

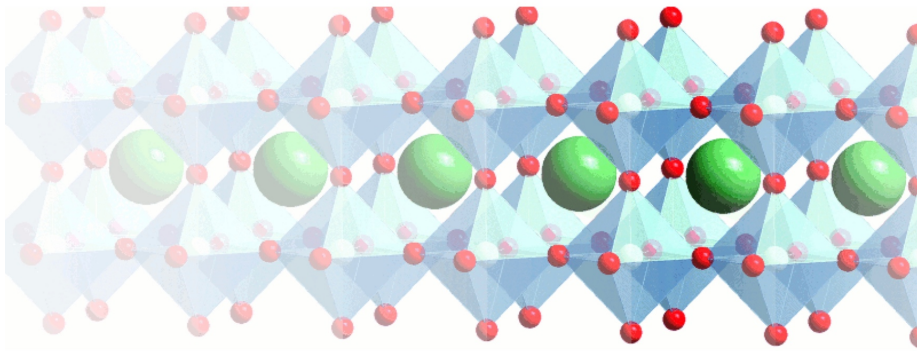
# JOURNEES PEROVSKITES HALOGENEES

**4ÈME ÉDITION**

**COLLOQUE DU  
GDR HPERO**

## **PROGRAMME**

14.05. Tutorials  
15.05. Présentations  
Session Poster  
16.05. Présentations  
Clôture



**JPH2018**

**RECUEIL DES  
RÉSUMÉS**

**14-16 mai 2018**

**Autrans (Grenoble)**

## **ORATEURS PLENIERS**

- Maksym Kovalenko (ETH Zürich)
- Sam Stranks (Cavendish Lab, Cambridge)
- Philip Schulz (NREL, IPVF)

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Peter Reiss



## Program

### 14-05-18

13:30	Arrival	
<b>14:30</b>	<b>Tutorials</b>	
14:30	Tutorial : synthesis, structure	Nicolas Mercier
15:15	Tutorial: electronic properties, simulation	Jacky Even
16:00	Break	
16:30	Tutorial: optical properties	Emmanuelle Deleporte
17:15	Tutorial: devices	Johann Bouclé
18:00	Registration	
18:30	Dinner	
20:00	HPERO Scientific Committee Meeting	

### 15-05-18

8:30	Opening	Emmanuelle Deleporte, Peter Reiss
<b>9:00</b>	<b>3D perovskites: synthesis, properties</b>	
9:00	Passivation routes toward eliminating non-radiative losses and ion migration in halide perovskite structures	Sam Stranks
9:45	Lead and iodide deficient (CH <sub>3</sub> NH <sub>3</sub> )PbI <sub>3</sub> , d-MAPI: the bridge between 2D and 3D hybrid perovskites	Antonin Leblanc
10:00	Comparative study of halide perovskite films obtained by liquid and dry processing	Chloé Dindault
10:15	Break	
<b>10:45</b>	<b>2D perovskites</b>	
10:45	Making and breaking the exciton in layered halide hybrid perovskites	M. Kepenekian
11:15	Layered cesium - guanidinium Sn(II) and Pb(II) bromides: C <sub>n</sub> [C(NH <sub>2</sub> ) <sub>3</sub> ]MnBr <sub>3n+1</sub> (M=Sn, Pb, n=1, 2)	Olga Nazarenko
11:45	Time-resolved microphotoluminescence study of 2D layered hybrid perovskites crystals. Correlation between the structural and optical properties	Damien Garrot
12:00	Highly efficient luminescence of hybrid perovskites	Maroua Ben Haj Salah
12:15	Biexciton Lasing in 2-Dimensional Lead Iodide Perovskites	Edward Booker
12:30	Lunch	
<b>14:00</b>	<b>0D perovskites: Nanocrystals</b>	
14:00	Colloidal APbX <sub>3</sub> nanocrystals [A=Cs <sup>+</sup> , CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup> , CH(NH <sub>2</sub> ) <sub>2</sub> <sup>+</sup> ] with bright photoluminescence spanning from ultraviolet to near-infrared spectral regions	Maksym Kovalenko
14:45	Magneto-optical spectroscopy of single lead halide perovskite nanocrystals	Philippe Tamarat

15:15	Lead substitution in halide perovskite nanocrystals	Dmitry Aldakov
15:45	Magnetoexcitons in colloidal MAPbI <sub>3</sub> nanoplatelets	A. Surrente
16:00	Electron-hole exchange energy and fine structure of excitons in Polymorphic CsPbBr <sub>3</sub> Single Nanocrystals	Laurent Legrand
16:15	Break	
<b>16:45</b>	<b>Poster session</b>	
19:00	Dinner	

### 16-05-18

<b>8:30</b>	<b>Devices</b>	
8:30	Interface Energetics in Halide Perovskites	Philip Schulz
9:15	Unravelling fine structure splitting of the bright exciton in a bulk MAPbBr <sub>3</sub> single crystal	Paulina Plochocka
9:45	Thin film perovskite solar cells by evaporation	Frederic Roux
10:00	Effect of chlorine addition on intrinsic stability of Perovskite solar cell	Manon Spalla
10:15	Break	
<b>10:45</b>	<b>3D perovskites, physics</b>	
10:45	Approaches towards perovskite industrialization: efficient 4-T Tandem integration and encapsulation techniques	F. Javier Ramos
11:15	Evidence of halide ion migration in CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub> (Cl) based perovskite solar cell and its effect on current-voltage hysteresis	Bernard Geffroy
11:30	Low temperature cation local dynamics in halogenated perovskites as seen by neutron backscattering spectroscopy	David Djurado
11:45	Emission properties of quantum dots in perovskite matrix	Justine Baronnier
12:00	Quantum modeling of electronic transport in MAPI : role of the dipole of the organic molecule	Antoine Lacroix
12:15	Low-frequency Raman spectroscopy and elastic softness of hybrid lead halide perovskites	Bernard Hehlen
12:30	Lunch	
14:00	Departure	

