolution of the solar cell performance was analyzed using ToF-SIMS profiling to unravel ion migration and possible redox processes occurring at the cathode and anode. The obtained results showed that the electrochemical stability of perovskite solar cells is largely affected by the used HTL materials. We also demonstrated influence of polarization conditions to the degradation on the example of PTAA hole-transport material. The revealed degradation pathways featured a crucial importance of controlling interfacial electrochemistry while designing highly efficient and stable perovskite solar cells.

# One-step printable hole transporting and absorbing layers fabricated by slot-die coater in ambient conditions for perovskite solar cells

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Despite the unprecedented progress in the growth of power conversation efficiency of lab-scale perovskite solar cells (PSCs) with a current record of 25.2 % [1], the realization of large PSCs through low-temperature processing is still challenging. The spin coating method typically used as the main route for the fabrication of lab-scale PSCs are limited in small size by the spatially inhomogeneous nucleation due to the radial gradient of oversaturation by dropping anti-solvents in the centre of film during coating [2]. Among many printing technologies, slot-die printing is a promising candidate for mass production such as roll-to-roll processing because of high coating speed, easy module patterning, and a pre-metered coating. Here, we introduce the application of the slot-die coating and vacuum-assisted solution process (VASP) on the fabrication of hole transporting (HTL) and absorbing (AL) layers without using toxic anti-solvents. Developed deposition routes were used for the fabrication of planar p-i-n perovskite solar cells including ITO/NiO/MAPbI<sub>3</sub>/PCBM/BCP/Ag.

The NiO HTL was printed on ITO glass from the water solution of tris(ethylenediamine) nickel acetate with replacing of ethylene glycol as a solvent of the spin coating route [3] to stabilize meniscus during head motion over the substrates. For the vacuum-assisted perovskite deposition, we found an optimal mixture of solvents with DMF:NMP (vol. ratio: 4:1) that gives excellent reproducibility and long operation window in the ambient conditions. The AL was slot-die printed on NiO-coated ITO glass with coating speed of 30mm/s. Then the wet printed films were kept in vacuum chamber for improving the crystallization of perovskite before being annealed at 100°C in 10 minutes to completely remove all remaining solvents. PCBM and BCP layers were deposited by spin coating, and finally, a 100nm-thick Ag electrode was thermally evaporated. For the comparison, we fabricated fully spin-coated devices as reference (AL was done with solvent engineering methods) and configurations with printed HTL/spin-coated AL (p-s devices); printed HTL/printed AL (p-p devices).

To estimate the output performance of the fabricated devices (reference we measured JV curves at standard conditions (1.5 AM G light spectrum with calibrated 100 mW/cm<sup>2</sup> intensity). The p-s devices had an efficiency around 16%, 1.01-1.05V of V<sub>oc</sub> and highest J<sub>sc</sub> 19.67mA/cm<sup>2</sup> and all output parameters were at the same level as for reference made of same materials. The efficiency of p-p devices was about 10% with 1.03V of V<sub>oc</sub> and 13mA/cm<sup>2</sup> of J<sub>sc</sub>. The reduced performance of the p-p devices was affected from high leakage current caused by not uniform coverage and film morphology of the perovskite layer and can be improved with special additives of chlorines and thiocyanates of organic cations for stabilization of crystallization rates during VASP treatment.

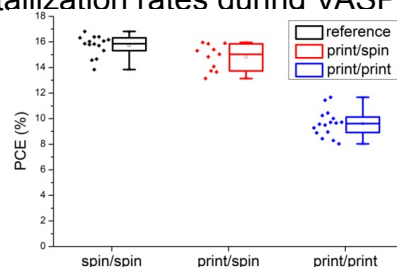


Figure 1: Efficiency comparison box chart of fabricated devices

PSCs with slot-die printed HTL and AL were successfully fabricated. The obtained results clarified that the slot-die printing and VASP methods can be effectively used for the upscaling of the devices with p-i-n planar structure including ITO/NiO/MAPbI<sub>3</sub>/PCBM/BCP/Ag.

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## Interface-induced degradation effects in perovskite solar cells

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In this work, we systematically explored a series of interfacial layers in p-i-n (bottom NiO<sub>x</sub>, PEDOT:PSS, PTAA and PTA) structures while using five different perovskite formulations. We investigated the effects of the aforementioned hole transport materials (HTLs) on the photochemical stability of the adjacent perovskite films in different sample geometries ranging from the simple ITO/HTL/perovskite bilayer stack to completed photovoltaic cells. Using a combination of complementary techniques such as optical spectroscopy, XRD, XPS, SEM, EDX, and TOF-SIMS allowed us to conclude on the interface-induced degradation effects in the investigated systems. We have shown that some interfacial materials actively interact with perovskite thus promoting their accelerated photochemical degradation. On the contrary, using certain HTLs improved remarkably the stability of the perovskite films and solar cells. Interestingly, this trend differs depending on perovskite composition. Revealed correlations between the chemical composition, structure and properties of the used charge-transport materials and the observed degradation effects at their interfaces with the complex lead halides pave a way to the development of perovskite solar cells with improved efficiency and operation stability.

# Precursor solution chemistry-controlled photostability of mixed-cation perovskite solar cells based on zinc oxide ETL

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The discovery of hybrid organic-inorganic complex lead halides with perovskite structure paved a way to a new generation of solar cells with the highpower conversion efficiency exceeding25%. However, the intrinsic instability of the perovskite-typeabsorber materialslimits theirpotential for further industrial application. A promising solution to extend lifetimeof perovskite solar cells is thorough engineering of the perovskite interfaces with electron and hole-transport layers.

In this work, we systematically investigated the behavior of the iterfaces between the bication perovskite  $\text{Cs}_{0.12}(\text{CH}(\text{NH}_2)_2)_{0.88}\text{PbI}_3$  and various electron transport layers (ETLs). We show that the n-i-p perovskite solar cells fabricated usingzinc oxideETL outperformed other types of devices assembled with titanium oxide, tin oxide, and cadmium sulfide as ETLs. Moreover, theZnO-based devices maintained more than 80% of the initial efficiency after 800 hours of light soaking at 65° C. Increase in the devices stability was attributed to the formation of a thin protective layer of a 2D perovskite at the ZnO/perovskite interface.

Other crucially important factor was recognized to be the chemistry occurring in the precursor solution upon storage.In particular, we have revealed a side reaction between the formamidinium iodide (FAI) and dimethylformamide (DMF) leading to the formation N'-(iminomethyl)-N,N-dimethylformimidamide (DMFI) , which was identified and characterized by 1D and 2D NMRspectorscopy. Furthermore, we have observed that the presence of DMFI in the precursor solution affectssignificantlyefficiency and stability of the perovskite solar cells.

To summarize, our findings highlight a profound impact of the interface and solution chemistry on the device photovoltaic performance and operational stability and provide additional insights for reaching long term operation stability of perovskite solar cells.



## Light Emitting Solar Cells Enabled by Ion Migration in Mixed Cation vs Mixed Halide Perovskites

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Organohalide perovskites (OHP) are ionic semiconductors, as opposed to covalently bonded conventional semiconductors, like Si or GaAs. As recently realized ionic migration plays important role in operation of all OHP based devices: solar cells and light emitting diodes (LED), photodetectors and other. Usually ionic migration despite its reversibility leads to losses of OHP-PV device performance, due to broad hysteresis in current-voltage characteristics, and in mixed halide OHP it is a reason for halide segregation effects, seen most clearly in photoluminescence.

In this talk we demonstrate that OHP with mixed ions can lead to dual functionality of optoelectronic devices: they can operate both as solar cells and as LED, depending on the dynamical poling effects, due to ionic migration in very low electrical fields [1,2]. If exposed to solar light in  $V_{oc}$  regime, the OHP-PV with mixed halides, turns itself to low threshold LED via ions accumulation at interfaces, which enables better charge injection, needed for electroluminescence. Similarly operating LED at low bias turns it to PV with higher  $V_{oc}$ , which slowly relax [1]. Moreover, we will discuss the difference in ionic migration effects in mixed halide and mono halide perovskites.

Mixed halide perovskites demonstrate both cation and anion migration whereas in monohalide perovskite only anion ions move. This is most clearly demonstrated in light emitting solar cells with PEDOT:PSS and C60 transport layers having high barrier for charge injection. In case of  $CH_3NH_3PbBr_2I$  perovskite layer device still can demonstrate low electroluminescence threshold voltage around 1.7V while in case of  $CH_3NH_3PbBr_3$  perovskite layer threshold voltage is much higher: around 2.9V. Therefore, nature of moving ions becomes important since perovskite organic cations methylammonium (MA) and formamidinium (FA) have non-zero dipole momentum of 2.29 Debye and 0.21 Debye respectively. Under applied external voltage MA and FA cations move towards the electron transport layer (ETL) and form dipole layer at the OHP/ETL interface. This dipole layer at the interface allows to easily adjust work functions between OHP and ETL. This ability to *in-situ* engineer the device band structure opens the way for development of dual-functional OHP devices based on simple design.

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## Ambipolar perovskite light emitting diodes

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Perovskite light-emitting diodes (PeLEDs) have recently attracted great research luminescence at room temperature in interest for their narrow emissions and solution processability. Remarkable progress has been achieved PeLEDs in recent years [1]. Here we present the new configuration of ambipolar transparent perovskite light emitting device. The combination of voltage induced p-i-n formation and ionically doped carbon electrodes and allows electroluminescence in forward and reverse bias. For this experiment high quality films of randomly oriented SWCNTs were produced by the aerosol (floating catalyst) chemical vapor deposition (CVD) method [1]. PeLEDs were assembled using a glass substrate with ITO stripes as bottom electrode; spin-coated  $\text{CsPbBr}_3/\text{I}_3$ :PEO composite as emissive layer; SWCNT deposited by a simple press transfer process at room temperature as top electrode.

