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Moscow Autumn Perovskite Photovoltaics  
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## ОРГАНИЗАТОРЫ



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Функциональные материалы на основе гибридных перовскитов в последнее десятилетие привлекают внимание научного сообщества благодаря своим уникальным физическим свойствам и огромному потенциалу для применения в солнечных элементах, светодиодах, фотодетекторах и материалах для генерации лазерного излучения.

MAPPIC – международная конференция, организованная МГУ имени М.В. Ломоносова (Факультет наук о материалах, Лаборатория новых материалов для солнечной энергетики). Основными задачами конференции являются установление контактов и обмен опытом между промышленностью, исследовательскими институтами и молодыми исследователями, работающими в области современных фотоэлектрических и светоизлучающих материалов.

В рамках конференции с основными и приглашёнными докладами выступили ведущие ученые в области солнечной энергетики из разных стран.

С пленарными докладами выступили:

Prof. Chen Qi	<i>Heterogeneity in halide perovskite solar cells</i>	Beijing University of Technology, China
Prof. Aldo Di Carlo	<i>Scaling up perovskite photovoltaic from cell to panels</i>	Tor Vergata University of Rome, Italy
Prof. Sergey A. Ponomarenko	<i>Recent advances in organic semiconductors for perovskite solar cells</i>	ISPM RAS, Russia
Prof. Shengzhong Liu	<i>Perovskite – a wonder material for solar cells</i>	Shaanxi Normal University, China
Prof. Shenghao Wang	<i>Opto-electronic properties of all inorganic ABX<sub>3</sub> perovskites and the solar cells</i>	Shanghai University, China
Prof. Zhengguo Xiao	<i>Large-area perovskite LEDs made by blade coating</i>	University of Science and Technology of China, China
Prof. Sai Bai	<i>High-performance light-emitting diodes and transistors based on metal halide perovskites</i>	University of Electronic Science and Technology of China, China
Dr. Pavel Troshin	<i>Engineering Stable Interfaces for p-i-n Perovskite Solar Cells</i>	IPCP RAS, Russia
Dr. Alexey Tarasov	<i>Structural disorder and stability issues – two heels of Achilles of layered hybrid halide perovskites</i>	Lomonosov Moscow State University, Russia

С приглашёнными докладами выступили:

Dr. Lubov Frolova	<i>Molecular modified all-inorganic perovskites with enhanced stability toward light and gamma rays exposure</i>	IPCP RAS, Russia
Prof. Sergey Makarov	<i>Perovskite microlasers: from material design to on-chip integration</i>	ITMO, Russia
Dr. Yury Kapitonov	<i>Lasing in halide perovskites</i>	St. Peterburg University, Russia
Dr. Sergey Adonin	<i>Supramolecular approaches towards the design of lead-free halometalate light absorbers</i>	Nikolaev Institute of Inorganic Chemistry of the Siberian Branch of the RAS, Russia
Dr. Narges Yaghoobi Nia	<i>High performance semitransparent perovskite solar cell and modules on flexible and rigid substrate for tandem application</i>	Tor Vergata University of Rome, Italy
Prof. Jixian Xu	<i>Materials interface engineering in perovskite-silicon tandems</i>	University of Science and Technology of China, China
Dr. Yuriy Luponosov	<i>Development of organic charge-transporting materials for perovskite solar cells</i>	ISPM RAS, Russia
Prof. Weidong Xu	<i>High-performance self-healable perovskite light-emitting diodes"</i>	Northwestern Polytechnical University, China
Prof. Weihua Ning	<i>Lead-free Perovskites for Optoelectronic and Spintronic Applications</i>	Soochow University, China
Dr. Danila Saranin	<i>Quantification of defect parameters and interface engineering for PCSs</i>	NUST MISiS, Russia
Prof. Jianjun Tian	<i>High efficiency and purity perovskite quantum-dot light-emitting diodes</i>	Institute for Advanced Materials Technology Beijing, China
Prof. Ivan Scheblykin	<i>Defect metastability in metal halide perovskites</i>	Lund University, Sweden
Prof. Mikhail Avdeev	<i>Structural studies of nanocomposite perovskite materials for photovoltaics at neutron and synchrotron sources</i>	Joint Institute for Nuclear Research, Dubna, Russia
Dr. Ivan Turkevych	<i>Strategies for efficiency improvement of rudorffite solar cells</i>	AIST, Japan

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## Структурные исследования нанокompозитных перовскитных материалов для фотовольтаики на нейтронных и синхротронных источниках

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В настоящее время большой интерес представляют нанокompозитные перовскитные материалы для фотовольтаики благодаря сравнительно простому и эргономичному процессу их изготовления в сочетании с возможностью тонкой регулировки электронных свойств. Наряду с оптимизацией материалов для многослойных структур (в отношении контакта и идеального выравнивания энергетических уровней между слоями) с целью улучшения характеристик конечных солнечных элементов, также остро стоит вопрос обеспечения структурной устойчивости их компонент в условиях повышенных температуры и влажности. Последнее ограничивает реализацию такого рода материалов в промышленных масштабах. В этой связи, важными являются структурные исследования, в том числе на основе методов рассеяния нейтронного и синхротронного излучений.

Настоящий обзор представляет основные идеи и наработки использования нейтронных и синхротронных методов в структурных исследованиях нанокompозитных перовскитных материалов для фотовольтаики, включая методы дифракции, рефлектометрии, малоуглового рассеяния и неупругого рассеяния. Полученные структурные и динамические данные позволяют устанавливать связь между структурой компонент фотоячеек на мезоскопическом уровне и их макроскопическими характеристиками в разных условиях. В свою очередь, понимание особенностей протекающих в них физико-химических процессов, позволяют формулировать рекомендации по составу и синтезу материалов для улучшения эффективности и стабильности перовскитных солнечных элементов.

Работа выполнена при поддержке гранта РФФИ [№22\_22\_00281].

## Влияние имплантация ионами Cs на атомный состав и структуру функциональных архитектур: стекло/ITO/TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>

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Гибридные органо-неорганические перовскитные материалы со смешанным катионом (ГОНП ПМСК) перспективны для применения в космической индустрии благодаря высокому коэффициенту поглощения фотонов оптического диапазона и массогабаритным характеристикам солнечных элементов на их основе (ПСЭ) [1]. В 2020 году немецкими физиками впервые было показана возможность работы ПСЭ в условиях космоса [2]. Представляет интерес идея создания таких структур на основе классических ГОНП (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>) путем имплантации высокоэнергетических ионов Cs. Цель данной работы заключалась в получении ПМСК из ГОНП с использованием ионной имплантации и исследовании ее влияния на атомный состав и кристаллическую структуру тонких пленок CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> на подложке стекло/ITO/TiO<sub>2</sub>.

Тонкие пленки CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> с планарной архитектурой были получены двухстадийным методом на подложке стекло/ITO/TiO<sub>2</sub>. Полученные пленки подвергались ионной имплантации ионами Cs<sup>+</sup> с энергией 100 и 200 кэВ с дозами 1 и 3•10<sup>13</sup> и 1 и 3•10<sup>14</sup>.

Рентгеноструктурный анализ показал, что при энергии имплантируемых ионов E<sub>Cs</sub> = 100 КэВ происходит увеличение количества тригональной фазы (соответствует PbI<sub>2</sub>) и уменьшение количества тетрагональной фазы (соответствует CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>). При энергии 200 КэВ наблюдается смещение основных пиков фаз, соответствующих PbI<sub>2</sub> и CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> в сторону меньших углов, что свидетельствует о частичном замещении атомов в узлах и увеличении межплоскостного расстояния.

Согласно данным ИК-анализа, облучение ионами Cs<sup>+</sup> не привело к деструкции органического катиона CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> в структуре CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. Показана пропорциональная зависимость глубины индуцированных имплантацией деструктивных изменений от величины энергии ионов.

С использованием энергодисперсионного спектрометра (EDS) показано наличие следующих элементов с соответствующим процентным содержанием: Pb – 32,16%; I – 56,04%; Ti – 4,00%; O – 2,94%; Sn – 4,86% в пленках перовскита, диоксида титана и ITO в составе многослойной структуры типа стекло/ITO/TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>.

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## Морфологические и оптические свойства перовскитных пленок $\text{MAPbI}_3$ , сформированных с использованием добавок

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Была изучена возможность модификации перовскитного слоя и улучшения его оптических характеристик с использованием углеродных точек и органических соединений в качестве добавок. Внесение добавок осуществлялось как их непосредственным включением в раствор прекурсора перовскита, так и добавлением в антирастворитель. Оба метода положительно повлияли на свойства пленки, о чем свидетельствует фотолюминесцентный анализ полученных слоев. На основе перовскитных слоев с улучшенными оптическими характеристиками были получены перовскитные солнечные элементы (ПСЭ) с более высокой эффективностью преобразования энергии.