## **Avant-propos**

JPH2018 désigne la quatrième édition des Journées Pérovskites Halogénées, rendez-vous maintenant bien établi, qui fait désormais office de réunion annuelle du GDR HPERO. C'est l'occasion d'aborder tous les aspects de la thématique : fabrication de couches minces, synthèse de nanocristaux, études des propriétés optiques, structurales et électroniques, simulations numériques jusqu'aux diverses applications (photovoltaïque, émission de lumière, détecteurs, etc.). L'objectif des JPH est de fédérer la communauté française comprenant physiciens, chimistes, théoriciens, ingénieurs et industriels. Cette édition 2018 est organisée pour la première fois en formule résidentielle avec hébergement, repas et présentations au même lieu dans le cadre pittoresque du Vercors, pour favoriser au mieux les échanges et discussions entre participants.

Au programme des JPH2018 nous avons le plaisir d'accueillir trois conférences plénières données par Sam Stranks (Cavendish Lab, Cambridge), Maksym Kovalenko (ETH Zürich) et Philip Schulz (IPVF), 20 communications orales et 27 communications par affiches.

Le comité d'organisation tient à remercier toutes les personnes qui l'ont aidé à mettre en place les JPH2018 ainsi que les partenaires et sponsors, grâce auxquels un tarif attractif a pu être proposé aux participants.

Bienvenue à Autrans !

Peter Reiss, pour le Comité d'Organisation

## **Preface**

JPH2018 designates the fourth edition of "Halide Perovskite Days", a meanwhile well-established national forum, which now also serves as the annual meeting of the GDR HPERO network. All aspects of the subject will be addressed, ranging from thin film fabrication and nanocrystal synthesis over studies of the optical, structural and electronic properties to numerical simulations and various applications (photovoltaics, light emission, detectors, etc.). The objective of the JPH is to federate the French community including physicists, chemists, theorists, engineers and industrials. To promote exchange and discussion between participants the 2018 edition is organized for the first time residentially with accommodation, meals and presentations at the same place, located in the scenic setting of the Vercors mountains.

The program comprises three plenary lectures given by Sam Stranks (Cavendish Lab, Cambridge), Maksym Kovalenko (ETH Zurich) and Philip Schulz (IPVF), 20 oral and 27 poster communications.

The organizing committee would like to thank all the people who helped putting in place JPH2018 as well as the partners and sponsors, thanks to which attractive inscription fees could be proposed to the participants.

Wishing you all an exciting meeting, welcome to Autrans!

Peter Reiss, on behalf of the Organizing Committee



## Plenary speakers



**Dr Sam Stranks** is a Royal Society University Research Fellow, TED Fellow, and Fellow of Clare College. He graduated from the University of Adelaide in 2007 with a BA, BSc and a University Medal. He completed his PhD as a Rhodes Scholar at Oxford University with Robin Nicholas, receiving the 2012 Institute of Physics Roy Thesis Prize. From 2012-2014, he was a Junior Research Fellow in Henry Snaith's group at Oxford University. From 2014-2016, he was a Marie Curie Fellow at the Massachusetts Institute of Technology working jointly with Vladimir Bulovic and Richard Friend (Cambridge). Sam is currently a PI leading a research group of 12 students and postdocs in the Cavendish Laboratory, University of Cambridge, with a focus on emerging PV and light emitting technologies. He received the 2016 IUPAP Young Scientist in Semiconductor

Physics Prize for "pioneering discoveries in the field of perovskite solar cells and optoelectronics through spectroscopy" and in 2017 was awarded the Early Career Prize by the European Physical Society and named by the MIT Technology Review as one of the 35 under 35 innovators in Europe.



**Dr Philip Schulz** joined the Centre National de la Recherche Scientifique (CNRS) in late 2017 on a Research Director position for Physical Chemistry and New Concepts for Photovoltaics. In this function, he is engaged in research activities at the Institut Photovoltaïque d'Île-de-France (IPVF) in Paris Saclay. At IPVF he leads the Interfaces and Hybrid Materials for PV project installed via the "Make Our Planet Great Again" initiative of the French President Emmanuel Macron.

From 2012 to 2017 Philip Schulz has been a postdoctoral researcher at the National Renewable Energy Laboratory (NREL) and the Surface and Interfaces Science Laboratory at Princeton University to study interface design in organic electronics and hybrid organic / inorganic solar cells. Philip Schulz received his Ph.D. in physics from the RWTH Aachen University in Germany in 2012.

His research fields cover organic and hybrid electronics, interface formation, thin-film analysis and electronic structure determination with a specific interest in the application for renewable energy generation – in particular emergent photovoltaic platforms.