SWCNT has a sensitive response of electrical properties to doping, due to having only one graphene layer. Any changes on the external graphene layer leads to sensitive response of CNT properties. In direct mode on LED device (+ITO/pero/SWCNT–) positively charged ions coat SWCNT. P-type doping leads to downshifting and change in the Fermi level, that helps to holes injection from SWCNT instead of ITO. Changing the direction of the electrical field coats the surface with oppositely charged ions.

We demonstrate a concept of stacked multicolor tandem pixel. Stack of transparent light emitting units might allow fine color tuning in parallel tandem connection without segregation compared to mixed halide perovskites. This configuration conforms pixel downsizing and make to fabrication of emissive multijunction pixels in a stack. Stacked pixel designs have potential application in head-up displays and augmented reality technologies, due to smaller pixel area compared to conventional display with active matrix.

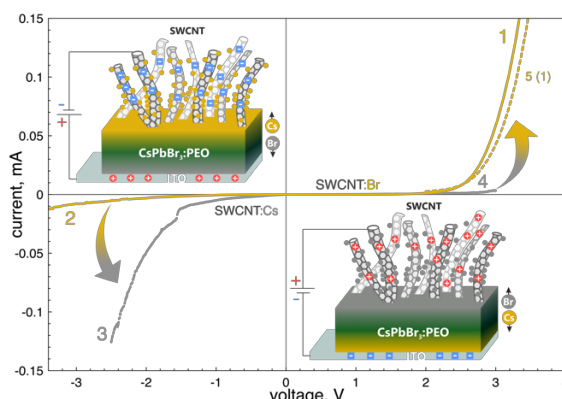


Figure 1: IV curve of single layer ambipolar PeLED (ITO/pero/SWCNT). Orange curves corresponds to forward sweep, SWCNT doped by  $\text{Cs}^+$  injects electrons; grey curves correspond to switched mode: SWCNT doped by  $\text{Br}^-$  injects holes. Switching realize by the voltage induced ions migration.

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## **Exciton to charge conversion in pristine non-fullerene acceptors: a computational study**

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Solar cell efficiencies can be boosted by replacing the fullerene acceptor with a dye, or a non-fullerene acceptor (NFAs). In fact, even pristine non-fullerene acceptors can convert excitons to charges, a process that obviously enhances the total solar cell efficiency. Here we explain why exciton dissociation into a charge transfer (CT) state and the splitting of the CT state into charge separated (CS) state is efficient in pristine NFAs.

To do this, we first evaluate dielectric solvation of an excited and CT states and show that there is enough driving force for the transition of the excited to CT state, due to a stronger dielectric stabilization of charges as compared to the localized excited state.

We then evaluate electrostatic potential at a disordered interface between NFA domains with different acceptor orientations and show that it provides electrostatic potential bending, sufficient to overcome the Coulomb binding energy of the CT state. Both effects can be traced back to molecular quadrupole moments and their long-range contributions to solid-state ionization energies and electron affinities. The presented study suggests several design rules for NFAs with efficient charge separation in photovoltaic applications.

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## **Novel Donor Small Molecules based on Benzodithiophene and Benzotriindole Cores for Organic Photovoltaics**

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Organic photovoltaics (OPV) is the one of the main science and technology part, which have been developed rapidly in the last decade. Nowadays, with well-designed and optimized molecular structure, the performance of organic solar cells (OSCs) have achieved the power conversion efficiency (PCE) to over 16% in case of single device architecture, and over 17% in case of tandem device architecture, which in turn makes OPVs more close to the theoretical prediction PCEs maximum. Most attention at the current time is paid to the development of OSCs based on non-fullerene acceptor materials (NFAs). Despite this, fullerene-based OSCs exhibit competitive PCE values, which suggests the need to develop both of these areas.

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

The work was financially supported by grant from the Russian Science Foundation (project № 19-73-10198). The work was performed in the framework of leading science school NSh-5698.2018.3

## Charge generation and recombination mechanisms in single component organic solar cells based on conjugated star-shaped oligomers

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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  $N(\text{Ph-nT-DCV-R})_3$  [3], which is very beneficial for SCOSC. In this work, we demonstrate a high potential of conjugated donor-acceptor molecules with general structure:  $N(\text{Ph-nT-DCV-R})_3$  for SCOSC. Photovoltaic properties were investigated in solution-processed SCOSC with the structure: glass/ITO/PEDOT:PSS/ $N(\text{Ph-nT-DCV-R})_3$ /Ca/Al. For SCOSC based on  $N(\text{Ph-2T-DCV-Et})_3$ , which showed the highest PCE of 1.2% and EQE of 24%, charge generation, recombination and transport properties were explored in details.

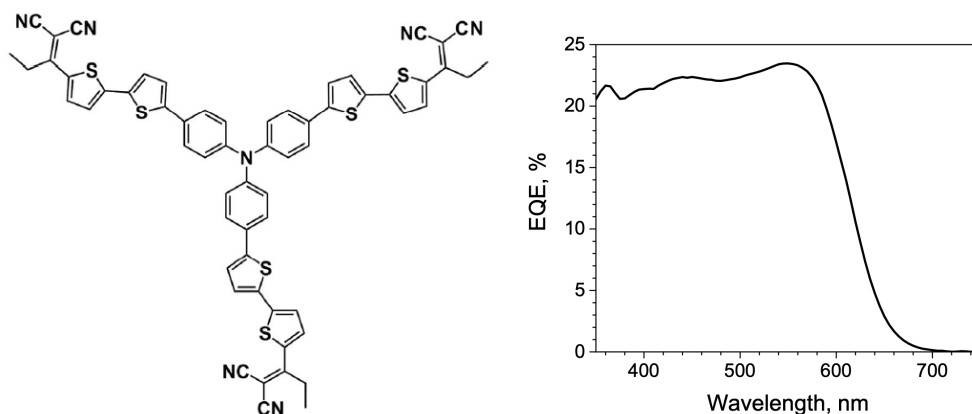


Fig. 1. Structural formula of  $N(\text{Ph-2T-DCV-Et})_3$  and EQE spectra for  $N(\text{Ph-2T-DCV-Et})_3$  solar cell.

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

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# **Poster Presentations**

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

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

In particular, hole transport layer (HTL) is responsible for multiple degradation pathways discovered for PSCs. State-of-art HTLs require additional p-doping with oxygen and hydroscopic Li-salts, which impairs ambient stability of PSCs [4]. Moreover, doped HTLs are intrinsically unstable in combination with complex lead halides since cationic species tend to oxidize I<sup>-</sup> to molecular iodine. Therefore, designing new p-type materials enabling decent transport of positive charge carriers without additional doping is crucially important.

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

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

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

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We report the first systematic assessment of intrinsic thermal and photochemical stability of a large panel of complex lead halides  $\text{APbX}_3$  incorporating different univalent cations ( $\text{A}=\text{CH}_3\text{NH}_3^+$ ,  $[\text{NH}_2\text{CHNH}_2]^+$ ,  $\text{Cs}^+$ ) and halogen anions ( $\text{X}=\text{Br}$ ,  $\text{I}$ ) using a series of complementary analytical techniques such as UV-vis spectroscopy, x-ray diffraction, x-ray photoelectron spectroscopy, EDX chemical analysis, atomic force and scanning electron microscopy, electron spin resonance spectroscopy and mass spectrometry. We show that both heat stress and light soaking can induce a severe degradation of perovskite films even under well-controlled inert atmosphere in the absence of oxygen and moisture. The stability of complex lead halides increases in the order  $\text{MAPbBr}_3 < \text{MAPbI}_3 < \text{FAPbI}_3 < \text{FAPbBr}_3 < \text{CsPbI}_3 < \text{CsPbBr}_3$ , thus featuring all-inorganic perovskites as the most promising absorbers for stable perovskite solar cells. An important correlation was found between the stability of the complex lead halides and the volatility of univalent cation halides ( $\text{AX}$ ) incorporated in their structure. In particular,  $\text{MAPbBr}_3$  has the lowest stability since it is comprised of  $\text{PbBr}_2$  and the most volatile  $\text{MABr}$ . On the contrary, all-inorganic  $\text{CsPbX}_3$  compounds show remarkable stability since  $\text{CsBr}$  and  $\text{CsI}$  are non-volatile under the solar cell operation conditions. The established relationship provides useful guidelines for designing new complex metal halides with immensely improved stability.

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



## CVD process for metal halide perovskite solar cells

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Metal halide perovskites are materials with unique semiconductor properties. Perovskites have a high optical absorption coefficient [1] and the diffusion lengths exceed 1  $\mu\text{m}$  for electrons and holes [2], direct well-tuned band gap. Low cost of perovskite precursors such as  $\text{CH}_3\text{NH}_3\text{I}$  and  $\text{PbI}_2$  and its solubility in some organic solvents (dimethyl formamide, dimethyl sulfoxide) makes perovskite an ideal absorber material for solar cells, photodetectors, light-emitting diodes.

Major trend in perovskite device fabrication is a solution process for thin films formation, which allowed to obtain high PCE on small SC in laboratory conditions, but upscaling of laboratory technique is expensive for industry due to necessity of introduction of new production machines. We propose using a chemical vapor deposition (CVD) for perovskite thin film formation. CVD is a common industrial method for obtaining semiconductor structures, it allowed to provide perovskite crystallization with tuned thickness and grains size [3].

In this work we were synthesized organic-inorganic halide perovskite  $\text{CH}_3\text{NH}_3\text{PbI}_3$  and full inorganic halide perovskite  $\text{CsPbBr}_3$  in one source, one step CVD on ITO substrates. Morphology of thin films and optical characteristics were investigated; the phase analysis were done with XRD.