## Дырочно-транспортные слои для перовскитных солнечных батарей на основе органических молекул с «якорными» группами

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Перовскитные солнечные батареи (ПСБ) имеют ряд преимуществ среди всех актуальных развивающихся фотоэлектрических технологий, поскольку могут достигать КПД сравнимых с неорганическими фотоэлементами на основе кремния, но при этом изготавливаться из дешевых материалов, малочувствительных к примесям и возможным дефектам с использованием современных экономичных печатных технологий производства. В современных ПСБ используются вспомогательные интерфейсные слои на основе органических материалов – электрон-транспортные и дырочно-транспортные слои. Они необходимы для улучшения транспорта зарядов, создания барьерного (от кислорода и влаги) эффекта, выравнивания разницы в энергетических уровнях между электродом и фотоактивным слоем и т.д. В случае дырочно-транспортных слоев острой проблемой является их плохая адгезия на поверхности неорганического электрода, поэтому для решения этой проблемы часто используют органические молекулы с «якорными группами», которые способны образовывать химическую или физическую связь с поверхностью металлов и их оксидов.

В ходе данной работы был проведен синтез 5-[4-(дифениламино)фенил]тиофен-2-карбоновой кислоты (ТРА-Т-СООН) на основе трифениламина – материала, обладающего подходящим уровнем ВЗМО и дырочной подвижностью в недопированном виде, с карбоксильной группой в качестве «якорной» функции для образования потенциально лучшей контактной поверхности с материалом электрода и/или перовскита в случае ПСБ, сопряженной с трифениламиновым фрагментом через тиофеновый спейсерный мостик. Изучены оптические, термические и электрохимические свойства молекулы. Полученные соединения были протестированы в качестве дырочно-проводящих материалов в недопированных перовскитных солнечных батареях, которые показали хорошие значения КПД - 20.3%, сравнимые с рекордными на текущий момент, а также стабильность приборных характеристик при воздействии внешних факторов деградации более 1000 ч.

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## Особенности переходных процессов в материале со смешанной проводимостью

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Исследование фотоэлектрических переходных процессов в перовскитных солнечных элементах является одним из многочисленных методических приёмов, применяемых для изучения физико-химических процессов ответственных за их высокую эффективность и все ещё недостаточную временную стабильность. Наиболее известные подходы такие, как импедансная спектроскопия и ее модификации, основаны на детектировании электрических сигналов в зависимости от частоты [1]. В данной работе изучаются процессы релаксации фотоэлектрического воздействия во временном домене, что приносит ряд преимуществ, таких как более высокая скорость измерений, так и возможность исследования близких по времени релаксационных процессов. В работе исследовался электрический отклик на ступеньку импульса света с микросекундными фронтами от светодиодов (AsGa,  $\lambda=450, 660$  нм,  $P=20-90$  мкВт.) Изучались ячейки следующего состава и конструкции: Glass/ITO/SnO<sub>2</sub>/PCVA/MAPi/PTA/VO<sub>x</sub>/Al/Glass.

Эквивалентные схемы получали путём подгонки тремя экспонентами различных участков кривых переходного тока. С помощью этой процедуры удалось выявить пять характерных времён релаксации, соответствующих пяти независимым накопителям энергии. Для эффективных ячеек имело место отсутствие длинновременных процессов, что можно объяснить малостью ионного вклада в процессы релаксации. В обоих типах ячеек (хранившихся 8 мес. на воздухе) проявилось также незначительное влияние ловушечных эффектов, часто имеющих доминирующее значение в органических фотодиодах, например, на основе фталоцианинов и фуллеренов [2]. Таким образом, так называемый метод расчленения или диакоптический подход [3] оказался весьма эффективным для исследования переходных процессов в перовскитных солнечных элементах. В результате было подтверждено значительное отрицательное влияние длинновременных процессов на характеристики изучаемых перовскитных элементов. Влияние глубоких ловушек на данном этапе старения образцов оказалось не существенным.

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## Supramolecular approaches towards the design of lead-free halometalate light absorbers

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Ability of halide complexes (hetero- or, more commonly, homoleptic) to form inclusion compounds with di- or polyhalogens via halogen bonding (XB) was noticed decades ago. Surprisingly, this feature was not systematically studied for years; after a long pause, this area experiences revival nowadays.

The talk covers the results obtained by our group within the last few years: the family of structurally diverse polyhalide-halometalates of bismuth, antimony, tellurium, tin, lead and some other elements, as well as their physical properties relevant to photovoltaics.

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## Temperature-Dependent Dynamics of the Light-Induced Degradation of MAPbI<sub>3</sub> and PbI<sub>2</sub> Thin Films

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The discovery of a family of semiconductor materials based on the complex halides of group 14 elements opened a big research arena and led to the emergence of a new perovskite photovoltaic technology. Impressive photovoltaic performances were demonstrated for perovskite solar cells based on lead halides, whereas their practical implementation is still severely impeded by the low device operational stability. Most importantly, complex lead halides were found sensitive to both light and heat, which are unavoidable satellites under the realistic solar cell operational conditions. Suppressing these intrinsic degradation pathways requires a thorough understanding of their mechanistic aspects. Herein, we explored the temperature effects in the light-induced decomposition of the model systems represented by MAPbI<sub>3</sub> and PbI<sub>2</sub> thin films under well-controlled anoxic conditions. We show that decreasing the sample temperature from 55 °C to 30 °C can extend the perovskite lifetime spectacularly by a factor of > 10-100 and also alter the material decomposition pathway. The analysis of the aging kinetics revealed that MAPbI<sub>3</sub> and PbI<sub>2</sub> photolysis have quite high effective activation energies of ~85 and ~106 kJ mol<sup>-1</sup>, respectively, which explain the observed strong effect of the temperature on the rate of the material photodecomposition. These findings suggest that controlling the temperature of the perovskite solar panels might be a key factor for reaching their long operational lifetimes (>20 years) required for the practical implementation of this promising technology.

## Benzotriindole-based donor-acceptor molecules: synthesis, properties and application in photovoltaic devices

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The design of novel organic semiconductor materials, as well as their use as an element base for the electronics and optoelectronic devices development has become an actively developing and economically justified area of fundamental and applied research in the last decade. Conjugated donor-acceptor organic materials have become an important class of materials owing to their unique optical and electronic properties and wide potential applications in organic electronic devices. 10,15-dihydro-5H-diindolo-[3,2-a:3',2'-c]carbazole (benzotriindole or triazatruxene) is a planar symmetric  $\pi$ -extended conjugated molecular structure that can be regarded as a symmetric indole cycle-trimer. Owing to both its planar electron-rich system and its easily modifiable NH moieties, this molecule offers great potential application in the field of organic electronic devices.

Here we report on an efficient synthesis and comprehensive properties studies of novel conjugated donor-acceptor benzotriindole-based oligomers. These molecules contain different electron-withdrawing groups, which are linked through oligothiophene  $\pi$ -spacer with benzotriindole electron-donor core. Their thermal, optical, and electrochemical properties, as well as the phase behavior were studied and compared. The analysis of the results obtained made it possible to establish a number of significant structurally inherent regularities and their influence on the efficiency of organic and perovskite photovoltaic devices in which the obtained small molecules were used as p-type organic semiconductors or hole transporting materials. [1,2]

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## **Vacuum evaporation of inorganic capping layers provides efficient encapsulation of perovskite solar cells**

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We introduce a simple and universal scalable encapsulation strategy for perovskite solar cells based on thermal vacuum evaporation of MgF<sub>2</sub> or MoO<sub>3-x</sub> capping layer followed by sealing the device with glass and UV-curable polymer. The proposed encapsulation method is beneficial to most of other known encapsulation approaches being fully harmless to perovskite and transporting layers and processible at room temperature. Vacuum deposition of the capping layer promotes efficient removal of water, oxygen and organic solvents residuals from the device prior to sealing and could be easily performed using standard equipment for metal electrodes deposition. The proposed strategy is transferrable to any lab-scale perovskite solar cells prototypes regardless their geometry and architecture and results in excellent stability of the devices in ambient air and long operating conditions. Upon the 1000 hours stability test at ambient air (30-60% RH), the cells preserved 92.9% of their initial efficiency in average under 1 Sun illumination at constant maximum power point tracking (MPPT, ISOS-L-1) and over 96% under storage in the dark (ISOS-D-1), thus evidencing for the high effectiveness of the proposed encapsulation approach.

## 2D-TMDs: an ideal blockbuster for interfacial layer to promote photo-induced charge transfer dynamics in PSCs

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Perovskite solar cells (PSCs) have come to the forefront in science as a highly promising alternative for renewable energy technologies, owing to their superb power-conversion efficiency along with cheap material cost, fascinating advantages of strong light harvesting, and particularly facile manufacturing techniques. However, due to the sandwich structure with multiple layers, the perovskite/charge transport layer (CTL) interfaces still remain the most sensitive part of the complete device by controlling the overall charge transfer dynamic and limiting both the device overall stability and performance.

The rapid pace of progress in graphene and atomic dimensionality-dependent unique properties in ultrathin graphene has led to an exploration of other 2D materials in the last few years. In particular, monolayers of transition metal dichalcogenides (TMDs) with lamellar structures have received significant attention in the scientific community owing to their exotic condensed-matter phenomena. 2D-TMDs are a promising class of direct bandgap semiconductors with outstanding chemical, physical and electronic properties, which can be further tuned by their synthesis route.