**Prof. M. V. Kovalenko** leads the Functional Inorganic Materials Group at the ETH Zurich (Swiss Federal Institute of Technology Zurich) and Empa (Swiss Federal Laboratories for Materials Science and Technology). Maksym Kovalenko has been an Assistant Professor of Inorganic Functional Materials at ETH Zürich since 2011, and Associate Professor from January 2017. On every step of his career journey, M. Kovalenko absorbed a range of diverse skills and knowledge that he now combines to lead an interdisciplinary research program. His Master's and Ph.D. theses revolved around the synthesis of infrared-luminescent colloidal nanocrystals (2003–2007). He earned his PhD degree in technical sciences (nanoscience and nanotechnology) in 2007 (with distinction) from the Johannes Kepler University Linz, Austria. During his postdoctoral training (2008–2011, University of Chicago), M. Kovalenko focused on the surface chemistry of colloidal nanocrystals and introduced inorganic surface functionalization of semiconductor nanocrystals, enhancing the prospects of fabricating nanocrystal solids for electronic and optoelectronic applications. During his independent career (2011–present), he expanded his research repertoire by initiating radically new (for him) research activities on electrochemical energy storage (*e.g.*, Li-ion and post-Li-ion batteries, located at the Empa branch) and, after his promotion to associate professor with tenure, by expanding the experimental infrastructure of his laboratory (*i.e.*, solid-state synthesis, radiation detection, advanced/comprehensive electronic and optical characterizations including single-dot spectroscopy, and the fabrication of light-emitting devices). He co-authored appr. 170 peer-reviewed research articles, 3 book chapters and 12 patents. He supervises a group of 10 postdoctoral fellows and 10 ongoing PhD projects; 3 PhD projects had been completed. He is the recipient of the ERC Starting Grant 2012, Ruzicka Preis 2013 and Werner Prize 2016. He delivered more than 100 invited, keynote and plenary presentation at international conferences and universities. He also serves as an associate editor of Chemistry of Materials.

The research activities of the **Functional Inorganic Materials** group, led by Prof. M. V. Kovalenko, cover various aspects of chemical synthesis, surface functionalization, self-assembly and applications of colloidal nanostructures aimed at developing novel functional materials for optoelectronics, as well as for energy supplying and energy storing purposes. The group had recently pioneered the synthesis of novel cesium lead halide nanocrystals ( $\text{CsPbX}_3$ ,  $X=\text{Cl, Br, I}$ , February 2015) and had been at the forefront of the studies on chemistry and physics of these novel photonic sources. Their photoluminescence spectra span the entire visible spectral range, with high quantum efficiencies reaching 90-95%. The simplicity of the synthesis and unnecessary for the electronic passivation, make such NCs highly promising optoelectronic materials. To date, these NCs have shown to be highly compelling competitors to conventional quantum dots, in particular, for applications in down-conversion (*i.e.* LCD-television displays) and as optical gain medium.

# List of sponsors



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# 3D perovskites : synthesis, properties

# Passivation routes toward eliminating non-radiative losses and ion migration in halide perovskite structures

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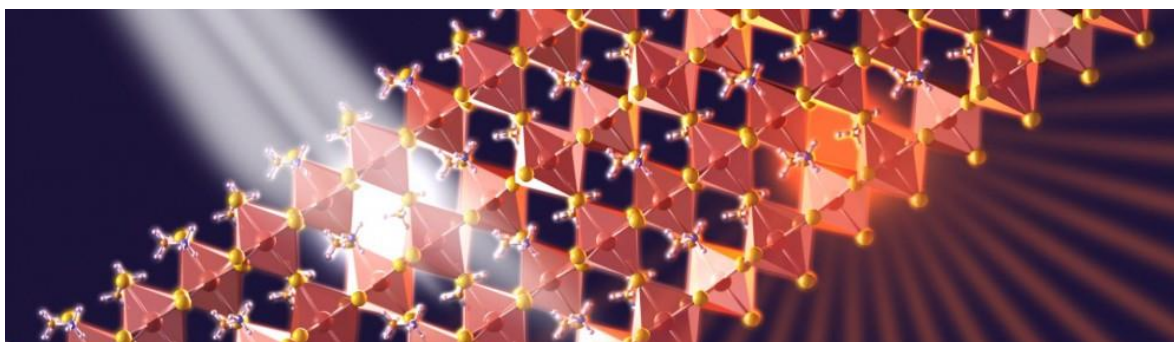
[sds65@cam.ac.uk](mailto:sds65@cam.ac.uk)

<https://www.stranks.oe.phy.cam.ac.uk/>

Halide perovskites are generating enormous interest for their use in solar photovoltaic and light-emission applications. One property linking the high performance of these devices is a high radiative efficiency of the materials; indeed, a prerequisite for these devices to reach their theoretical efficiency limits is the elimination of all non-radiative decay. However, there still exists substantial parasitic non-radiative losses and ionic migration in the materials, both of which lead to performance limitations and instabilities<sup>1</sup>.

Here, I will focus on understanding and eliminating non-radiative losses in perovskite structures. I will present new methods to image the time-resolved luminescence through 3D tomography. I will then detail several new and promising passivation approaches through additives aimed at eliminating these problematic processes in a range of. One method uses post-treatments in which the films are exposed to light and atmospheric molecules<sup>2, 3</sup>, while the other combines alkali halide additives into the precursor solutions<sup>4</sup>. In both approaches, we find internal photoluminescence quantum efficiencies over 90% along with the removal of transient photo-induced ion migration processes without compromising charge carrier mobility.

This work reveals promising approaches to fabricate metal halide thin films with the highest optoelectronic quality. The work also provides further evidence that non-radiative decay and ionic motion are intimately related, generalizing the conjecture that there are common solutions to both problems.