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# Phenyl-C<sub>61</sub>-butyric acid as an interface passivation layer for highly efficient and stable perovskite solar cells

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In recent years, hybrid organic-inorganic materials based on complex lead halides with perovskite type crystal structure have attracted a particular attention of the photovoltaic community. Despite the high efficiencies of perovskite solar cells, one of the major obstacles for further development of this technology is related to intrinsic instability of the interfaces between the most common metal oxide electron transport layers and the perovskite absorber. Unfavorable interfacial chemistry leads to reduced power conversion efficiencies (PCE) and stability of perovskite solar cells. Surface modification of the electron transport layer (ETL) is one of the most effective ways to improve the performance of perovskite solar cells.

In particular, bare zinc oxide and tin oxide ETLs widely used in photovoltaics<sup>1</sup> can cause a severe degradation of perovskite upon annealing<sup>2</sup>. To mitigate this problem, we introduce an additional passivation coating<sup>3</sup> of [6,6]-phenyl-C<sub>61</sub>-butyric acid (PCBA) atop zinc and tin oxides. We found that PCBA binds to the oxide surface forming presumably a monolayer, which blocks the direct contact of perovskite with the ETL. The passivation of tin oxide with PCBA dramatically improved the charge extraction properties of the ETL resulting in an increase of solar cell PCE from 12% to 20.3%. Compared to the conventionally used PCBM<sup>2</sup>, an application of PCBA layer resulted in higher PCE, which was attributed to a better adhesion of the PCBA to the oxide surface due to its anchoring COOH groups. Moreover, PCBA layer can be deposited using 40-times less concentrated solution as compared to PCBM, thus providing a more cost-effective approach to oxide interface passivation.

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## Top or Bottom: Decoupling the Contributions of Hole- and Electron-Transport Layers to Light-Induced Degradation of p-i-n Perovskite Solar Cells

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Perovskite solar cells (PSCs) have demonstrated impressive performances, while their operation stability still requires substantial improvements before this technology can be successfully commercialized. There is a growing evidence that stability of PSCs is strongly dependent on the interface chemistry between the absorber films and adjacent charge transport layers, while the exact mechanistic pathways remain poorly explored.<sup>[1,2]</sup> Here we present a straightforward approach for decoupling the degradation effects induced by the top electron transport layer (ETL) of the fullerene derivative PC<sub>61</sub>BM and various bottom hole-transport layer (HTL) materials assembled in p-i-n perovskite solar cells configurations. We show that chemical interaction of MAPbI<sub>3</sub> absorber with PC<sub>61</sub>BM most aggressively affects the operation stability of solar cells. However, washing away the degraded fullerene derivative and depositing fresh ETL leads to restoration of the initial photovoltaic performance when bottom perovskite/HTL interface is not degraded. Following this approach and refreshing ETL after light soaking of the samples and before completing the solar cell architectures, we were able to compare the photostability of stacks with various HTLs. It has been shown that PEDOT:PSS and NiO<sub>x</sub> induce significant degradation of the adjacent perovskite layer under light exposure, while PTAA provides the most stable perovskite/HTL interface. ToF-SIMS analysis of fresh and aged samples allowed us to identify chemical origins of the interactions between MAPbI<sub>3</sub> and HTLs. The proposed research methodology and the revealed degradation pathways pave a way to the future development of efficient and stable perovskite solar cells.

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# Pyrrolo[3,4-c]pyrrole-1,4-dione-based ultra-narrow bandgap conjugated polymers: promising electron-transport materials for perovskite solar cells

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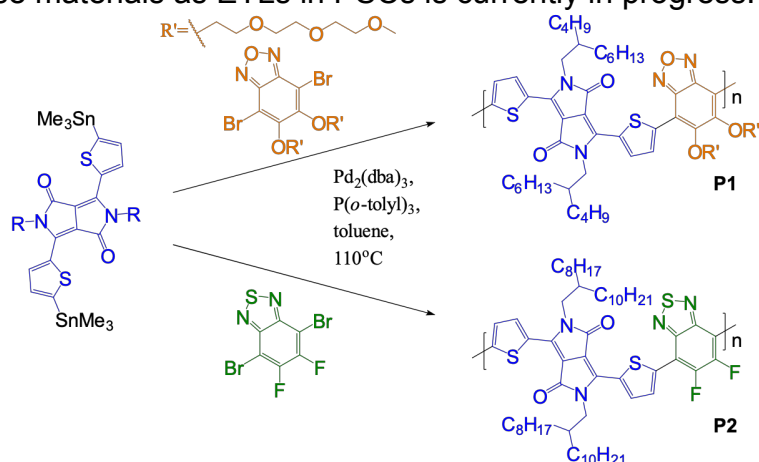
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The power conversion efficiency of perovskite solar cells (PSCs) has rapidly increased from 3.8% [1] in 2009 to record values of 25.2% in 2019 [2]. At the same time, PSC exhibited low operational stability owing to degradation of complex lead iodides (e.g.  $\text{CH}_3\text{NH}_3\text{PbI}_3$ ) used as absorber materials in PSCs [3]. The main decomposition pathways are associated with the reaction of complex lead halides with moisture, oxygen and intrinsic light- or heat-induced decomposition with the formation of gaseous products in the course of solar cell operation [4]. One of the possible ways to mitigate such degradation is using polymeric electron- and hole-transport materials that form high-quality and dense films, thereby suppressing the diffusion of aggressive environmental species inside the active layer of the device and evaporation of volatile aging products outside thus giving them time to react and reform the perovskite absorber material.

In this work we present the synthesis of two conjugated polymers based on pyrrolo[3,4-c]pyrrole-1,4-dione, which can be considered as promising electron transport layer (ETL) materials in PSCs. Polymer **P1** was assembled using benzo[c][1,2,5]oxadiazole block with triethylene glycol monoethyl ether side chains to improve the interface contact between the ETL and the perovskite. Fluorine-substituted benzo[c][1,2,5]thiadiazole acceptor block was introduced in **P2** to decrease LUMO energy for better matching of the absorber conduction band. Polymers were synthesized by Stille coupling reaction with moderate yield of 50-55%. Weight-average molecular weights estimated using gel-permeation chromatography were found to be 162 kDa and 146 kDa for **P1** and **P2**, respectively. Both polymers have narrow bandgaps of about 1.3 eV as estimated from their optical spectra. The LUMO energies of the polymers were -4.01 eV for **P1** and -4.46 eV for **P2**. Evaluation of these materials as ETLs in PSCs is currently in progress.



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## **MAPbBr<sub>3</sub> single crystal for use in photodetector structures**

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Organic-inorganic halide perovskites (OIHP) are a well-known material as an absorbing layer of solar cells. Also, this class of semiconductors showed promising performance in photodetection in comparison to traditional semiconductor materials.<sup>[1]</sup> The high trap density of polycrystalline thin films accounts for the lower carrier mobility and shorter carrier diffusion length. Thus, perovskite single crystals could be optimal solution for application in photodiode, photoresistors and detector devices structures.

Perovskite single crystals have outstanding optoelectronic and electrophysical properties for devices in demand in the field of imaging, optical communication, and medicine due to the high carrier lifetimes (to 15  $\mu$ s) and diffusion length (to 175  $\mu$ m).<sup>[2]</sup> Also, the high absorption coefficient of OIHP provides high photosensitivity and short response time.

Novel approach in growth of monocrystals with retrograde solubility method (50-110°C temperature and 5-6 hours growth period) that was demonstrated <sup>[3]</sup> in 2015<sup>th</sup> opened new opportunities in commercialization of devices based on perovskite single crystals. Those conditions provide low-cost fabrication in compare to Si, GaAs, etc. technology. In this work, we fabricated and studied photodetector based on MAPbBr<sub>3</sub> perovskite single crystal.

Inverse temperature crystallization technique used to growth the MAPbBr<sub>3</sub> single crystal. J-V measurements were done in the dark, under the light with intensity 50 mW/cm<sup>2</sup> and 100 mW/cm<sup>2</sup>. Device shown photosensitivity which was 0.023 A/W. Calculated from time-of-flight measurements mobility of photogenerated carriers was 2 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>

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## Conjugated polymers: promising hole-transport materials for dopant-free perovskite solar cells

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Perovskite solar cells (PSCs) represent a rapidly emerging photovoltaic technology, which recently exceeded 25% efficiency threshold and continues to rise [1]. One of the most important components of PSCs is a hole transport material (HTM). To date, most of efficient HTMs require hydroscopic dopants, which impair the device operation stability [2]. However, there are few promising families of conjugated polymers, which demonstrated decent performances in dopant-free n-i-p devices.

In this work, we systematically explored a broad range of HTMs in order to reveal the impact of their molecular structure and properties on the PSCs performance and operation stability. While selecting the screening candidates, we paid special attention to the HTMs with a proper HOMO alignment with respect to the perovskite valence band. The passivation effect of HTMs on perovskite films and their encapsulation properties were examined in thin films and multilayered stacks by using a series of complementary instrumental techniques such as UV-vis and PL spectroscopy, XRD analysis, ToF SIMS, probe microscopy and SEM. Finally, we fabricated completed n-i-p PSCs with different HTMs and explored their operation stability under continuous light illumination. The obtained set of results allowed us to identify the most promising HTMs and outline some basic principles for their future rational design.

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

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## Inverted perovskite solar cell with SnO<sub>2</sub> interlayer

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To date, the power conversion efficiency (PCE) of hybrid perovskite solar cells reached 25.2 % [1]. Despite the competitive values of PCE in comparison to commercially available analogues - Si; CIGS and CdTe, technology of PSCs has promising potential in mass production with use of solution methods for deposition – slot -die; doctor blade; ink-jet printing with integration to roll to roll or sheet to sheet fabrication lines [2].