We introduce a few atom thick 2D-TMDs as an interfacial layer on perovskite to minimize the energy barrier, suppress the charge accumulation, and recombination while promoting charge transfer dynamics in the PSCs. By combining the interfacial layer in dopant-free PSCs, we achieved a pro-long stabilized efficiency with a significantly enhanced open-circuit voltage and fill factor. Our work put forward the deep experimental understanding of 2D-TMDs as an interfacial agent toward stabilized performances.

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## Structure, optical and scintillation properties of hybrid bromocuprates (I) based on methylammonium and formamidinium cations

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In recent years, inorganic halide cuprates (I) of composition  $A_mCu_nX_{n+m}$  ( $X = I^-, Br^-$ ;  $A = K^+, Rb^+, Cs^+$ ) have been proposed as promising materials for application in various fields of optoelectronics, including light-emitting diodes, photodetectors, and scintillator materials. These materials demonstrate record high light yields, good stability to external factors (moisture and oxygen), photoluminescence quantum yields close to 100%, and a large Stokes shift excluding self-absorption [1]. An alternative to these materials is hybrid halocuprates (HHs), in which the alkali cations is replaced with organic cations. This class of materials also demonstrates excellent optical properties; however, little is known about the possibility of using HHs as scintillation materials.

In this work, hybrid bromocuprates containing organic cations of methylammonium ( $CH_3NH_3^+ - MA^+$ ) and formamidinium ( $HC(NH_2)_2^+ - FA^+$ ) were studied for the first time. In particular, phases of the composition  $MA_2CuBr_3$  [2],  $FA_3CuBr_4$ ,  $MACu_2Br_3$ ,  $FACu_2Br_3$ ,  $MACuBr_2$ ,  $FACuBr_2$  were obtained in the forms of single crystals, powders and thin films.

The crystal structures parameters of the obtained compounds were determined by XRD. All crystal structures are either one-dimensional (endless chains of edge-sharing  $[CuBr_4]$  tetrahedra) or zero-dimensional (isolated  $[CuBr_4]$  tetrahedra); the dimensionality of the phases reduces with increase of the A:Cu ratio. The absorption edge of the studied phases was estimated to be in the range of 300-410 nm. It was demonstrated that the  $ACuBr_2$  and  $ACu_2Br_3$  compounds exhibit photoluminescence only at low temperatures (70-120 K,  $\lambda_{max} = 600-610$  nm for  $ACu_2Br_3$ ,  $\lambda_{max} = 480-540$  nm for  $ACuBr_2$ ), while the  $MA_2CuBr_3$  phase demonstrates bright green photoluminescence at room temperature ( $\lambda_{max} = 515$  nm) with PL QY up to 90%. The clear trend of the bandgap broadening and  $PL_{max}$  blue shift with the A:Cu ratio increase (and corresponding reduce of dimensionality) can be observed for both  $MA^+$ - and  $FA^+$ -containing phases.

Under the radiation of X-ray tubes with silver and copper anodes  $MA_2CuBr_3$  exhibits bright radioluminescence ( $\lambda_{max} = 520$  nm) even at room temperature. The light yield of the  $MA_2CuBr_3$  was estimated as 13700 photons/MeV, which is a relatively high value for a hybrid and polycrystalline material [3]. At present,  $MA_2CuBr_3$  is the second discovered hybrid halocuprate exhibiting radioluminescence at room temperature. The obtained results demonstrate the perspective of using hybrid bromocuprates, in particular the  $MA_2CuBr_3$ , as materials for scintillation detectors.

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## FT-IR spectroscopic studies of hybrid perovskite

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Hybrid organic-inorganic perovskites, with the general chemical formula  $ABX_3$  (A being the organic cation, B – Pb, and X – Br or I) exhibit a rich structural and electronic behavior which is influenced by the complex interactions between the organic and inorganic subunits.

The method of infrared (IR) spectroscopy in combination with special devices, such as vacuum variable-temperature cells and reactors, makes it possible to obtain unique information about the interactions and transformations in dispersed solids.

In our work, we have applied an IR cell specially developed in our laboratory [1] which is used to register the spectra of fine powders, molecules adsorbed on their surface, and of surface species during heterogeneous catalytic and photocatalytic reactions.

Here experimental setup details were presented. IR spectroscopic study of powder samples of methylammonium lead halide ( $MAPb(I_3/Br_3)$ ) and pyridinium lead halide ( $PyHPb(I_3/Br_3)$ ) perovskites were carried out at room temperature. All samples studied were synthesized in our laboratory.

For the  $MAPbBr_3$  perovskite sample, the kinetic dependencies of its IR spectrum during the photoexcitation of solid in different spectral regions were obtained.

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## Solubility of hybrid perovskites and their precursors in aprotic solvents

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Hybrid perovskites with a general formula APbX<sub>3</sub> (A = CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>, HC(NH<sub>2</sub>)<sub>2</sub><sup>+</sup>, Cs<sup>+</sup>; X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>) represent a promising class of compounds for application in photovoltaics and optoelectronics. Based on perovskite materials, a new type of highly efficient solar cells with record efficiency 25.7% [1] are produced.

Dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and gamma-butyrolactone (GBL) are the most frequently used solvents to obtain hybrid perovskites, either in a form of polycrystalline films or as single crystals.

Although perovskite solutions with concentrations > 1 M are commonly used, the solubility of single precursors, as well as the perovskites with different compositions, are almost never reported.

In this study, we present a complete set of solubility data for MAPbI<sub>3</sub>, FAPbI<sub>3</sub>, MAPbBr<sub>3</sub> and FAPbBr<sub>3</sub> perovskites in DMF and DMSO, and rationalize the observed differences in solubility by analyzing the donor numbers of the solvents and halide anions.

The solubilities of MAPbI<sub>3</sub> and FAPbI<sub>3</sub> in DMF were found to increase with temperature up to 90 °C, unlike MAPbBr<sub>3</sub> and FAPbBr<sub>3</sub> which demonstrate the retrograde solubility behavior and lower solubility values. The solubilities of MAPbI<sub>3</sub>, FAPbI<sub>3</sub> and FAPbBr<sub>3</sub> in DMSO are found to increase with temperature while the solubility of MAPbBr<sub>3</sub> demonstrates a maximum at 60–75 °C and slightly decreases upon further temperature increase.

To further understand the effect of mixed compositions on the total solubility of the perovskite, we also measured the solubility of (MAPbBr<sub>3</sub>)<sub>0.15</sub>(FAPbI<sub>3</sub>)<sub>0.85</sub> at 30 °C and 90 °C in DMF and DMSO. The results show that the solubility in DMF and DMSO at 30 °C is higher than that for the pure components FAPbI<sub>3</sub> and MAPbBr<sub>3</sub>. Contrastingly, the solubility in DMSO at 30 °C lies between the solubilities of the pure components. At 90 °C, the solubility of the perovskite in DMF is also much higher than that for the pure components reaching, whereas it is almost the same in DMSO as the solubility of FAPbI<sub>3</sub>. The solubility of (MAPbBr<sub>3</sub>)<sub>0.15</sub>(FAPbI<sub>3</sub>)<sub>0.85</sub> in a mixed DMF/DMSO solvent was found to be slightly larger than that in pure DMF [2].

Based on the results obtained we conclude that solutions formed by a solvent with a relatively large donor number and a perovskite with a relatively high donor number of the halide anions demonstrate a direct solubility behavior. A relative increase in the halide donor number leads to the inverse solubility behavior when also taking into account the difference in the lattice energies of perovskites with different compositions and formation of intermediate phases [3]. Eventually, solvents with lower donor numbers (i.e., GBL) are unable to dissolve hybrid perovskites with halides of higher donor numbers which simultaneously have stronger interactions in a solid state. Relatively small donor numbers of a solvent, with respect to the donor number of a halide of a corresponding perovskite, lead to the insolubility of such perovskite phases, while a relatively high donor number of the halide anions would result in direct solubility behavior.

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## Unveiling the microstructural and optical properties of graphene-derived metal oxide-based all-inorganic CsSnBr<sub>3</sub> layer for ecofriendly flexible perovskite solar cell applications

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The growing energy need and rapid consumption of conventional energy resources motivated researchers to find feasible and cheap alternative resources. The wafer-based crystalline silicon photovoltaics is a commonly used solar cell technology, but it has high-cost and limited stock. Nowadays, perovskite solar cells have emerged as a promising next-generation photovoltaic technology due to their low cost. A remarkable power-conversion efficiency (24.7%) has been demonstrated for organic-based perovskite solar cells. Still, these are most degradable and less stable as the performance degrades rapidly because these perovskite materials decompose under ambient (moisture and elevated temperature) conditions. Therefore, the instability of perovskites is a significant challenge in commercializing this solar cell technology. Since different solvent and material engineering can tailor the material properties and power-conversion efficiency, a study on the microstructural and optical properties of graphene-derived metal oxide-based all-inorganic CsSnBr<sub>3</sub> perovskite layer is undertaken herein using Al<sub>2</sub>O<sub>3</sub> as an efficient scaffold layer to enhance the stability and performance. The fundamental aim is to improve the long-term stability and power conversion efficiency of CsSnBr<sub>3</sub> halide-based flexible perovskite solar cells through material engineering. An efficient Al<sub>2</sub>O<sub>3</sub> scaffold layer engineers CsSnBr<sub>3</sub> halide perovskite material to attain efficient charge transport and long-term stability. In different processing conditions, the self-optimized microstructural and optical properties of conventional and inverted graphene-derived metal oxide-based all-inorganic CsSnBr<sub>3</sub> interface structures are exploited to deposit a thin active absorber layer with larger grains and low trap state density to enhance the performance further. By doing so, we wish to significantly improve the stability of highly efficient eco-friendly flexible perovskite solar cells.