1. Stranks SD. Nonradiative Losses in Metal Halide Perovskites. *ACS Energy Letters* 2017, **2**, 1515-1525.
2. Brenes R, Guo D, Osherov A, Noel NK, Eames C, Hutter EM, *et al.* Metal Halide Perovskite Polycrystalline Films Exhibiting Properties of Single Crystals. *Joule* 2017, **1**, 155-167.
3. Brenes R, Eames C, Bulovic V, Islam MS, Stranks SD. The Impact of Atmosphere on the Local Luminescence Properties of Metal Halide Perovskite Grains. *Advanced Materials* 2018, in press, DOI: 10.1002/adma.201706208.
4. Abdi-Jalebi M, Andaji-Garmaroudi Z, Cacovich S, Stavrakas C, Philippe B, Richter JM, *et al.* Maximizing and stabilizing luminescence from halide perovskites with potassium passivation. *Nature* 2018, **555**, 497-501.

## Lead and iodide deficient ( $\text{CH}_3\text{NH}_3$ ) $\text{PbI}_3$ , *d*-MAPI: the bridge between 2D and 3D hybrid perovskites

**Antonin Leblanc,<sup>a</sup> Nicolas Mercier,<sup>\*a</sup> Magali Allain,<sup>a</sup> Jens Dittmer,<sup>b</sup> Vincent Fernandez,<sup>c</sup> Thierry Pauporté<sup>\*d</sup>**

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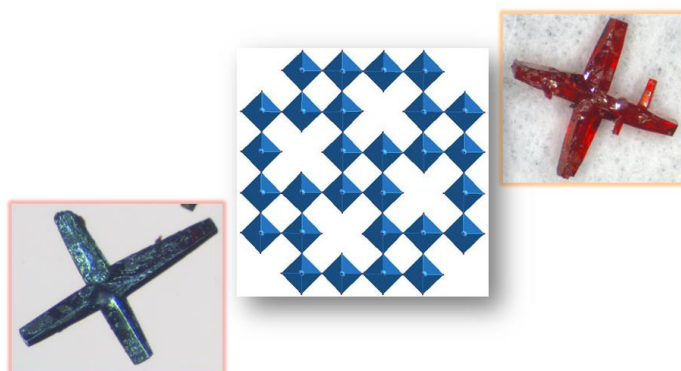
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The last years, the Hybrid Perovskite solar cells showed a high photoconversion efficiency (PCE) up to 22,7%.<sup>[1]</sup> The best performances were obtained with the three-dimensional  $\text{CH}_3\text{NH}_3\text{PbI}_3$  and derivatives such as mixed small cations and mixed halogens (Rb,Cs,FA,MA) $\text{PbI}_3$  compounds, where  $\text{MA}^+$ =methylammonium and  $\text{FA}^+$ =formamidinium.<sup>[2]</sup>

Very recently, we have discovered a new family of hybrid perovskites, named *d*-MAPI, which can be prepared as single crystals, crystallized powders and crystallized thin films. A *d*-MAPI phase is lead and iodide deficient compared to MAPI ( $\text{CH}_3\text{NH}_3\text{PbI}_3$ ): a  $(\text{PbI})^+$  unit being substituted by an organic monocation, while keeping a 3D architecture. By using two kinds of organic cations, the methylammonium and the ethanolanmonium ( $\text{HEA}^+$ ), a series of *d*-MAPI compounds whose general formulation is  $(\text{MA})_{1-2.48x}(\text{HEA})_{3.48x}[\text{Pb}_{1-x}\text{I}_{3-x}]$  ( $0 < x < 0.20$ ) has been obtained. The substitution of  $(\text{PbI})^+$  unit leads to the formation of channels along *c* axis.



**Fig. 1** Crystals pictures & an inorganic structure view of the new phase *d*-MAPI.

Channels of this network can be filled by extra  $\text{Pb}^{2+}$  and  $\text{I}^-$  ions and organic cations (when  $x < 0.20$ ) or only by organic cations (when  $x = 0.20$ ). First experiments using *d*-MAPI layers for an application as absorber materials in regular FTO/compact-TiO<sub>2</sub>/meso-TiO<sub>2</sub>/Perovskite/SpiroOMeTAD/Ag PSCs have shown that *d*-MAPI ( $x = 0.10$ ) exhibits a PCE of 6%. Moreover, a relative stability test of thin films of MAPI and *d*-MAPI ( $x = 0.10$ ) has revealed that *d*-MAPI thin films are more stable than the MAPI ones. This new type of hybrid perovskite  $(\text{A}, \text{A}')_{1+x}[\text{Pb}_{1-x}\text{X}_{3-x}]$  ( $\text{A} = \text{MA}^+$ ,  $\text{A}' = \text{HEA}^+$ ) offers increased flexibility of its chemical composition with potential substitutions on the A, A', Pb and X sites.

1) NREL efficiency chart: <https://www.nrel.gov/pv/assets/images/efficiency-chart.png>

2) Michael Gratzel, *Acc. Chem. Res.*, **2017**, *50*, 487-491.

3) Antonin Leblanc, Nicolas Mercier, Magali Allain, Jens Dittmer, Vincent Fernandez, Thierry Pauporté, *Angew. Chem.*, **2017**, *129*, 16283-16288.

# Etude comparative de films de perovskites halogénées obtenus par voie liquide et voie sèche

Chloé DINDAULT<sup>a,b</sup>, Sufal SWARAJ<sup>c</sup>, Bernard GEFROY<sup>b,d</sup>, Jean-Eric BOUREE<sup>b</sup>, Rachid BELKHOUCHE<sup>c</sup>, Yvan BONNASSIEUX<sup>b,a</sup>, Philip SCHULZ<sup>e,a</sup> & Denis TONDELIER<sup>b,a</sup>

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Les perovskites halogénées sont depuis plusieurs années sous le feu des projecteurs dans le domaine du photovoltaïque. Si la course aux rendements concentre la majeure partie des efforts de recherche, les méthodes de fabrication à grande échelle font elles aussi l'objet de nombreux travaux. En effet, le faible coût des matières premières et les excellentes performances obtenues en laboratoire font de ces matériaux d'excellents candidats pour des applications industrielles.