However, commercialization of PSCs is still so far because of several major factor of devices instabilities. One of the main problems for the stability of interfaces in the devices is contact between the metal cathode and electron transport layer [2-3]. Typically electron transport junction suffer from the chemical interaction with metal film and diffusion in depth of the device. As result, interface degrades with forming of shunts, chemical compounds (typically metal halides) and recombination centers, which leads to decrease value of the solar cells output characteristics (PCE, FF,  $J_{sc}$ ,  $V_{oc}$ ) [4].

In this work, we introduced an inorganic buffer layer SnO<sub>2</sub> between the organic n-type transport layer (PCBM) and the metal electrode (Ag). The work present output characteristics data and maximum power point tracking (MPPT). In the result output parameters had equal values in comparison with references, but MPPT showed an increase of the device stability by 19 %.

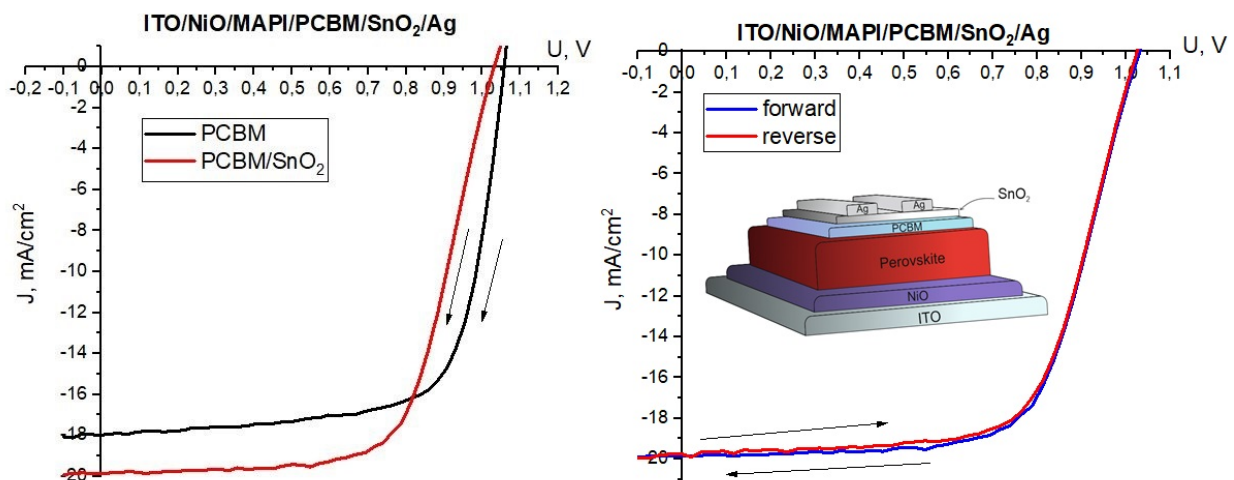


Fig. 1 –a) Current-voltage characteristics without and with SnO<sub>2</sub>; b) Forward and reverse current-voltage characteristics of devices with buffer layer

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# Impact of overstoichiometric $\text{PbI}_2$ on photovoltaic performance and photostability of $\text{MAPbI}_3$ perovskite films

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Lead halide perovskite solar cells represent now one of the most rapidly developing fields of scientific research. Unique optoelectronic properties of the absorber materials such as high extinction coefficient, long carrier diffusion lengths and high power conversion efficiencies make perovskite solar cells a highly promising future generation photovoltaic technology. Unfortunately, it is still far away from commercial application due to intrinsically low photochemical and thermal stability of the used absorber materials. This problem can be mitigated through compositional and interfacial engineering of all components within the photovoltaic cell.

While considering the modification of the perovskite absorber, the effects of stoichiometry between the lead iodide and univalent cation halides should be particularly considered. Some previous reports suggest that introducing overstoichiometric amounts of lead iodide ( $\text{PbI}_2$ ) in the active layer leads to its accumulation at the grain boundaries and induces their passivation [2]. Other reports, on the contrary, demonstrated that  $\text{PbI}_2$  can be responsible for the formation of structural defects, which have a strongly negative impact on the perovskite photostability [1]. These contradictions in the results reported by different groups point to the need for a systematic study of the stoichiometry effects on the stability of  $\text{MAPbI}_3$  thin films and photovoltaic devices.

In this study, we explored the influence of overstoichiometric amount of  $\text{PbI}_2$  (up to 15% by weight) on the behavior of perovskite films and solar cells. We found that the addition of 10% of lead iodide improved the perovskite solar cell performance as compared to the reference stoichiometric  $\text{MAPbI}_3$  system. However, the effect of overstoichiometric lead iodide on the photostability of perovskite films was found to be strongly dependent on the solvent used for processing of thin films. In particular, stability of the perovskite films processed from DMF precursor solution was strongly impaired by overstoichiometric  $\text{PbI}_2$ . On the contrary, the films coated from DMF-NMP solvent mixture were very tolerant to the presence of excessive amount of  $\text{PbI}_2$  presumably due to its integration in the adduct  $\text{PbI}_2 \cdot \text{NMP}$  [3-5]. Thus, we conclude that the presence of crystalline phase of  $\text{PbI}_2$  in perovskite films strongly accelerates their photodegradation, while using NMP as a co-solvent improves photostability of the coated films owing to the complexation of overstoichiometric lead iodide.

The obtained results explain controversial data presented in the previous publications and feature the crucial effect of the solvent used for absorber film processing on the operational stability of perovskite solar cells.

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## **On the way to develop scalable techniques for deposition of multication perovskite films and solar cells**

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During the last decade hybrid organic-inorganic perovskite solar cells attracted great attention due to their outstanding performance achieved at projected low fabrication cost. Power conversion efficiency (PCE) of small-area perovskite solar cells surpassed recently 25%, which features great commercialization of this emerging PV technology. Among different absorber material formulations, multication systems comprising cesium, formamidinium (FA) and optionally methylammonium are now the most intensively studied due to their advanced optoelectronic properties and good stability [1]. However, deposition of large-area films of such multication perovskites is more challenging compared to conventional MAPbI<sub>3</sub> system. Therefore, in this work we aimed at the development of reliable procedures for coating multication perovskite films and evaluation of their performance in solar cells.

Blade coating is a very popular technique for large-area films deposition. This technique was successfully used for single-step MAPbI<sub>3</sub> perovskite processing [2], while its application for single step coating of multication perovskites under ambient conditions is more challenging. Physical vapor deposition represents a scalable, reproducible and safe method for perovskite film formation, though it is associated with the need to use more sophisticated equipment and consume more energy.

In this work, we initiated optimization of blade coating and PVD techniques for deposition of multication perovskites. Using XRD, AFM, UV-Vis absorbance measurements we have shown that the films with the decent morphology and desired phase composition might be obtained by both of these methods. However, application of the coated films in solar cells requires further optimization. Currently, we reached PCEs of 7-9%, which have to be doubled in the future experiments.

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## **Influence of partial Pb<sup>2+</sup> substitution in APbI<sub>3</sub> perovskites on their photovoltaic performance and photostability**

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Perovskite solar cells represent one of the most promising photovoltaic technologies. Over the past few years, the performance of perovskite solar cells was gradually improved up to >25%, which is close to the characteristics of crystalline silicon photovoltaics. However, high toxicity and low stability of complex lead halides used as absorber materials hamper commercialization of this technology. Compositional engineering of lead perovskites was actively pursued in order to improve their stability and/or performance. In particular, a partial or full replacement of Pb<sup>2+</sup> in APbX<sub>3</sub> is highly desirable in terms of developing more environmentally friendly materials.

Here we present a systematic study of lead substitution in MAPbI<sub>3</sub> and CsFAPbI<sub>3</sub> with >20 different cations introduced in atomic concentrations ranging from 10<sup>-4</sup> to 20-30%. It was shown that replacing even minor fraction of lead could change significantly the perovskite film crystallinity and morphology. Importantly, the efficiency and stability of p-i-n and n-i-p solar cells were improved considerably by appropriate modification of perovskite active layer. Moreover, important relationships were established between the nature of the substituting ions (e.g. ionic radius or charge) and their effects on electronic properties and photovoltaic performance of the resulting hybrid perovskites. The obtained results should facilitate the rational design of more stable and less toxic absorber materials for advanced perovskite solar cells.

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

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

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

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# Development of the all-inorganic perovskite-like chalcogenide metal complexes of Cd, In, Sb and Bi and investigation of their semiconductor and photovoltaic characteristics

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The field of photovoltaics is undergoing a surge of interest following the recent discovery of the lead halide perovskites as a remarkable family of solar absorber materials demonstrating outstanding efficiencies in solar cells. However, the intrinsic instability of complex lead halides under exposure to light limits severely the lifetime of the solar cells based on these materials. Many of the excellent properties seen in hybrid perovskites are thought to derive from the  $ns^2$  electronic configuration of lead, a configuration seen in a range of post-transition metal compounds, such as Sb(III) and Bi(III) halide and chalcogenide complexes [1]. In this work, a series of covalent all-inorganic chalcogenide complexes of Sb and Bi was considered in terms of promising photoactive semiconducting materials with appropriate photovoltaic characteristics.

The materials considered have the general composition of  $A_xB_yQ_mX_n$  (A, B – metals; Q = S, Se; X = Cl, Br, I), with pseudo-3D- and 2D-crystal structures. The synthesis of these complexes was carried out by thermal sintering of simple or binary compounds mixtures in vacuum-sealed ampoules under the argon atmosphere [2]. Their semiconductor and photoelectrical properties were investigated in thin films deposited on glass substrates by thermal evaporation of the target material or its precursors. The elemental and phase composition of the materials were characterized using atomic absorption spectroscopy and XRD methods, respectively.