**s-SNOM investigation of photodegradation process in MAPI films**

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We applied IR s-SNOM technique for the first time to follow the nanoscale dynamics of the light-induced decomposition of MAPbI<sub>3</sub> films under well-controlled anoxic conditions inside the glove box.

The obtained results revealed that the light-induced aging of the MAPbI<sub>3</sub> films has a spatially heterogeneous character. The perovskite decomposition is started at the grain boundaries and is accompanied by the formation of core-shell structures, where the perovskite grains are covered with a “skin” of PbI<sub>2</sub>, which is the MAPbI<sub>3</sub> main aging product.

## Effect of intrinsic defects on photoluminescence of pristine and doped CsPbBr<sub>3</sub> perovskite

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We explored the effect of irradiation within fundamental absorption spectral range on excitonic photoluminescence in both pristine and doped micro-dispersed CsPbBr<sub>3</sub> halide perovskite. Heterovalent doping of CsPbBr<sub>3</sub> was achieved with Ag<sup>+</sup> and Bi<sup>3+</sup> cations at different dopant concentrations. It was demonstrated that light irradiation results in significant quenching of excitonic photoluminescence in pristine and Ag doped halide perovskite while for Bi doped CsPbBr<sub>3</sub> this effect is rather negligible.

It was demonstrated that photoluminescence quenching is strongly correlates with the number of photoinduced intrinsic defects in pristine and Ag doped CsPbBr<sub>3</sub> and the number of intrinsic defects compensating excess of the positive charge brought by Bi<sup>3+</sup> cations in Bi doped CsPbBr<sub>3</sub> [1]. Absorption spectra of photoinduced and Bi doping induced intrinsic defects demonstrate an apparent similarity that infers that they have similar origin [2]. The observed correlations between the number of the intrinsic defects and excitonic photoluminescence quenching suggest that exciton decay at the intrinsic defects is a reason for the luminescence behavior caused by either photoirradiation or Bi doping.

The correlation parameters (correlation slopes) indicate that effect of luminescence quenching depends on the type of cations at the defect site and increases as: Ag<sup>+</sup> < Pb<sup>2+</sup> < Bi<sup>3+</sup>. In other words, the higher is a positive charge of the cations at the defect sites, the less is a stability of the excitons and the higher is the efficiency of the exciton decay leading to luminescence quenching. In turn, it may imply that interaction between cations and electron component of excitons at the defect site is responsible for the exciton decay.

This finding can be used to manipulate a stability of the excitonic states and efficiency of photoluminescence in CsPbBr<sub>3</sub> perovskite. Particularly, the effect can be used for spatial modulation of excitons and excitonic luminescence in CsPbBr<sub>3</sub> using photolithography.

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## Self-assembled monolayer treatment of charge selective layers and usage as single ETL for p-i-n planar PSSC

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Perovskite solar cells (PSCs) are an emerging thin-film photovoltaic technology and exhibit high output characteristics (PCE > 25 %). To maximize the PCEs and stability of the inverted PSCs, the optimization of the electron and hole selective layers (ETLs and HTLs) and both interfaces is critical to promote an efficient charge transfer.

The recognized hole-transporting material for p-i-n PSCs is inorganic nickel oxide (NiO<sub>x</sub>) due its suitable characteristics: high mobilities of the holes (up to 101 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>), optimal valence band position (in range of - 5.4...5.2 eV) and large band gap (> 3.4 eV). However, NiO<sub>x</sub> layer has weak adhesion with perovskite absorber and induces formation of pinholes and trap states at the hole collection interface. In order to tune the NiO<sub>x</sub>/perovskite interface, we designed PSCs with self-assembled monolayer (SAM) – 2PACz.

SAMs have aroused extensive attention owing to unique ability to manipulate interfacial property, as well as simple solution processing, minimal parasitic absorption, scalable fabrication. The chemical structure of 2PACz ([2-(9H-Carbazol-9-yl)ethyl]phosphonic acid) included carbazole bodies with phosphonic acid anchoring groups permits to form specific 2 nm thick monolayers on various oxides (in our case is NiO<sub>x</sub>) and treat surface nonbonded atoms or surface dangling bonds making them robust interlayers and provide favourable conditions for charge extraction. Moreover, the stability of solar cells has been increased under light-soaking and thermal tests and prolonged more than 1400h. In another case 2PACz showed promising results as co-ETL to inorganic C<sub>60</sub> layer. Interestingly, that 2PACz can be deposited before C<sub>60</sub> and after ETL by spin-coating. The efficiency of the devices showed equal values 17.78 % and 17.85 % for (2PACz+C<sub>60</sub>) and (C<sub>60</sub>+2PACz) configurations.

And another point is ETL-free fabrication of ITO/NiO/2C/2PACz/Cu solar cells with 2PACz monolayer between perovskite and metal electrode with achieved 14.66 % of efficiency. Such behaviour of the PSCs suggests that the metal work function has been favorably altered by SAM incorporation, that created an energetically aligned interface to the perovskite absorber without non-radioactive losses.

Presented results demonstrated an effective strategy for improving the performance of a SAM-based perovskite solar cells.

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## Lasing in halide perovskites

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Halide perovskites are a promising medium for creating semiconductor lasers. Many of them are direct-gap semiconductors with efficient photoluminescence. With an increase in the optical pump intensity, one can observe amplified spontaneous emission, and the laser could be made by placing the material in a resonator. Numerous examples of microlasers based on halide perovskites are described in the literature. The main approaches are the creation of lasers based on perovskite films with external resonator, or microcrystalline lasers, when the crystal itself act as a resonator. In such systems, lasing can be observed at room temperature using pulsed optical pumping with kHz repetition rates. In most of these works, the lasing mechanism has not received sufficient attention. Spectroscopic studies could help shed light on the mechanisms of laser generation. In semiconductors, such studies are performed at cryogenic temperatures, which makes it possible to suppress thermal broadening. Single crystals could be used to reduce the inhomogeneous broadening. However, due to the complexity of mechanical processing of halide perovskites, the creation of resonators with single crystalline active medium is not possible.

In our group, we undertook a detailed study of the optical properties of single crystals of 3D halide perovskites at cryogenic temperatures. At such temperatures, the state with the highest oscillator strength is the free exciton [1]. Using photoluminescence excitation spectroscopy, it was found that the bound exciton state [2], which accounts for the photoluminescence maximum, is located lower in energy and is followed by the defect-related tail [3]. An unexpected solution for observing lasing in halide perovskite single crystals was random resonators formed on crystal cleavages. The random lasing was observed both in MAPbBr<sub>3</sub> [4] and MAPbI<sub>3</sub> [5] single crystals. The spectral position of the lasing clearly shows that the main lasing mechanism is the recombination on defect-related states, where the balance between gain and medium transparency is achieved.

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## Oxidative polymerization of triaryl amines as an efficient and scalable approach to the synthesis of HTL materials for perovskite solar cells

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Perovskite solar cells (PSCs) have achieved tremendous progress in terms of power conversion efficiencies (PCE) during the last decade which features a high commercialization potential of this PV technology. To achieve high PCE, significant efforts have been made to design and investigate new hole-transport layer (HTL) materials. Along with the spiro-OMeTAD, polytriaryl amines (PTAAs) represent one of the most commonly used families of HTL materials. However, even the most promising HTL materials delivering high PCEs will not bring PSCs towards commercialization if their high cost is not taken into consideration. Unfortunately, both spiro-OMeTAD and PTAA are prohibitively expensive materials with the current price of ~500 and ~2000 \$/g respectively.

Spiro-OMeTAD is expensive due to its multistep synthesis that requires low temperature, sensitive and aggressive reagents, and costly sublimation purification. The high cost of PTAA is driven by both complexity of the utilized synthetic methods, which often require several synthetic steps, and the high cost of metal-based catalysts, including noble metal complexes. For example, Pd-catalyzed Suzuki reaction has been actively utilized as the method of polycondensation of triaryl amines with halogen and boron-based functional groups. Unstable and pricey Ni(COD)<sub>2</sub> has also been utilized for the polymerization of brominated triaryl amines. Although the oxidative polymerization of aryl amines has been actively utilized for the synthesis of materials for electroluminescent devices, the application of this approach for the synthesis of HTL materials for perovskite solar cells remains still unexplored. Herein, we report a straightforward synthesis of a series of polytriaryl amines using an efficient and cheap FeCl<sub>3</sub>-assisted oxidative polymerization. This simple yet efficient synthetic approach allowed us to obtain a series of polytriaryl amines. These polymers outperformed commercial PTAA, which was utilized as a reference, when used as HTL materials in MAPbI<sub>3</sub>-based n-i-p perovskite solar cells. In particular, reproducible PCEs of >18% were reached for ITO|SnO<sub>2</sub>|PCBA|MAPbI<sub>3</sub>|HTL|VO<sub>x</sub>|Ag device configuration.