S'il existe parmi les méthodes en voie liquide des techniques de dépôt grandes surfaces prometteuses ; comme le *slot-die*<sup>[1]</sup>, le *doctor-blade*<sup>[2]</sup>, le *spray*<sup>[3]</sup> ou encore l'impression jet d'encre<sup>[4]</sup> ; les procédés en voie sèche semblent cependant être les plus adaptés à l'industrialisation de cette technologie. En effet, ces derniers permettent ; selon toute logique ; l'obtention de films homogènes et denses, de façon reproductible et sur de larges surfaces.

Dans ce contexte, nous présentons ici une étude comparative voie liquide/voie sèche de films de perovskites halogénées. Ceux-ci sont caractérisés par des techniques plutôt classiques (DRX, MEB, I-V, etc...) mais aussi, de façon inédite, par une technique 'grands instruments' : la microscopie STXM (*Scanning Transmission X-ray Microscopy*) disponible sur la ligne HERMES au Synchrotron SOLEIL<sup>[5]</sup>. Cette technique permet d'obtenir des informations spectroscopiques et chimiques avec une résolution spatiale de l'ordre de la dizaine de nm. Le rayonnement Synchrotron d'énergie accordable (sur HERMES typiquement entre 250 et 1500 eV) irradie les échantillons et le signal transmis est mesuré. Le traitement des images par analyse de clusters permet de mettre en évidence plusieurs zones au sein de la couche de perovskite (Figure 2) et d'en extraire les spectres d'absorption. En comparant l'intensité des pics du Plomb et de l'iode selon les zones isolées, nous pourrions étudier l'évolution du ratio Pb/I à travers le profil Interface inférieure / Perovskite / Interface supérieure.

Nous discuterons autour des résultats de ces différentes caractérisations afin de comparer les deux méthodes de dépôt utilisées dans cette étude.

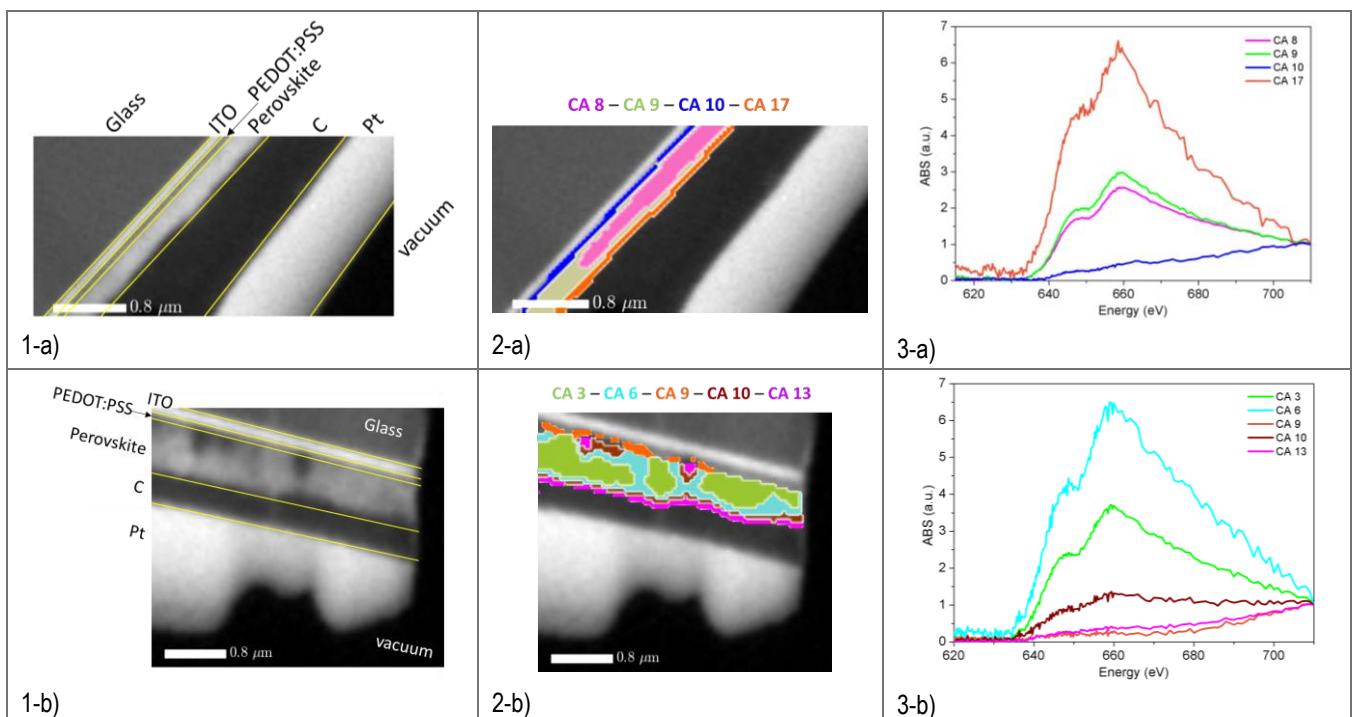


Figure 1 : Pour a) une perovskite par voie sèche et b) une perovskite par voie liquide : 1) image obtenue par STXM de la section transversale de l'échantillon à 660 eV (le C et le Pt viennent de l'affinement des échantillons STXM par FIB) ; 2) masques de différentes régions dans la couche de perovskite isolées par analyse de clusters et 3) les spectres d'absorption correspondants (à 648,8 eV pic du Pb et à 660 eV pic de l'iode)