Some materials, such as  $CdSb_2Se_3Br_2$  (1),  $InSb_2Se_4Br$  (2) and  $InBi_2Se_4I$  (3) demonstrated significant increase in conductivity under illumination. The revealed photoconductivity opens wide opportunities for designing lateral photodetectors using these materials. The laboratory prototypes of solar cells with the general configuration of ITO/ETL(HTL)/Photoactive material (1) or (2)/HTL(ETL)/Ag were fabricated and subsequently optimized in order to reach optimal photovoltaic characteristics. The highest power conversion efficiency (~0.5%) in solar cells was obtained for material (2). We believe that further improvements can be achieved while optimizing the material structure, processing conditions and device geometry.

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## **Tellurium complex polyhalides: narrow bandgap photoactive materials for electronics**

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Complex metal halides are intensively explored primarily in the context of their potential applications as absorber materials for perovskite photovoltaics. Despite a significant progress achieved with perovskite solar cells based on complex lead halides, it is still unclear if they can be practically useful because of the unresolved so far severe operational stability issues. At the same time, the success and challenges faced with lead-based perovskites stimulate active screening of other complex metal halides in order to develop more stable and, probably, even more efficient absorber materials.

In this work we explored for the first time a family of Te(IV) polyhalides  $A_2TeX_6I_2$ , where A represents organic cation and X denotes Br or I. The crystal structures of these compounds feature  $[TeX_6]$  octahedra interconnected by  $I_2$  bridge molecules. These compounds can be synthesized using a simple single-step procedure, which makes them available on a large scale. The tellurium complex bromides and, particularly, iodides exhibited interesting optical properties favoring their photovoltaic applications (e.g. band gaps below 1.5 eV). Thin films of the tellurium halides showed semiconductor behavior and revealed strong photoconductivity effects enabling their application as active materials in efficient photodetectors.

# Synthesis of novel conjugated polymers based on benzodithiophene and their application in polymer solar cells

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Polymer solar cells (PSCs) are considered as a promising photovoltaic technology due to their unique characteristics such as mechanical flexibility, lightweight and solution processability using high-throughput printing technologies [1]. The highest power conversion efficiencies (PCEs) were achieved for PSCs incorporating conjugated benzodithiophene-based polymers [2] highlighting a great potential of this type of materials for organic electronics application. Recently we showed that the polymers with extended DADAD type monomer units possess optimal optoelectronic properties [3] in comparison with widely used (X-DAD)<sub>n</sub> analogues.

In this work, we designed and synthesized three novel (X-DDADADD)<sub>n</sub> conjugated polymers based on benzodithiophene (X), benzothiadiazole (A) and thiophene (D) using Stille cross-coupling polycondensation reaction (Fig.1).

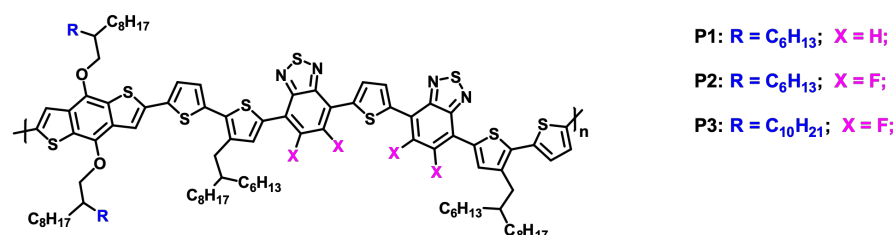


Figure 1. Molecular structures of conjugated polymers **P1–P3**

Optoelectronic properties of synthesized polymers **P1–P3** were studied using absorption spectroscopy and cyclic voltammetry. All compounds possess medium bandgaps of 1.65 – 1.67 eV and HOMO energies in the range of -5.51 – -5.56 eV. Photovoltaic properties of polymers **P1–P3** were investigated in organic solar cells with conventional architecture. The fullerene derivative [60]PCBM was used as acceptor component of the photoactive blend. The best PCEs of > 6% ( $V_{OC}$  = 769 mV,  $J_{SC}$  = 11.4 mA/cm<sup>2</sup>, FF = 68%) showed OSCs based on polymer **P2**. The performance of devices might be significantly improved by using non-fullerene acceptors due to reduced  $V_{OC}$  losses, that is currently in progress in our group.

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## Design of additives to suppress degradation of photoactive materials in organic solar cells

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Organic solar cells (OSCs) have a unique combination of characteristics, which makes them highly competitive with respect to a number of applications. The performance of OSCs has been rapidly increasing owing to the development of new donor and acceptor materials. However, one of the main obstacles for their commercialization is relatively fast degradation of both active materials and photovoltaic devices under realistic operational conditions.

In this work, we present new stabilizing additives improving significantly stability of organic semiconductor materials used in the active layer of OSCs. Thermal and photochemical stability of conjugated polymers **P1-P3**, fullerene derivatives **F1-F3** and their blends with stabilizing additives **D1-D4** was investigated in detail. The degradation of thin films of pristine semiconductor materials and their composites with **D1-D4** in the presence of trace amounts of oxygen was monitored by photoluminescence (PL) spectroscopy and electron spin resonance spectroscopy (ESR) [1-3].

The performed studies revealed that stabilizing additive **D3** demonstrates the best performance. This compound effectively suppresses degradation of polymers and fullerene derivatives in the course of annealing at 130°C under ambient conditions, which simulates OSCs encapsulation conditions. In addition, **D3** more than twice decreased the concentration of radical species accumulated in organic materials under UV-irradiation as revealed by ESR.

In conclusion, the proposed additives substantially improved ambient and photochemical stability of organic semiconductors and, hence, are expected to extend significantly the operational lifetimes of OSCs based on these materials.

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## Scalable organic solar cells based on novel (X-DADAD) polymers processed using layer-by-layer technique

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Organic solar cells (OSCs) demonstrate rapidly growing power conversion efficiencies (PCE) now reaching >17% for double-junction devices [1]. High OSCs performances were achieved using spin-coating technology for the active film deposition after thorough optimization in terms of blend composition, using processing additives, etc. However, commercialization of organic solar cells requires more straightforward and scalable film deposition technologies. Moreover, novel materials with specific properties are required to enable reliable processing of the films through roll-to-roll solution printing and coating industrial techniques.

Here we present OSCs processed using blade-coating with layer-by-layer deposition of electron donor and electron acceptor materials (LBL). The novel (X-DADAD)<sub>n</sub> medium bandgap polymer **P1** was used as a promising electron donor absorber material, while PC<sub>61</sub>BM was used as a fullerene-based acceptor.

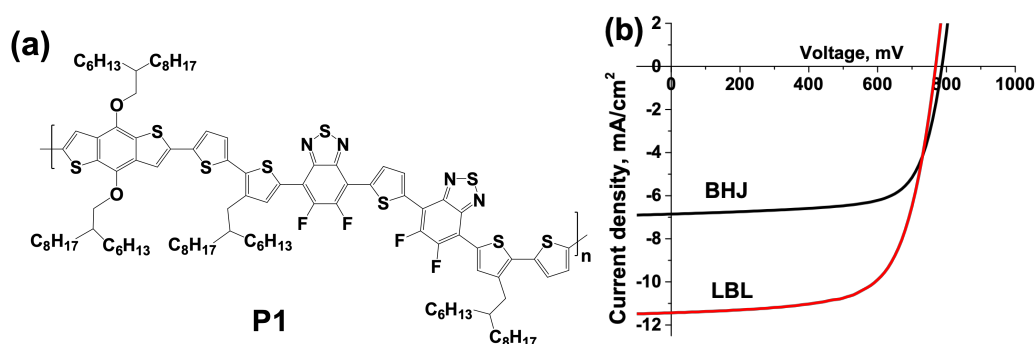


Figure 1. (a) The chemical structure of **P1**. (b) The current-voltage characteristics of BHJ and LBL OSCs based on the **P1** and PC<sub>61</sub>BM.

It has been shown that layer-by-layer fabricated OSCs possess enhanced photovoltaic performance compared to traditional bulk heterojunction solar cells. The current density was improved from 6.9 mA/cm<sup>2</sup> to 11.4 mA/cm<sup>2</sup> and the efficiency reached 6%. We believe that improved vertical morphology of the active layer is responsible for improved performance of LBL OSCs.

We emphasize that blading is a scalable film deposition technique, while the reached efficiency of 6% is among the best values reported for large-area roll-to-roll coated polymer solar cells. Further optimization is expected to lead to improved efficiencies since the used material combination can potentially deliver PCE of >13%.

[1] L.X. Meng, Y.M. Zhang, X.J. Wan, C.X. Li, X. Zhang, Y.B. Wang, X. Ke, Z. Xiao, L.M. Ding, R.X. Xia, H.L. Yip, Y. Cao, Y.S. Chen, *Science*, 361, **2018**, 1094

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# Novel Conjugated Polymers Based On Thiazolothiazole For Organic and Perovskite Solar Cells

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Conjugated polymers represent a promising type semiconductor materials for organic solar cells (OSCs). The commercially competitive power conversion efficiencies (PCE) of >17% [1] were achieved using state-of-the-art conjugated polymers in double-junction device geometry. However, the synthesis of these materials is usually a multistep and complicated process impeding the commercialization of OSCs.

In this work, we designed novel conjugated polymer Tz-T4BTB based on thiazolothiazole (Fig. 1a). A straightforward synthesis of Tz-T4BTB allows to produce this polymer on a large scale and at low cost.