## Efficiency and stability enhancement of all slot die printed inverted perovskite solar cells with Mxene in electron transporting layer

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The current power conversion efficiency (PCE) record of perovskite solar cells (PSCs) has reached 25.7 % [1], that is comparable to the efficiency of other commercial solar cells. Nevertheless, the short lifetime and instability of device characteristics are the main reason hindering its development toward commercialization. Among promising strategies for the prolongation of stabilization of PSCs, interface engineering attracts considerable attention due to simple application in solution processing, preventing chemical decomposition induced by external agents and promoting fast charge transfer. Recently, MXenes, a class of two-dimensional inorganic compounds with various functionalization (=O, -F, -OH), demonstrated significantly effective improvement for the n-type charge collection in spin-coated PSCs [2]. Herein, we demonstrate the application of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> Mxene in solution processed electron transporting layers in the all slot-die printed PSCs with p-i-n structure for efficiency enhancement and long stability.

The four functional layers of devices, including NiO<sub>x</sub> (hole transporting layer - HTL), CsFAPbI<sub>3-x</sub>Cl<sub>x</sub> (absorber) and PCBM – BCP (electron transporting layers - ETLs), are printed in ambient conditions. By adding small amount of Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> into the PCBM and BCP solutions to form dispersions for printing process we found that, the interlayer BCP:Mxene and ETL based on PCBM:Mxene can slightly improve the device PCE from 17.7 % to nearly 18.2 % effectively enhance its stability. The Mxene device PCE reached the T80 point after 1700 hours under continuous light-soaking, while in the same measurement condition the device without Mxene exhibited less than 200 hours. The archived results proved that the BCP:MXene and PCBM:Mxene interaction with perovskite layer results in passivation of the surface states of Mxenes, which could slow down the degradation of the printed devices, thus, prolonged its lifetime in ambient condition.

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## Development of organic charge-transporting materials for perovskite solar cells

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Perovskite solar cells (PSCs) have several advantages among all the developing photovoltaic technologies: high power conversion efficiency (PCE) over 25 %; (ii) possibility of large-scale production using low-cost printing technologies; (iii) they can be produced from cheap materials having low sensitivity to impurities and defects [1]. The further enhancement of PSCs performance and more importantly their stability can be achieved through the usage of efficient hole-transporting layers (HTLs) based on novel dopant-free hole-transporting materials (HTMs).

In this talk a short overview of existing organic charge transporting materials diversity will be combined with our last results on developing of novel p-type and n-type organic semiconductors for perovskite and organic solar cells. The p-type materials will be presented by several classes including donor-acceptor small molecules of various architecture [2-4], triphenylamine-based polymers [5] and small molecules with “anchoring” groups. The n-type materials will be represented by fused A-D-A small molecules with low-lying LUMO levels [6]. Detail of the synthesis, investigation, and comparison of properties along with the results of testing of these materials in organic (PCE up to 17.7%) and perovskite (PCE over 20%) solar cells will be given as well [4,6].

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## Random lasing in MAPbI<sub>3</sub> halide perovskite single crystals

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Halide perovskites are a well-studied material for the production of solar cells. However, much less research is devoted to the study of halide perovskites as a radiating medium, in particular, as an active medium for lasers. Many studies devoted to lasing do not give a clear understanding of the mechanism of lasing due to the use of polycrystalline samples in them and the study at room temperature. In such a situation, the inhomogeneous and thermal broadenings are observed, respectively. The study of random lasing at cryogenic temperatures in single-crystal samples makes it possible to avoid these problems.

In this work spectral, temporal, polarimetric, and threshold measurements on MAPbI<sub>3</sub> single crystal are demonstrated to facilitate isolating random lasing from the photoluminescence background. Spectral localization of the lasing lines points to defect-related states emission as the lasing origin. Time-resolved photoluminescence study shows that the random lasing is emitted as an ultrashort pulse with a duration below 10 ps, and the photoluminescence background as a long 100 ps afterglow. The results obtained are the next step towards understanding, and, therefore, control of the mechanism of lasing in halide perovskites.

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## Investigation of the rational approach to improve stability of hybrid halide perovskite using 1,4-butanediammonium iodide

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Perovskite solar cells (PSCs) demonstrate remarkable power conversion efficiencies (PCE) up to 25.7%, being one of the most perspective types of thin-film photovoltaic devices. However, PSCs still suffer from low exploitation stability mostly due to the degradation of light harvesting perovskite materials. There are several approaches to protect hybrid perovskites from degradation under light, moisture, and heat including application of 2D perovskites or 2D/3D heterostructures as well as the control of surface and bulk defects in perovskite materials and interfaces. Diammonium cations are considered as a promising passivating agent as well as a perspective component of 2D perovskites, due to the low deprotonation ability and the absence of van der Waals gap in 2D perovskite structures. However, there are still a lack of experimental data regarding the use of diammonium cations in PSCs, and the available results are controversial in terms of the most effective approach to introduce diammonium cations into light harvesting material for the enhancement of both the performance and long-term stability of PSCs.

In this study, we verify the possibility of solution synthesis of 1,4-butanediammonium-based (BDA)(MA)<sub>n-1</sub>Pb<sub>n</sub>I<sub>3n+1</sub> phases with  $n = 2, 3$ . We found that only (BDA)PbI<sub>4</sub> structure with  $n=1$  could be obtained both as a film and as a single crystal. However, higher  $n$  members of (BDA)(MA)<sub>n-1</sub>Pb<sub>n</sub>I<sub>3n+1</sub> compositional row demonstrate thermodynamic instability in favor of simultaneous crystallization of 3D MAPbI<sub>3</sub> and 2D (BDA)PbI<sub>4</sub> phases. This result was obtained by several independent experiments supporting the presence of a thermodynamic barrier to obtain BDA-based layered compounds with  $n > 1$ .

Another approach to introduce BDA<sup>2+</sup> cations into perovskite material is a bulk passivation of 3D perovskite films with small amounts of BDAI<sub>2</sub> additive. This type of additive can passivate vacancies  $V_A'$  and  $V_I'$  and accumulate at grain boundaries in polycrystalline perovskite films. We investigated the effect of BDAI<sub>2</sub> bulk additives on crystal structure, optical properties, and stability of hybrid perovskites with different composition (FA<sub>0.75</sub>MA<sub>0.25</sub>PbI<sub>3</sub> and FA<sub>0.85</sub>CS<sub>0.15</sub>PbI<sub>3</sub>). We found a threshold amount of BDAI<sub>2</sub> equal to 1% allowing to maintain proper charge carrier lifetimes, average grain size, and PCE of PSCs. The photostability of both perovskite films and PSCs noticeably increases already after 0.25% additive amount and proportionally enhances with further BDAI<sub>2</sub> addition. All the passivated devices preserve from 50 to 80% of the initial PCE after 400 hours of continuous 1 sun irradiation with stabilized temperature 65°C while control devices completely lose their performance already after 170 hours of the experiment.

Summing up, 1,4-butanediammonium iodide is a unsuitable spacer cation for 2D hybrid perovskites with  $n > 1$ . The more perspective application of such diammonium cations is a bulk passivation of 3D lead iodide perovskites with small amounts of BDAI<sub>2</sub> (<1% with respect to Pb) which allows to simultaneously increase PCE and photothermal stability of PSCs.

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## Single-step chemical vapor deposition of methyl ammonium lead halide perovskite for p-i-n solar cells

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Metal halide perovskite solar cells being one of the fastest emerging technology for renewable energy still has to become more industry friendly in a way that will allow using it for thin film modules or in tandems with conventional silicon devices. The simplest way to achieve this is to use chemical vapor deposition (CVD) technique for tandem production. In this work, we show a method for a single step production of MAPbI<sub>3</sub> films in a simple two-zone CVD reactor from lead diacetate and methylammonium iodide powders. Obtained films show highly ordered cubic MAPbI<sub>3</sub> phase with a thickness of 400-500 nm, good photoluminescence response and absorption band edge similar to spin-coated film. We used those films to produce p-i-n solar cells with ITO/NiO/MAPbI<sub>3</sub>/C60/Cu structure. The best pixels showed negligible 0.23 % PCE right after the manufacturing but significantly improved to 5.5 % PCE after 8 hours of storage in the dark. The main limiting factor affecting the efficiency is low current density, which we attribute to non-optimized growth conditions; however, our approach is a first step to a single step CVD deposition of MAPbI<sub>3</sub> on any type of substrates including texturized silicon subcells for better overall efficiency.