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# 2D perovskites

**Layered cesium - guanidinium Sn(II) and Pb(II) bromides:  
Cs<sub>n</sub>[C(NH<sub>2</sub>)<sub>3</sub>]M<sub>n</sub>Br<sub>3n+1</sub> (M=Sn, Pb, n=1, 2)**

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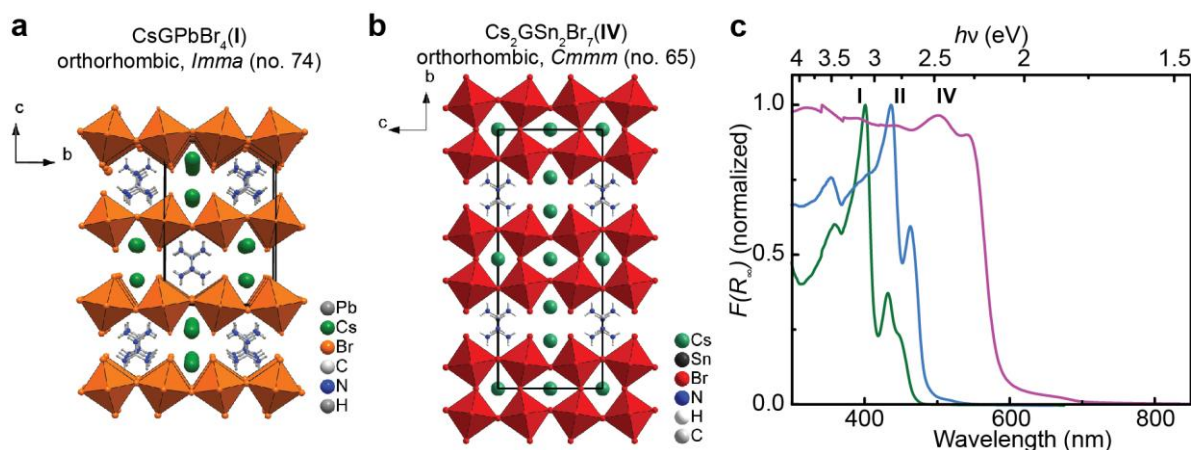
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Layered hybrid perovskite-related metal halide compounds are under a focus of researchers due to their tunable optoelectronic properties and tailorable structures. The crystal structure of such compounds is made of perovskite layers, consisting of corner sharing metal-halide octahedra, and organic ammonium cations situated in the interlayer space (an isolating layer). Perovskite slabs are commonly parallel to (100), (110) and (111) planes. (100) compounds with A<sub>n+1</sub>B<sub>n</sub>X<sub>3n+1</sub> general formula and a simplest member (n=1) adopting K<sub>2</sub>NiF<sub>4</sub> crystal structure, are called Ruddlesden-Popper phases. To modify the thickness of slabs (n>1) a mixture of cations is used: small cations, *i.e.* methylammonium (MA) for A<sub>n+1</sub>Pb(Sn)<sub>n</sub>X<sub>3n+1</sub>, which fill the voids within the layers, and large A-type cations filling the interlayer space.

In our study, we eliminated bulky organic amines and replaced typically used MA by Cs<sup>+</sup> expecting higher thermal and chemical stability.[1-2] As an interlayer component a small and highly symmetric guanidinium cation ([C(NH<sub>2</sub>)<sub>3</sub>]<sup>+</sup>, G) was chosen due to its thermodynamic stability, high basicity (pK<sub>a</sub>=13.6), and strong hydrogen-bonds capabilities. The G cation, owing to its ionic radii, can't sustain a three-dimensional perovskite network (ABX<sub>3</sub>) and could situate itself in the interlayer space.[1-3] Two families of layered compounds were obtained: cesium G lead and tin bromides. CsGPbBr<sub>4</sub> (I) (Fig. 1a), Cs<sub>2</sub>GPb<sub>2</sub>Br<sub>7</sub> (II) are air stable compounds that possess a good temperature stability (up to 300 °C), and are emissive upon moderate cooling.[1] Photoresponsivities in the range of 1-10 mA·W<sup>-1</sup> were measured with II. Compounds CsGSnBr<sub>4</sub> (III) and Cs<sub>2</sub>GSn<sub>2</sub>Br<sub>7</sub> (IV) (Fig. 1b) promise lower toxicity, as their lead analogues. IV has smaller band gap than II (Fig. 1c).[2] The later is probable due to higher electronegativity of Pb and differences in distortions in the inorganic crystal lattices. Small ionic radii of G enables short interlayer Br...Br contacts, 4.070 Å in IV, allowing for weak Br...Br interactions, allegedly increasing the density of the electronic states.



**Fig. 1** (a) Crystal structure of CsGPbBr<sub>4</sub>(I). (b) Crystal structure of Cs<sub>2</sub>GSn<sub>2</sub>Br<sub>7</sub>(IV). (c) Kubelka–Munk function  $F(R_{\infty})=(1-R_{\infty})^2/2R_{\infty}$  ( $R_{\infty}$ -diffusive reflectance). The measurements were performed on the microcrystalline powder.