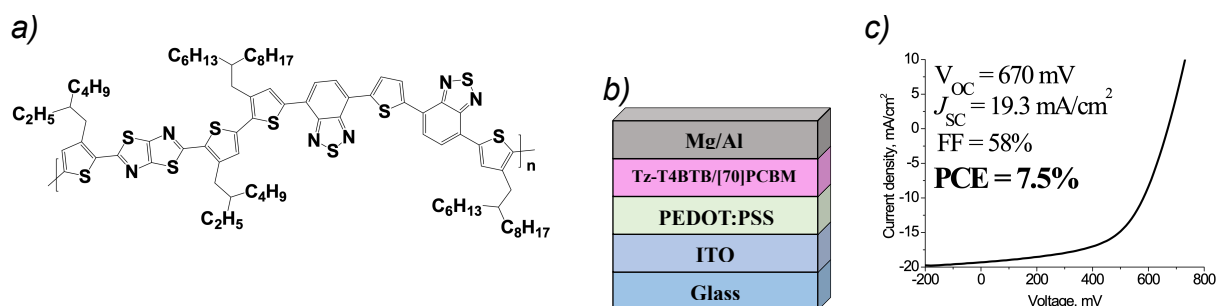


Figure 1. (a) Molecular structure of Tz-T4BTB. (b) The architecture of photovoltaic cells. (c) The voltage-current characteristics of OSCs based on the Tz-T4BTB/[70]PCBM blends.

Organic solar cells based on Tz-T4BTB/[70]PCBM blends delivered high short-circuit current densities of 19.3 mA/cm<sup>2</sup> with decent fill factors of ~60% and PCE > 7% (Fig. 1c). We believe that further molecular optimization of Tz-T4BTB structure (e.g. using fluorine substitution) and using appropriate non-fullerene acceptors might deliver higher efficiencies required for commercially feasible organic photovoltaics.

[1] L. Meng, Y. Zhang, X. Wan, C. Li, X. Zhang, Y. Wang, X. Ke, Z. Xiao, L. Ding, R. Xia, H.-L. Yip, Yong Cao, Y. Chen, *Science* **2018**, *361*, 1094–1098

This work was financially supported by the Russian Foundation for Basic Research, (project No. 18-33-20025)

# Design of low molecular weight electron donor molecules based on thiophene and benzothiadiazole for solar cell applications

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Conjugated small molecules have attracted a lot of attention with respect to their potential application in organic electronics because of their well-defined composition and structure, low batch-to-batch variation of their properties, easier energy level control. Small molecules (SM) were successfully used as both donor [1] and acceptor materials [2] in organic solar cells (OSC). Here we report the synthesis and investigation of novel small molecule **M1** comprised of thiophene and benzothiadiazole units (Fig.1a).

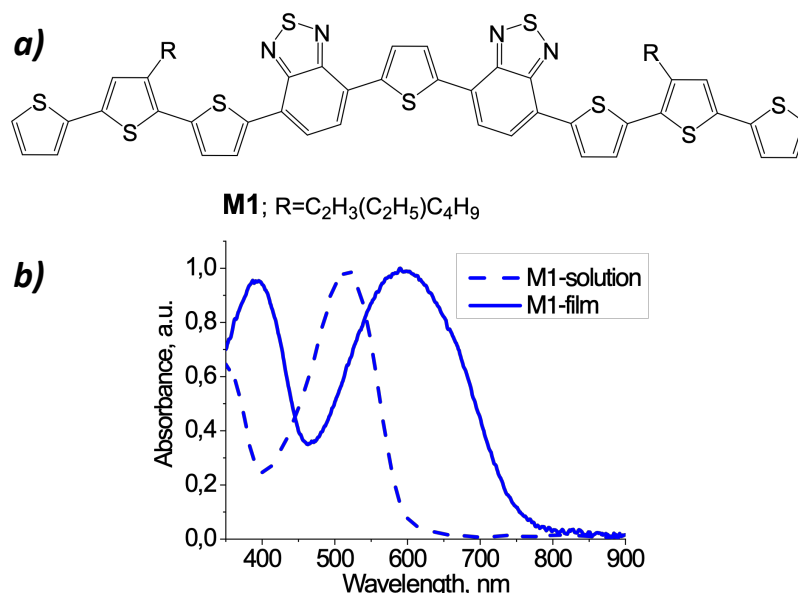


Fig.1. Molecular structures of **M1** (a) and absorption spectra of this compound in solution and solid film (b)

The obtained materials demonstrate efficient self-ordering in thin films as suggested by the bathochromic shift (~150 nm) of the absorption band in optical spectra while going from solution to the solid state. The optical band gap of **M1** was estimated as 1.63 eV, while HOMO energy is ca. -5.44 eV. The optical and electronic properties of this novel small molecule are optimal for its using as promising semiconductor for organic electronics and, in particular, in solar cells. Relevant studies are currently in progress.

This work was supported by RFBR (project № 18-33-00667).

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# Synthesis of novel donor-acceptor conjugated polymers comprising thiazolothiazole units for photovoltaic applications

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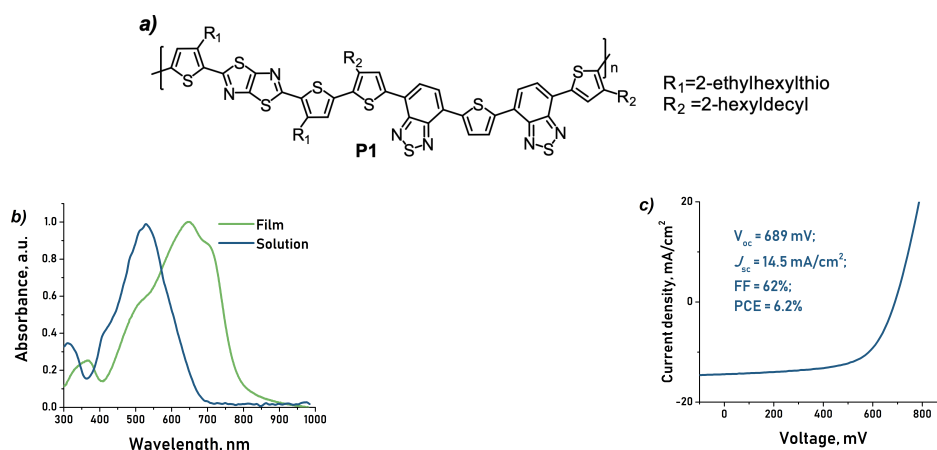
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Solution-processible bulk-heterojunction organic solar cells have attracted tremendous attention because of their multiple advantages such as low cost, lightweight, mechanical flexibility, easy manufacturing process and potential for designing semi-transparent light harvesting devices for e.g. smart windows. However, state-of-the-art large-area OSCs demonstrate still low power conversion efficiencies (PCEs). Non-optimal morphology of the absorber films is one of the crucial factors limiting the PCEs of large-area devices [1]. This problem might be solved using crystalline polymers displaying very ordered chain packing in solid state as observed particularly for thiazole-based materials. It is known that thiazolothiazole fused rings can increase the rigidity of the macromolecules, enhance their  $\pi$ - $\pi$  stacking and thereby significantly improve the crystallinity of the polymer [2].

In our work, we developed novel thiazolothiazole-based conjugated polymer **P1** comprising DADAD system comprised of thiophene (D) and benzothiadiazole (A) fragments (Fig.1a). Polymer **P1** shows a tendency to strong self-organization in thin films as can be concluded from a large bathochromic shift in optical spectra while going from solution to solid state (Fig.1b). First investigation of photovoltaic properties of **P1** in OSCs with fullerene-based acceptor [60]PCBM showed encouraging PCEs of 6.2%, which can be improved by optimization of the device fabrication conditions (Fig.1c). Evaluation of the performance of **P1** as hole-transport material for polymer solar cells is currently in progress.



**Fig.1.** Molecular structure of **P1** (a), absorption spectra of **P1** in 1,2-dichlorobenzene and thin film (b),  $J$ - $V$  characteristics for the solar cells based on **P1**/[60]PCBM blends (c).

This work was supported by the Russian Foundation for Basic Research (project No.18-33-20025)

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## Novel dioxyphenylene-TBTBT copolymer for application in solar cells

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Bulk heterojunction organic solar cells have attracted attention due to their light weight, low cost, and flexibility [1]. Donor-acceptor (D-A) conjugated polymers have been widely employed as active layer components in organic solar cells because of their tunable band gap, frontier energy levels and charge transport characteristics. It has been shown recently that (X-DADAD)<sub>n</sub> type polymers demonstrate improved optoelectronic characteristics compared to conventional (X-DAD)<sub>n</sub> type structures [2].

In this work, we synthesized and investigated a novel polymer **P1** with 1,4-bis((2-hexyldecyl)oxy)benzene (X), benzothiadiazole (A) and thiophene (D) units (Fig.1a).