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## Diffuse reflectance spectroscopy with dilution: a powerful method for halide perovskites study

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Halide perovskites and their low-dimensional analogs are promising semiconductor materials for solar cells, light-emitting diodes, lasers, detectors and other applications in the field of photonics. The most informative optical property of photonic materials is the absorption spectrum, which makes it possible to observe the fundamental absorption edge, exciton structure, defect bands, etc. Traditionally, when studying halide perovskites, this spectrum is obtained using thin film absorption spectroscopy or diffuse reflection spectroscopy of powders. The first method is applicable only to compounds with the developed technology of thin-film deposition, and in the second case, a large absorption coefficient narrows the observations to the transparency region. We demonstrate diffuse reflectance spectroscopy with dilution as a method for obtaining the full reflectance spectrum from halide perovskite powders and its application to practically important cases. Grounded single crystals of halide perovskites, such as MAPbI<sub>3</sub>, MAPbBr<sub>3</sub> and MAPbBr<sub>3</sub> doped with bismuth, as well as one-dimensional perovskite PyPbI<sub>3</sub> were chosen as the samples under study. When diluted, the true structure of the diffuse reflectance spectra becomes visible, otherwise hidden behind the strong absorption of the material. Further processing based on the Kubelka-Munk transformation and the Bouguer-Lambert law makes it possible to obtain absorption spectra that are consistent with the literature data for thin films. The dependence of the phase transition in MAPbI<sub>3</sub> between the tetragonal and orthorhombic phases was also studied, which found agreement with the literature data.

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## Highly efficient light-trapping electrode for the perovskite solar cells

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Perovskite materials possess excellent optical and electrical characteristics, and hence, their use for solar cells attracts tremendous interest [1]. The simplest design for solar cells is a one-sided (monofacial) structure with front traditional electrodes based on transparent conducting oxides, such as FTO and ITO, and a non-transmitting metallic contact. Such solar cells exhibit high efficiency up to 25.7% [2]. Meanwhile, bifacial perovskite solar cells (PSCs) structures consist of two transparent electrodes and have recently drawn growing attention [3]. A bifacial structure increases the solar cell efficiency by harvesting the reflected light. However, the use of such PSCs is hindered by their low light absorption in the active layer due to high optical losses, which leads to a photocurrent reduction and, as a result, a decrease in the power conversion efficiency. These losses arise due to significant parasitic absorption of transparent conducting oxides (ITO, FTO). Moreover, due to the high transparency of such electrodes and their refractive index values of  $n = 1.8$ , similar to those of photoactive perovskites, unabsorbed photons can easily escape the device volume, making the conventional PSCs less efficient than cells with metallic top contact. Replacing ITO with a highly reflective material is a sensible strategy to keep the radiation in the structure. In addition, ITO and FTO have a high sheet resistance, which reduces the power conversion efficiency. Metals, especially Al and Au, have better optical and electrical properties than ITO, which makes them effective for use in solar cells [4].

Moreover, to increase the generation rate in the perovskite photoactive layer and enhance the energy conversion efficiency of PSCs, light-trapping structures improving the light absorption in the active layer can be introduced. The efficiency of antireflective PSCs increases by 8.6% compared to the planar reference solar cells [5].

In our work, we introduce a method using a light-trapping electrode (LTE) implemented as a perforated metal electrode with densely packed dielectric nanospheres. In semi-transparent PSCs, this structure can serve as an alternative to the traditional transparent electrodes based on conducting oxides such as ITO or FTO. We have performed optical and electrical modeling of our PSCs and show that our structures significantly improve the efficiency of light conversion and current generation. We have observed an 11% improvement in the light absorption for the monofacial PSCs, and a 15% for the bifacial PSCs. The best theoretical results of efficiency for our PSCs are 27.9% (monofacial) and 33.4% (bifacial). Thus, our electrode based on the light-trapping strategy is one of the best candidates to replace the classic transparent conducting oxides such as ITO or FTO. We show that our structure has excellent characteristics, improving the efficiency of light conversion and current generation.

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## Using azaadamantane derivatives for improving thermal and photochemical stability of multication lead halide perovskites

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Complex lead halides incorporating simultaneously a few univalent cations such as cesium (Cs<sup>+</sup>), methylammonium (MA<sup>+</sup>) and formamidinium (FA<sup>+</sup>) represent highly promising materials for perovskite solar cells delivering record-high power conversion efficiencies. Unfortunately, these materials demonstrate insufficient stability, which limits their practical implementation; therefore, improving the photochemical and thermal stability of multication lead halide perovskites is an urgent task, which needs to be addressed to achieve sufficiently long operational lifetimes of perovskite solar cells which are required for their massive real-life applications. Herein, we present a comparative study of two azaadamantane-based molecular modifiers as stabilizing additives for Cs<sub>0.10</sub>MA<sub>0.15</sub>FA<sub>0.75</sub>PbI<sub>3</sub> and Cs<sub>0.12</sub>FA<sub>0.88</sub>PbI<sub>3</sub> perovskite formulations. An iodide of N-methylated 1,3,5,7-tetraazaadamantane known as urotropine (MAdI) showed a modest stabilizing effect reflected in a decreased amount of PbI<sub>2</sub> formed as the decomposition product from Cs<sub>0.10</sub>MA<sub>0.15</sub>FA<sub>0.75</sub>PbI<sub>3</sub> and suppressed light-induced crystallization of Cs<sub>0.12</sub>FA<sub>0.88</sub>PbI<sub>3</sub>. On the contrary, 4,6,10-trihydroxy-1,4,6,10-tetraazaadamantane hydrochloride (NAdCl) strongly enhanced the stability of both lead halide perovskites and prevented the formation of metallic lead Pb<sup>0</sup> as a photolysis product. Different stabilizing effects caused by MAdI and NAdCl were related to their different localization within the perovskite films as evidenced by nanoscale infrared (IR) s-SNOM microscopy.

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## Synthesis and properties of new non-fullerene organic n-type materials as electron transport layers based on A-D-A conjugated oligomers

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Perovskite photovoltaics is an intensively developing area. In perovskite solar cells (PSCs), the electron transport layer (ETL) extracts and transports electrons from the perovskite light absorption layer to the cathode, which plays an important role in improving the performance and long-term stability of the devices. Traditionally, the widely used ETL materials in PSCs are fullerenes (C60, C70) and their soluble form phenyl-C61-butyric acid methyl ester. However, compared with fullerene derivatives, non-fullerene n-type organic semiconductors have some unique advantages, such as molecular structure diversity, easy in modification, adjustable frontier molecular orbitals, good solubility in different organic solvents, and optimal thermal stability.

Recently, non-fullerene electron transport materials (ETMs) have attracted more and more attention as efficient ETLs in PSCs. This work presents the synthesis of three novel non-fullerene acceptor molecules: BTPT-OD, BTPT-4F-OD, TPIIC, which are conjugated compounds of donor-acceptor structure with a central condensed electron-donor fragment and end strong electron-acceptor groups. The chemical structure of the compounds were proved by <sup>1</sup>H NMR, <sup>13</sup>C NMR techniques and by MALDI mass spectrometry analysis. Experimental optical and electrochemical properties, thermal stability, phase behavior as well as electron transport characteristics have been extensively investigated and compared.

The compounds are characterized by a high thermal and photo stability, efficient sunlight absorption in the red and near-infrared spectral ranges, good solubility combined with a high degree of crystallinity and possess appropriate energy levels of HOMO and LUMO levels to be used as ETL in PSCs. The data obtained in the analysis of charge transport properties show, that new non-fullerene acceptor molecules achieve high electron mobility and outstanding power conversion efficiency (up to 17.7%) in organic solar cells and potentially can be used as ETLs in PSCs.

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## There's plenty of phases at the bottom: remarkable diversity of formamidinium-based low-dimensional perovskites

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Hybrid halide perovskites (HHPs) are a growing class of semiconductors, attracting great and increasing attention of the world scientific community owing to their unique set of optical and electronic properties, such as direct band gaps, high optical absorption coefficients, long charge carrier lifetime, and remarkable tolerance to defects, making them almost ideal materials for photovoltaics and optoelectronics. Another unique feature of the halide perovskite family is the unprecedented structural flexibility expressed in the ability to adopt dimensionally reduced structures across the full range of 3D to 0D inorganic frameworks.

The majority of structural design strategies for hybrid compounds are based on the concept of achieving the desired dimensionality by introducing bulk organic cations that act as a template for the structure. In this research we show alternative concept of dimensionality reduction through successive “cleavage” of the anionic framework of the parent perovskite compound  $\text{FAPbI}_3$  ( $\text{FA}^+ =$  formamidinium) by addition of AI salt ( $\text{A} = \text{FA}^+$  or  $\text{MA}^+$ ) to form a derivative low-dimensional perovskites (LDPs) with formula  $\text{A}_n\text{PbX}_{x+n}$ . Particularly, we isolated and characterized for the first time three new formamidinium-based LDPs: the 1D  $\text{FA}_3\text{PbI}_5$ , the 2D  $(\text{FA}_{1-x}\text{MA}_x)_2\text{PbI}_4$  (110)-oriented layered perovskite and the “hollow” perovskite  $(\text{FA}_{1-x}\text{MA}_x)_{1.5}\text{PbI}_{3.5}$  with intermediate dimensionality between 3D and 2D. All phases were synthesized in powder form under mild equilibrium conditions via transport reaction in toluene using iodine as mass transfer mediator. The equilibrium nature of the was proved by synthesis from different precursors (binary iodides or ternary iodoplumbates) which allow us to identify the areas of homogeneity of different phases and to construct the first phase diagram of the  $\text{PbI}_2$ -MAI-FAI system.