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- 3) Nazarenko et al., J. Am. Chem. Soc., submitted



## Making and breaking the exciton in layered halide hybrid perovskites

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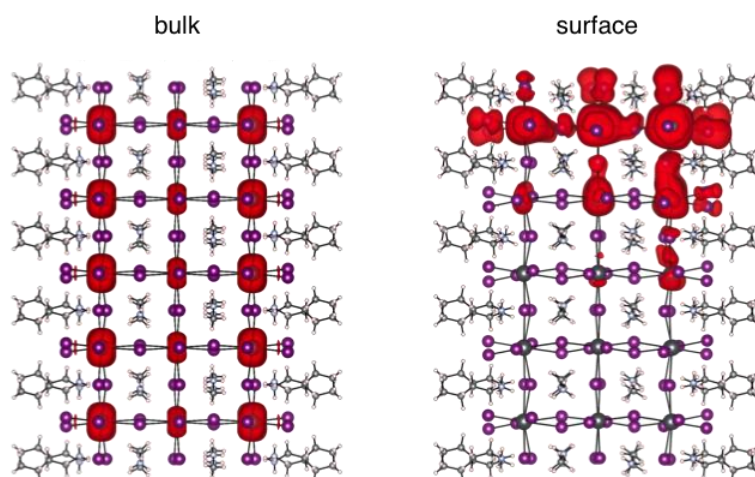
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The well-known environmental fragility of halide hybrid-based solar cells lies in the way of their success. A path around this fragility has been proposed with the use of layered perovskites [1], which have recently demonstrated improved photostability and humidity resistance with a power conversion efficiency of 12.5 % [2]. Interestingly, the performances of the latter can be traced back to extremely efficient internal exciton dissociation through edge states identified on thin films and single crystals [3].



**Fig. 1** In the case of thicker layered perovskites  $(\text{BA})_2(\text{MA})_{n-1}\text{Pb}_n\text{I}_{3n+1}$  ( $n > 2$ ), the surface leads to the localization of the conduction band conducting to the breaking of the exciton.<sup>3,7</sup>

Layered perovskites present fascinating features with inherent quantum and dielectric confinements imposed by the organic layers sandwiching the inorganic core, and computational approaches have successfully help rationalized their properties (excitonic, Rashba effects, etc.) [4-6]. Here, we propose a joint spectroscopic and computational investigation to unravel the origin of the recently identified layer-edge states in layered Ruddlesden-Popper phases with inorganic layers containing  $n = 1$  to 4 octahedra. We show that for  $n > 2$ , the system presents a localized surface state within the band gap.<sup>7</sup>

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# HIGHLY EFFICIENT LUMINESCENCE OF HYBRID PEROVSKITES

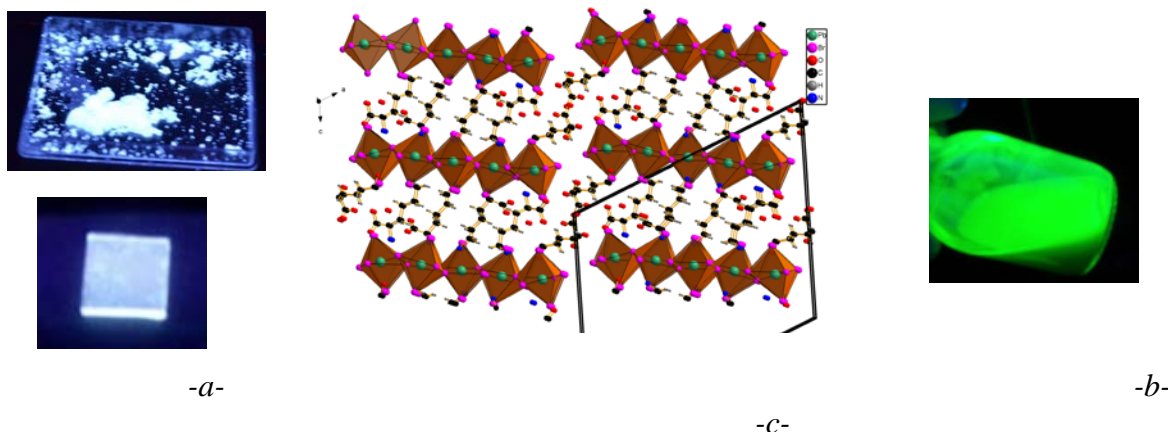
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**Summary:** Organic-inorganic perovskite hybrids are attracting increasing attention among scientists because the molecular hybridization offers the potential of combining the best parts of characteristic properties of the two chemical entities as well as generating new properties arising from the molecular interactions between the two building block.

The rapid progress in material synthesis and device fabrication has promoted the development of optoelectronic applications including solar cells, transistors and photodetectors<sup>[1]</sup>. Moreover, (A)PbX<sub>3</sub> HPs have received great attention recently due to their potential application in the fabrication of very efficient light emission devices (PeLEDs for Perovskite LEDs), particularly when HPs are nanocrystals (NCs). Depending on the halide composition (X= I, Br, Cl or mixed Cl/Br, Br/I), the emission can be tuned in the all visible range.<sup>[2]</sup> Finally, the potentiality of intrinsic white-light emission by layered bromo- and chloro-plumbate HPs have been recently showed.<sup>[3]</sup> *In this communication*, we report the results of our effort to prepare new materials for PeLEDs applications : **1-** a family of 2D HPs (CO<sub>2</sub>H-(CH<sub>2</sub>)<sub>n-1</sub>-NH<sub>3</sub>)<sub>2</sub>Pb(X,X')<sub>4</sub> (X= Br, Cl) exhibiting white luminescence with Photo Luminescence Quantum Efficiency (PLQE) reaching 15% which constitutes a record, and promising results in PeLEDs (Fig. 1a); **2-** a series of four hybrids materials based on 1D perovskite networks Pb<sub>n</sub>Br<sub>(4n+2)</sub><sup>(2n+2)-</sup> with n= 2, 3, 4, 5 (Fig. 1b), allowing to establish property(luminescence)-structure relationships for hybrid perovskites whose network varies from 1D to 2D (n= ∞); **3-** Highly luminescent properties of nanocrystals of the lead and bromide deficient (CH<sub>3</sub>NH<sub>3</sub>)PbBr<sub>3</sub> compound, (MA,HEA)<sub>1+x</sub>[Pb<sub>1-x</sub>Br<sub>3-x</sub>] (MA<sup>+</sup> methylammonium, HEA<sup>+</sup> hydroxyethylammonium) for PeLEDs applications (Fig. 1c). These compounds are bromide derivatives of a new family of hybrid perovskite, dubbed d-HPs, (MA,HEA)<sub>1+x</sub>[Pb<sub>1-x</sub>I<sub>3-x</sub>] (0.10≤x≤0.20), that has been recently discovered in our group for PSCs applications.<sup>[4]</sup>