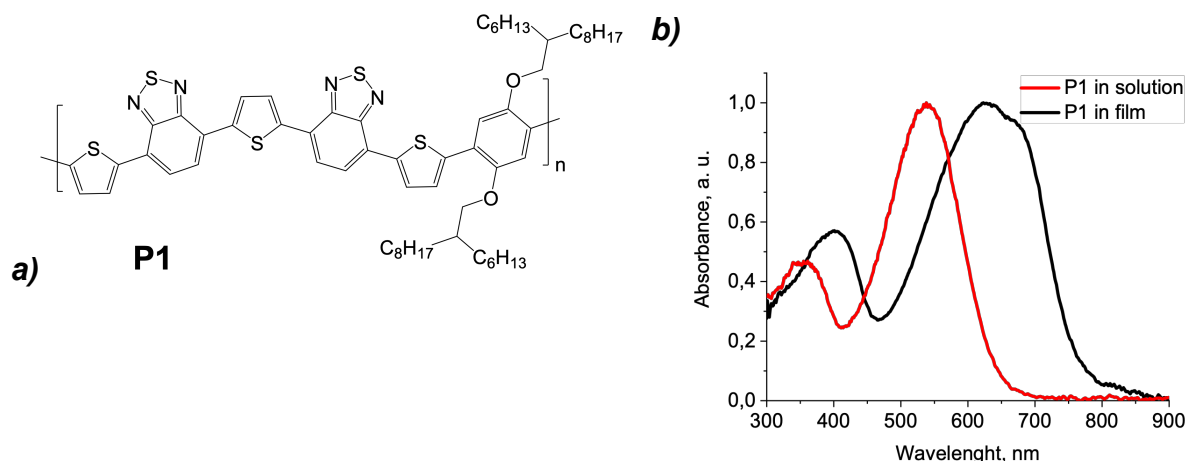


Fig.1. Molecular structure of **P1**(a) and its optical spectra in solution and in thin film (b)

Polymer **P1** demonstrated strong self-assembling and intermolecular interactions in solid state as can be concluded from a spectacular red shift of its absorption band while going from solution to thin films (Fig. 1b). **P1** has reasonably low bandgap ( $E_g^{\text{opt}}$ ) of ~1.6 eV and HOMO energy of -5.3 eV, as estimated from the absorption onset and electrochemical measurements. Organic solar cells based on **P1**/[60]PCBM have been fabricated and their photovoltaic characteristics explored. The devices showed power conversion efficiencies of ~4% with short-circuit current densities of 10.2 mA cm<sup>-2</sup>, open-circuit voltages of 587 mV, and fill factors of 63%. We believe that further optimization of the polymer structure and methodology of the solar cells fabrication will allow us to reach better device performance.

This work was supported by RFBR (project № 18-33-00667).

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# Self-powered Organic IR Photodetectors Based on Low Bandgap Polymer / Fullerene Composites

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Sergey Babenko<sup>3</sup>, and Pavel Troshin<sup>1,2</sup>**

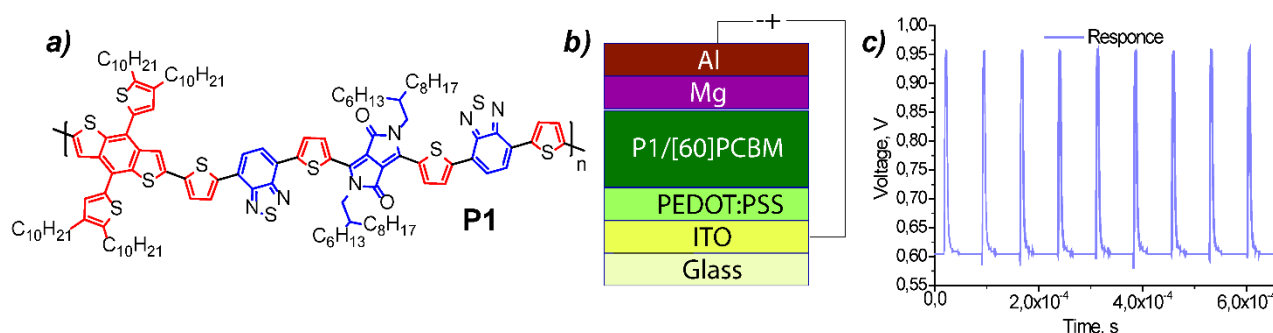
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Organic photodetectors represent a promising thin-film technology with a number of envisioned applications in position sensing and remote-control devices, chemical or biological sensors and etc. [1]. A considerable attention is paid now to infrared (IR) photodetectors. Conjugated polymers with a broad and intense near-IR absorption bands are actively explored as light sensitive materials for thin film photodetectors.

In this work, we designed and synthesized novel low bandgap conjugated polymer comprising benzodithiophene and diketopyrrolopyrrole units (**Fig.1a**) and explored it as absorber material in organic photodetectors. of 1.3 eV and exhibited broad absorption in visible-NIR region up to 930 nm.



**Figure 1.** Molecular structure of polymer **P1** (a), layout of the photodetector device (b) and its dynamic response to a series of light pulses (c).

The photovoltaic cells with the standard configuration glass/ITO/PEDOT:PSS/**P1**: fullerene derivative/Mg/Al (**Fig. 1b**) were fabricated. Three different fullerene derivatives were evaluated as acceptor materials to achieve the best blend morphology and photovoltaic performance. The device based on **P1**/[60]PCBM blend was applied as photodetector delivering a high detectivity of  $1.26 \times 10^{12}$  Jones and operation frequency of up to  $5.0 \times 10^5$  Hz (**Fig.1c**) at zero applied potential, which means zero power consumption by the photodetector.

Thus, we designed organic photodetectors based on conjugated polymer **P1**, which demonstrated encouraging performance and might find some practical applications. Further improvement in the device characteristics is potentially possible via development of new materials and optimization of the device architecture.

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## **Electron-selective transparent electrodes and buffer layer materials for efficient standard and inverted organic solar cells**

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To achieve efficient and stable performance of organic photovoltaic cells it is necessary to apply proper charge-selective buffer layers at the interfaces between the photoactive layer and cathode or anode. Intensive research has been performed in that direction which resulted in the development of many promising buffer layer materials. Nevertheless, most of the existing materials failed to provide simultaneously high efficiency and long-term operation stability in the devices.

Semitransparent indium-tin oxide (ITO) and fluorine-doped tin oxide (FTO) electrodes exhibit greater selectivity towards positive charge carriers due to their high work functions (4.7-5.2 eV). We have developed a simple method for lowering the ITO and FTO work functions, which make them highly selective towards negative charge carriers (electrons) [1]. These electrodes were shown to be suitable for designing efficient and stable inverted organic solar cells.

Standard bulk heterojunction solar cells comprising ITO/PEDOT:PSS anodes require also n-type buffer layers at the cathode/active layer interface. We will present a family of multifunctional [60]fullerene derivatives, which behave as superior hole-blocking electron-transport materials improving the efficiency of organic solar cells by 20-35%. A mechanism of the operation of the fullerene-based cathode buffer layers has been revealed for the first time and will be particularly discussed.

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This work was supported by RFBR (project № 18-33-01086/19\_mol\_a).

## **Novel low molecular weight semiconductor materials comprising alternating benzothiadiazole and thiophene units**

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Low molecular weight materials have been intensively investigated in organic solar cells and field-effect transistors within the last decade [1]. In present work, we report the synthesis of novel low molecular weight photoactive semiconductor material TBTBT comprising electron-deficient benzothiadiazole units (B) and electron-rich thiophene rings (T). This material showed excellent ambient stability and resistance to the light-induced photooxidation, which features it as a promising material for air-stable electronics. TBTBT demonstrated ambipolar semiconductor behavior when investigated in OFETs with charge carrier mobility of  $\sim 4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .

TBTBT was also explored as electron donor material in organic solar cells in combination with [60]fullerene as an acceptor counterpart. Optimization of the device structure and active layer processing conditions delivered modest power conversion efficiency of 2.5%.

The application of TBTBT as electron transport material in p-i-n perovskite solar cells delivered competitive power conversion efficiency and device operation stability.

This work was supported by the Russian Foundation for Basic Research (grant No. 18-33-00667).

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# Novel benzodithiophene-based lowbandgap polymers for organic solar cells and modules

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New organic semiconductor materials for organic solar cells (OSCs) are intensively developed within the last two decades. The impressive power conversion efficiencies of >17% were achieved recently for single junction and tandem OSCs [1]. Theoretical simulations showed that PCE values exceeding 20% could be expected for devices based on materials with improved optoelectronic and charge-transport characteristics [2]. These results are very encouraging in terms of OSCs commercialization. However, solar cells based on new materials should also show the tolerance to upscaling without severe performance losses.

In this work, we report the synthesis of novel (X-DADAD)<sub>n</sub> conjugated polymer **P1** based on benzodithiophene units with alternating donor(thiophene) and acceptor(benzothiadiazole) blocks (Fig. 1). Previously we showed that (X-DADAD)<sub>n</sub> polymers demonstrate optimal characteristics for application in solar cells according to theoretical models [3]. We investigated photovoltaic properties of **P1** in OSCs, which were fabricated using laboratory spin coating and roll-to-roll (R2R) compatible doctorblade technique.

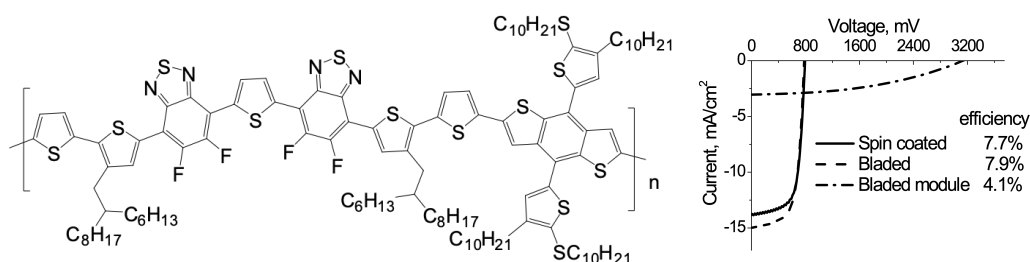


Fig. 1 Molecular structure of **P1** polymer and current-voltage characteristics of **P1**-based organic solar cells and modules.

As can be seen from Fig.1, solar cells fabricated using doctorblading demonstrate even better photovoltaic performance as compared to devices based on spin coated films. We also assembled modules (active area of 16.3 cm<sup>2</sup>) based on **P1**/[70]PCBM blends using doctor blade film coating in ambient air. The obtained results suggest that synthesized polymer **P1** is a promising material for industrial fabrication of large-area photovoltaic modules.