The experimentally determined optical bandgap, photoluminescence maximum, and exciton binding energy of the formamidinium-based LDPs steadily increase with lowering the structural dimensionality. The observed trends are explained by fundamental dependence of the monotonic reducing of the electronic dimensionality with decreasing of the structural dimensionality. The performed ab-initio DFT calculations corroborate the increasing the bandgap in series  $3\text{D} < \text{“Hollow”} < 2\text{D} < 1\text{D}$  and also predict less dispersive the VBM and CBM for low-dimensional phases.

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## Refraction index near the excitonic resonance in MAPbI<sub>3</sub>

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The study of the optical properties of halide perovskites is necessary to understand the behavior of these materials in various optoelectronic devices. In this paper, we measured the optical reflection spectrum of MAPbI<sub>3</sub> single crystal under normal incidence of light.

In this configuration, the dependence of the reflection coefficient  $R$  on the photon energy  $E$  of bulk MAPbI<sub>3</sub> at liquid helium temperatures is characterized by the presence of a typical excitonic resonance curve. The position of the resonance is determined by the difference between the value of the band gap of MAPbI<sub>3</sub> and the binding energy of the exciton and is approximately 1.64 eV at the temperature  $T = 4$  K.

In our experiment, in addition to the exciton resonance, we observed oscillations at photon energies below the position of the resonance in the reflection spectrum of MAPbI<sub>3</sub>. We assume that a Fabry-Perot microresonator was formed as a result of the natural splitting of MAPbI<sub>3</sub> single crystal, and the observed oscillations are Fabry-Perot modes. Knowing the positions of the Fabry-Perot mode maxima and the cavity width makes it possible to determine the refractive index near the exciton resonance in MAPbI<sub>3</sub>.

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## Challenges for using CuSCN as hole transport material for perovskite solar cells

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In less than 15 years, halide perovskites have been one of the most studied material for optoelectronic and photovoltaic applications and have demonstrated remarkable results: in single-junction solar cells, their conversion efficiency has been increased from few percent to more than 25% close behind to the record efficiency of reference silicon devices [1,2], and in tandem solar cells, their combination with silicon absorber managed to overcome the theoretical limit of efficiency for single junction silicon cell with the certified efficiency approaching 30% [1,3].

Nevertheless, it remains many challenges for these materials: upscaling, stability, and choice of materials. For the later, one significant issue is to find alternative hole transport material (HTM) that could replace usual HTM such as PTAA and Spiro-OMeTAD that are costly. Among possibilities, copper(I) thiocyanate (CuSCN) appears as a promising material. Indeed, this inorganic p-type semiconductor has numerous advantages: low-cost, good electrical, optical properties, and thermal stability, well aligned work function with perovskite absorbers and low temperature deposition [4].

Despite these advantages, the use of CuSCN in perovskite devices remains low. First reports highlighted a potential degradation process at the interface between CuSCN and the perovskite [5]. But later Arora et al. showed the instability originated from the CuSCN/Au contact interface and demonstrated an efficiency of 20.8% by adding a reduced graphene oxide spacer at this interface [6]. In inverted structure, there are few reports, and with modest efficiencies ~17% [7].

In this work, we present the challenges of using CuSCN as hole transport material for perovskite solar cells. The interaction between this HTM and the perovskite solution is first shown. Then different solutions to overcome this problem are investigated.

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## Quantification of defect parameters and interface engineering for PCSs

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The long-term stability of halide perovskite solar cells (PSCs) is still the challenge for real exploitation. Defects formed in the thin-film perovskite films – vacancies, antisites and interstitials were considered as a main trigger for corrosion of the interfaces and electrochemical degradation of the electrodes. The quantification of the defects in the semiconductor devices is well established topic however It's still not widely used for PSCs. The complexity of different corrosion processes in the device architecture require analysis for the numerical parameters of the defects associated with external stress. In this investigation we performed the complex analysis using admittance and deep-level transient spectroscopy (DLTS) for p-i-n PCSs under continuous light soaking stress. We found the various doping methods tunes the activation energy of the defects and despite the gain of the performance have the impact to the long-term stability. The analysis showed that hybrid perovskite compositions with iodide at X-site position of the ABX<sub>3</sub> molecule have tendency to form three kinds of the charged with range of E<sub>a</sub> from 0.30 up to 0.80 eV. Identification of the defects demonstrated that doping interface engineering methods realized for the multi-cation PSCs suppressed the formation of the antisite defects and interstitials. The changes in the defect's energy levels after continuous light soaking stress with respect to different doping/passivation methods were discussed. The present work provides new insights for the defect behavior of PSCs under continuous external stress, reveals the critical points for the passivation of the defects.

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## **Modulation of charge carrier lifetimes through the perovskite interfacial engineering**

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The presence of defects in the perovskite layer and its interfaces within a lead halide perovskite solar cell (PSC) is detrimental for its durability and performance, and therefore should be controlled or even eliminated. One of the defect types having a major effect on the stability and photovoltaic efficiency of PSC is iodine vacancy. However, its role in the PSC degradation and performance loss is still not understood, and only few synthetic approaches are proposed to tackle with the problem of VI formation and its detrimental impact. In this work, the formation of shallow and deep trap states of VI at the surfaces and interfaces of FAPbI<sub>3</sub> is investigated. The formation energies, charge transition levels and polaron structures associated with VI are modelled from the first principles, and the impact of these parameters on the charge carrier recombination process, which ultimately affects the PSC efficiency and longevity, is analyzed. Then, the approaches for the interfacial engineering aiming at the reduction of vacancy concentration are considered and their impact on the electron structure and charge carrier recombination process is analyzed from the theoretical perspective.

## Semi-transparent perovskite solar cells with Ion Beam Sputtering top-contact and anti-reflection coating

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The perovskite photovoltaics (PV) is a prominent part of modern technologies reduces the strain in the conventional energy generation approach and endorses the prospectiveness of renewable energy. From the power conversion efficiency standpoint of view, perovskite solar cells are consistently improving, and more and more exciting challenges are encountered [1].

One such a crucial challenge is to increase the photon availability for PV conversion. This challenge solved by using texturized surfaces or antireflection coatings (ARCs) as mono- and multi-layers [2]. The main disadvantage of ARC monolayer is that it reduces reflectance only at a specific wavelength and ARCs efficiency decrease as the angle of light incidence varies from normal incidence due to the difference in optical path length at oblique angles relative to a normal angle [3]. There is limitation of materials, suitable for using as a single layer with a low reflectance index [4].

In this work as a photo-absorbing layer we used multi-cation perovskite  $\text{Cs}_{0.2}\text{FA}_{0.8}\text{Pb}(\text{Br}_{0.25-x}\text{I}_{0.75}\text{Cl}_x)_3$  (band gap - 1.73 eV) and triple-cation perovskite  $\text{FA}_{0.85}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.85}\text{Br}_{0.15})_3\text{Cs}_x$  (band gap - 1.59 eV). We fabricated opaque perovskite solar cells (PSC) and semi-transparent PSCs using NaF (1.5 and 3 nm) as an adhesion layer and  $\text{MgF}_2$  as the ARC layer. For the semitransparent structures, we used the transparent ITO electrode (210 nm) deposited with the ion-beam sputtering technique (low temperature method).

The use of  $\text{MgF}_2$  showed a great increase of current density. The PSCs with NaF 1.5 and 3 nm without ARC - PCE=8.4/4.1 %,  $V_{oc}$ =0.92/0.65 V,  $J_{sc}$ =17.6/18.5 mA/cm<sup>2</sup> and FF = 52/34 %. The PSCs with NaF 1.5 and 3 nm with ARC - PCE=9.5/12.3 %,  $V_{oc}$ =0.86/0.88 V,  $J_{sc}$ =23.5/24.2 mA/cm<sup>2</sup> and FF = 47/58 %. To confirm the received data we also obtained EQE spectra where the structures were measured from top and back sides. The PSCs with NaF 3 nm without ARC  $J_{sc}$ =17.36/15.57 mA/cm<sup>2</sup> and for PSCs with NaF 3 nm with ARC  $J_{sc}$ =20.85/19.67 mA/cm<sup>2</sup>. These results will help advance the fabrication of PSCs that maximize the conversion of sunlight.

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## High efficiency and purity perovskite quantum-dot light-emitting diodes

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We achieved high efficiency pure-blue and -red LEDs based on the perovskite QDs:

(1) Pure-blue (electroluminescence at 469 nm) PeLEDs with full-width at half-maximum (FWHM) of 21 nm, high external quantum efficiency (EQE) of 10.3 %, luminance of 12,060 cd/m<sup>2</sup>, and continuous operation half-life (T50) of 59 hours at initial luminance of 100 cd m<sup>-2</sup>, representing the best performance for the pure-blue perovskite LEDs.

(2) Pure-red (emitting at 636 nm) PeLEDs with Commission Internationale de l'Eclairage (CIE) coordinates (0.703, 0.297) meeting the Rec. 2020 standard, high EQE of 20.8%, luminance of 3,775 cd/m<sup>2</sup> and excellent stability, representing one of the best pure-red perovskite LEDs.