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



# Synthesis of novel (X-DADAD)<sub>n</sub> conjugated polymer based on thiophene and benzothiadiazole and its application in organic and perovskite solar cells

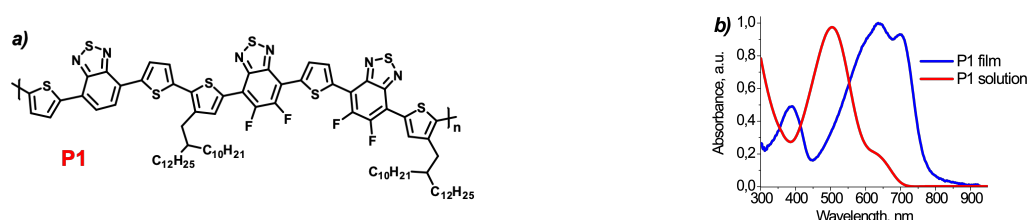
**Alina Lolaeva<sup>1</sup>, Alexander Akkuratov<sup>1</sup>, Petr Kuznetsov<sup>1</sup>,  
Marina Tepliakova<sup>2</sup>, and Pavel Troshin<sup>2,1</sup>**

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A great progress has been made in increasing power conversion efficiencies (PCEs) of polymer solar cells (OSCs) from 1% in the beginning of 2000s to >16% reached recently [1,2]. Further development of new photoactive materials can improve efficiency and stability of devices that is necessary for commercialization of OSCs. Conjugated polymers comprising thiophene and (difluoro)benzothiadiazole building blocks are recognized as the most successful families of semiconductor materials for highly efficient OSCs [3,4]. We have reported recently a promising approach to design of (X-DADAD)<sub>n</sub>-type copolymers with improved optoelectronic properties in comparison with well-known (X-DAD)<sub>n</sub> structures [5].



In this work, we present synthesis and investigation of optoelectronic properties of novel (X-DADAD)<sub>n</sub> conjugated polymer **P1** based on alternating benzothiadiazole (A) and (bi)thiophene (D) units (Fig.1). The alternation of electron donor thiophene and electron acceptor benzothiadiazole or 5,6-difluorobenzothiadiazole blocks enables reasonably low band gap of **P1** due to so-called push-pull effect. Branched 2-decyltetradecyl side chains were introduced to provide good solubility of polymer **P1** in common organic solvents.

Figure 1. (a) Molecular structure of polymer **P1**; (b) absorption spectra of **P1**

Resulting polymer **P1** exhibited broad absorption spectrum with the  $\lambda_{\text{edge}}$  at 772 nm in solid film that corresponds to bandgap of 1.6 eV (Fig. 1). Cyclic voltammetry measurements suggested that polymer **P1** possesses deep-lying HOMO energy level of -5.6 eV that is beneficial for reaching high open-circuit voltages in OSCs.

Investigation of **P1** as absorber in organic and hole-transport material in perovskite solar cells is currently in progress.

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## Fabrication of multi-cation planar PSC via sequential deposition in ambient conditions

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Despite the fact that the efficiency of small-area perovskite solar cells exceeded the value of 25%, the issue concerning for module – size devices remains unresolved[1]. One of the most promising crystallization methods for large area perovskite solar cells is two-step crystallization, which involves initial deposition of lead halide with subsequent conversion into black phase of perovskite with organic cation solution. A comprehensive and in-depth understanding of the nucleation and growth process during perovskite crystallization is imperative for the further research and development of high-quality perovskite solar cells.

This work presents a two-stepdeposition method of high performing stable perovskite layer in ambient condition on the top of inorganic hole transport layer (nickel oxide) in inverted planar structure [2]. We observed the following results with the first report about 2-step crystallization on the top of inorganic HTL (NiO).

The JV measurementsfor glass/FTO/NiO/Perovskite/PCBM/BCP/Ag structure (p-i-n), were performed underABA solar simulator and showed hysteresis-free plots. The efficiency values were obtained at the level of 12.5% (SC based on triple  $\text{Cs}_{0.05}(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$  – perovskite) and 9.5 % (SC based on  $\text{MAPbI}_3$ ). Achieved results demonstrated superior enhancement of the performance in comparison to previous works presented in the literature for inverted solar cells fabricated with 2 – step method [3],[4],[5]. It was revealed that critical parameters of the technological process are temperature control and timing for immersed substrates in 2nd step. We showed that shelf-life of devices based on triple perovskite is more stabled than in tri- iodide single cation configuration.

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## **All-Inorganic CsPbI<sub>3</sub> Perovskite Solar Cells with Long-Term Stability Enabled by Functional Additives**

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Low operation stability of hybrid perovskite solar cells currently is the main obstacle for their practical implementation. Replacing fragile organic moieties with robust inorganic cations represents a promising approach to designing more stable absorber materials. Inorganic lead-halide based perovskites CsPbI<sub>3-x</sub>Br<sub>x</sub> (x=0-3) have demonstrated improved thermal and photochemical stability. Among them, CsPbI<sub>3</sub> is considered as the most promising inorganic perovskite for photovoltaic cells due to its narrow band gap. Unfortunately, the cubic  $\alpha$ -phase of CsPbI<sub>3</sub> undergoes fast transition to a non-active yellow  $\delta$ -phase under realistic solar cell operation conditions thus limiting practical application of this material. Efforts of many research groups working on improving CsPbI<sub>3</sub> perovskite phase stability resulted in a certain progress in this field achieved very recently.

Here we addressed the problem of poor  $\alpha$ -phase stability of CsPbI<sub>3</sub> by introducing stabilizing additives in the film structure. A group of additives was identified that suppress significantly the phase transition effects in CsPbI<sub>3</sub>. The lifetime of the stabilized CsPbI<sub>3</sub> perovskite exceeded 1000 h under 1 sun illumination at elevated temperatures. In addition, solar cells based on CsPbI<sub>3</sub> films modified with properly chosen additives showed reasonably high power conversion efficiencies. These results pave a way to design of stable and efficient all-inorganic perovskite solar cells.

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## DFT Studies of Nonstoichiometric Hybrid Perovskites

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Hybrid Perovskites  $\text{XCSPbI}_3$  in the cubic phase (where X are various organic cations) have many desirable photovoltaic properties which make them promising candidates for a new generation of solar technologies. However, they have a major drawback which is their low stability under prolonged light exposure. One large challenge for these perovskites is to improve their stability to levels which would allow the technology to become commercialized. In the present work we jointly cooperated with experiment to deduce the structure of a nonstoichiometric perovskite  $\text{FA}_x\text{CsPbI}_{3+x}$ . The resulting unit cell for  $x = 0.5$  was a tight, layered monoclinic cell which had a structure similar to the ones that had been hypothesized in experiment and in previously published work [1]. We noted that the structure appeared to change significantly depending on the rotations of the formadinium species and these geometrical changes significantly affected stability. We also calculated the phase-segregation thermodynamics of both the pure and hybrid materials:  $\text{CsPbI}_3$  and  $\text{FAPbI}_3$  were both exothermic according to both our data and literature data [2]. Meanwhile, the nonstoichiometric  $\text{FA}_x\text{CsPbI}_{3+x}$   $x=0.5$  had endothermic phase segregation energy which was in agreement with the special stability this species is observed to have in experiment.

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## New conjugated block co-polymers as hole-transport layer materials for efficient perovskite solar cells

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Global energy demand grows exponentially and it is mainly fulfilled by combustion of fossil fuels leading to significant environmental impacts and frightening climate changes. Therefore, the development of renewable energy resources is a major challenge for humanity to minimize greenhouse gas emission and combat the global warming effects. Perovskite solar cells (PSCs) represent the most promising emerging technology for solar energy conversion. Power conversion efficiency of PSCs recently exceeded 25% threshold and has a promise to grow even further coming close to the performance of crystalline silicon solar cells (26.7%) [1]. However, commercialization of PSCs is impeded by their low stability.

PSC is comprised of photoactive layer sandwiched between charge transport layers. In classical n-i-p configuration perovskite is covered with hole transport layer (HTL), which provides hole transport, prevents contact between perovskite layer and electrode, and serves as a barrier for oxygen and moisture of the environment. State of art HTLs have insufficient transport properties. Their application requires additional p-doping with Li-salts and oxygen of the air, enhancing photovoltaic characteristics of PSC [2]. However, the hygroscopic nature of these salts leads to mitigation of the operation stability. That is why a search for new perspective HTLs is of a great importance.

In this context, conjugated block copolymers (CBCPs) are particularly interesting because of their ability to undergo efficient self-assembling in thin films into periodically ordered nanostructures thus enabling potentially efficient vertical charge transport [3]. In this work, we systematically investigated a set of CBCPs as hole-transport materials in PSCs. The deposition conditions for each material were thoroughly optimized to achieve optimal film thickness and photovoltaic performance. The best-performing CBCP delivered light conversion efficiencies of >18% in solar cells using MAPbI<sub>3</sub> as absorber layer.

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## Impact of photoactive layer/electrode interface on organic solar cells degradation

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Organic photovoltaics (OPVs) represents an exciting solar energy conversion technology [1]. Organic semiconductor materials can be solution-processed onto flexible substrates, enabling fast and inexpensive manufacturing of OPV modules. Both the capital expense and energy payback period of OPVs are projected to be less than that of other photovoltaic products [2-4]. The efficiencies of the best laboratory prototypes of single-junction organic solar cells have reached >17% [5], while their commercial application is hampered by a number of factors including low operation stability of organic solar cells [3,7].

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

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

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