## Mie-resonant halide perovskite superlattices

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Lead halide perovskites present a new class of promising materials with outstanding optoelectronic properties which applied as light-emitting devices [1] and solar cells [2]. Additionally, perovskite nanocrystals have a high quantum yield of photoluminescence [3], which is an important characteristic for creating a light nanosource. By self-assembling, these nanocrystals can form ordered three-dimensional arrays also known as superlattices [4]. Due to a relatively high refractive index of lead halide perovskites, it is possible to apply Mie resonances to enhance emitting properties [5]. In this work, we study the photoluminescence of lead halide superlattices supporting Mie resonances in the optical range.

We have synthesized lead halide perovskites spherical superlattices assembled from CsPbBr<sub>3</sub> nanocrystals obtained the hot injection method with diameters from 100 nm to 400 nm. We studied photoluminescence from separated superlattices with different size at the temperature of 6K. All nanoparticles demonstrated two peaks in photoluminescence spectra, that exhibited redshift with the increase in particle size. We attribute this shift to the polaritonic effect in such an ordered array of quantum dots, which was theoretically described earlier [6]. Our experimental results have good agreement with the theoretical calculations based on the model mentioned.

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## Strategies for efficiency improvement of rudorffite solar cells

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Perovskite photovoltaics (PV) is becoming a competitive technology to CIGS, CdTe and crystalline Si solar cells. However, the issue of Pb toxicity still remains an obstacle that can hinder potential of perovskite PV. In my presentation I am going to review recent progress in photovoltaic cells based on non-toxic iodobismuthates with rudorffite structure. In contrast to double-perovskites  $C_2ABX_6$  ( $C=Cs, MA; A=Ag, Cu; B=Bi, Sb; X=Br, I$ ) consisting of corner shared  $AX_6$  and  $BX_6$  octahedra and hybrid  $C_3B_2X_9$  halides, such as  $MA_3Bi_2I_9$ , consisting of isolated face-shared  $B_2X_9$  bioctahedra, materials with rudorffite structure have a general formula of  $A_aB_bX_x$  ( $A=Ag, Cu; B=Bi, Sb; X=Br, I$ , and  $x=a+3b$ ) with the crystal lattice consisting of edge-shared  $AX_6$  and  $BX_6$  octahedra. Several members of this family, such as  $Ag_3BiI_6$ ,  $Ag_2BiI_5$ ,  $AgBiI_4$ ,  $AgBi_2I_7$ , have been extensively studied for solar cell applications during the last five years. Ag-Bi-I rudorffites are characterized with direct bandgaps in the range of 1.76-1.83 eV corresponding to possible PCE of up to 18% for optimized solar cells by assuming typical optical and electronic losses. It turns out, however, that rudorffite solar cells do not follow the rapid PCE improvement trend that we observed for Pb-based hybrid perovskites. In contrast to electronically clean hybrid perovskites, where native point defects usually do not create mid-gap recombination levels, rudorffites are not blessed with defect tolerance. Furthermore, the solvent-assisted fabrication methods inevitably produce morphologically defective rudorffite films due to high content of solvent molecules in the intermediary adducts. In addition, Ag-Bi-I rudorffite films are not stable in contact with tert-butyl pyridine and acetonitrile, which are necessary additives for the effective doping of spiro-OMeTAD with LiTFSI, which turns the fabrication of effective hole-transport layers into a difficult issue. Here I am going to present strategies for the fabrication of morphologically perfect rudorffite layers through iodination of Ag-Bi bimetallic films and application of pre-doping of spiro-OMeTAD with subsequent removal of the detrimental additives for the fabrication of highly conductive hole transport layers, combination of which resulted in the significant improvement of photoconversion efficiency to 6.4% for the cells with planar FTO/c-TiO<sub>2</sub>/AgBiI<sub>4</sub>/sp-OMeTAD/Au architecture.

## Compact zwitter-ions as a promising passivators for hybrid halide perovskites with increased stability

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Low stability of hybrid perovskites as a light-harvesting materials in solar cells to exploitation factors (e.g. light, heat, humidity) is the most vital problem in perovskite photovoltaics. A wide range of different origins of hybrid perovskites degradation has been discussed in the literature. All of them can be generally divided into two groups: (1) the loss of volatile components and (2) the high concentration of surface defects. Up to now there is no sufficient data about the rational determination of the most critical degradation factor, and accordingly the most effective approach to the stability improvement of perovskite materials and solar cells based on them.

In the current work we experimentally demonstrate that for hybrid perovskites the loss of volatile components leads to the fast and irreversible materials degradation while the high concentration of defects is a less significant factor. This primarily sets a requirement to form capping layers on the perovskite surface. Since hybrid perovskites have relatively high concentration of charged defects, the most promising type of organic passivators are multifunctional molecules. Zwitterions are an example of such molecules which can simultaneously passivate both negatively ( $V_A'$ ,  $I_i'$ ), and positively charged defects ( $V_I\bullet$ ,  $Pb^{\delta+}$ ). The use of compact zwitterions could also allow to form dense capping layers on top of perovskite films which is less possible by using bulkier zwitterions with long non-functional carbon chains, previously reported in the literature.

In this work we provide a detailed study of the effect of compact zwitterions (c-ZIs) on the perovskite materials and solar cells based on them. We use the following zwitterions – 3-(2,2,2-trimethylhydraziniumyl) propionate and (3R)-3-hydroxy-4-(trimethylammonio) butanoate namely meldonium and L-carnitine. We also investigate passivation with butylammonium iodide (BAI) as a typical passivator known to effectively decrease defects concentration and unable to form dense capping layer on perovskite surface. Passivation was carried out by spin-coating of passivator solution in isopropyl alcohol onto perovskite films.

According to the photoluminescence (PL) data, all used passivators lead to the decrease of nonradiative recombination proportional to the concentration of the used passivator solution. On the surface of perovskite films passivated by zwitterions was revealed the formation of small particles at low concentration of zwitterion (<10 mM) and a dense capping layer at higher concentration ( $\geq 10$  mM). This feature occurs only on the film surface with retaining the average grain size in the film volume. The observed small particles possibly originate from the formation of delta-polytype with c-ZIs located between 1D octahedral lead-iodide chains. The formation of capping layers by c-ZIs also leads to the film color change, which is absent in the case of BAI. Instead, a well-known 2D  $BA_2MA_{n-1}Pb_nI_{3n+1}$  phases are formed during passivation with BAI.

The light soaking of perovskite films in both types of atmospheres – inert and oxidizing, demonstrates a pronounced increase in perovskite stability in the case of zwitterions in contrast to the BAI-passivated materials retaining the same degradation rate as a reference perovskite film: PL intensity

of meldonium and L-carnitine passivated films preserve more than 60% of initial intensity after 90 hours of light irradiation in an inert atmosphere, while BAI-passivated and pristine samples demonstrate a significant drop of PL signal already after 24 hours of aging. The same degradation rates are observed under oxidizing atmosphere.

The use of c-ZIs in perovskite solar cells leads to the PCE increase mainly due to defects passivation, as evidenced by the increase of open-circuit voltage by up to 0.2V. On the other hand, an increase of meldonium concentration monotonically reduces short-circuit current density due to the growth of the thickness of capping layer with low conductivity. Continuous MPP tracking of assembled devices under 1 sun and 65°C demonstrates an increase of PSCs long-term stability with meldonium passivation in contrast to control devices and devices with BAI passivation which proves the effectiveness of zwitter-ionic perovskite passivation for both the PCE and stability increase.

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## Design of Perovskite Formulations with Improved Photostability by Partial Substitution of $\text{Pb}^{2+}$ in $\text{CsPbI}_3$

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Over the past few years, the performance of perovskite solar cells was gradually improved up to >25%, which is close to the characteristics of crystalline silicon photovoltaics. However, high toxicity and low stability of complex lead halides used as absorber materials hamper commercialization of this technology. Compositional engineering of lead halide perovskites was actively pursued in order to improve their stability and/or performance. In particular, a partial or full replacement of  $\text{Pb}^{2+}$  in  $\text{APbX}_3$  is highly desirable in terms of developing more environmentally friendly materials.

Herein, we present a systematic study of lead substitution in  $\text{CsPbI}_3$  with >30 different cations introduced in atomic concentrations ranging from 1 to 20-30% [1]. It was shown that a series of 25 cations enables the formation of the black orthorhombic  $\gamma$ -phase of  $\text{CsPb}_{1-x}\text{M}_x\text{I}_{3-x}$  at relatively low temperatures of 100-200 °C, whereas non-modified  $\text{CsPbI}_3$  is obtained as a black polymorph above 300 °C. The most promising systems surviving > 500 h of continuous light soaking (0.85 sun) were identified. Using XRD and EDS we have revealed possible localization of  $\text{Mn}^+$  cations, thereby coming closer to the understanding of stabilization mechanism of halide perovskites.  $\text{CsPb}_{1-x}\text{M}_x\text{I}_{3-x}$  formulations with the superior photostability were tested as a light absorber materials in solar cells and showed good performance: e.g.  $\text{CsPb}_{0.9}\text{Ba}_{0.1}\text{I}_3$  – based devices provided PCE of 11.4%. Thus, the  $\text{Pb}^{2+}$  replacement strategy has a high potential for fabrication efficient and stable perovskite solar cells.