**Fig. 1** a) White luminescence of powder and thin film of (CO<sub>2</sub>H-(CH<sub>2</sub>)<sub>3</sub>-NH<sub>3</sub>)<sub>2</sub>PbBr<sub>4</sub>; b) Crystal structure of the 1D Pb<sub>5</sub>Br<sub>22</sub> perovskite network (n= 5) based compound (A)<sub>6</sub>Pb<sub>5</sub>Br<sub>22</sub> (A= Lysine dication); c) Photoluminescence of NCs of (MA,HEA)<sub>1+x</sub>[Pb<sub>1-x</sub>Br<sub>3-x</sub>] upon UV irradiation.

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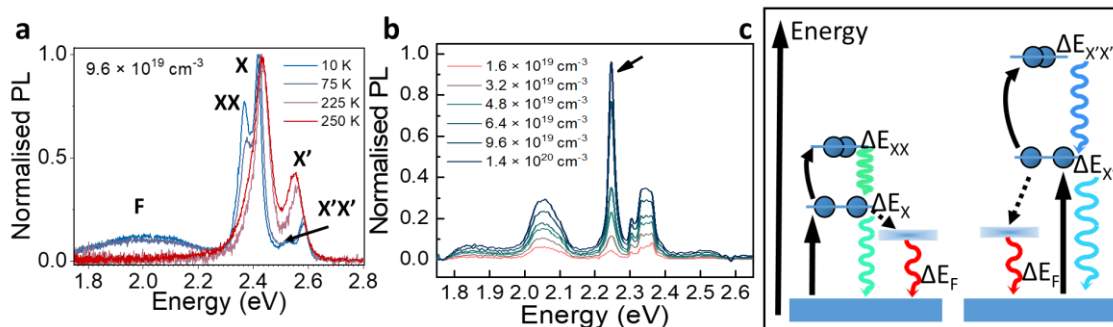
## Biexciton Lasing in 2-Dimensional Lead Iodide Perovskites

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2D hybrid organic/inorganic metal-halide perovskites show increased exciton binding energies compared to 3D perovskites. Carrier confinement and Coulomb interactions play a strong role in raising the biexciton binding energy to 50 meV. We report photoluminescence at a range of temperatures and carrier concentrations in thin films of the layered perovskite material  $(C_{12}H_{25}NH_3)_2PbI_4$ . We directly observe biexcitons up to a sample temperature of 225 K. We construct an optical cavity (comprising a distributed Bragg reflector and a metal mirror), with photonic resonances tuned to the biexciton energy. We observe optically-pumped biexciton lasing up to 125 K, with a threshold peak excitation density of  $1 \times 10^{19} \text{ cm}^{-3}$ . The demonstration of biexciton lasing above liquid nitrogen temperatures is a crucial step for the application of layered perovskites in photonic applications.



**Fig. 1:** a) Temperature dependence of photoluminescence spectra from dodecylammonium lead iodide. F is frenkel defect emission previously seen by Booker et al.,[10] XX is biexciton emission, X is exciton emission, X' is high energy exciton emission and X'X' is high energy biexciton emission. b) Power dependence of cavity of dodecylammonium lead iodide. The arrow indicates proposed biexciton laser emission. c) Proposed state diagram of dodecylammonium lead iodide.

2D perovskites have been studied extensively due the physics they exhibit as self-assembled alternating organic and inorganic sheets.[1],[2] and also due to their potential device applications (field-effect transistors,[3] LEDs,[4] and solar cells[5]), wavelength tunability. [6]

Here we investigate dodecylammonium lead iodide,  $(C_{12}H_{25}NH_3)_2PbI_4$  ( $DA_2PbI_4$ ), which consists of lead iodide octahedra sheets separated by dodecylammonium ions. The dodecylammonium gives electronic confinement in the inorganic layers, resulting in a large exciton binding energy,[7,8] which in this material has previously been determined to be 320 meV.[9]

We investigate the many-body interactions of excited species in the quantum wells formed in  $DA_2PbI_4$ , and identify biexciton formation with a binding energy of 50 meV. Biexcitons make interesting prospective lasing media due to their intrinsically reduced self-absorption compared to excitonic laser systems. Recent findings of energy-tunable amplified spontaneous emission (ASE) in 3D perovskites[12] and ASE in mixed 2D-3D perovskites[13] biexciton lasing has previously been reported at 16 K with laser pump powers.[14] Here we demonstrate cavity lasing above liquid nitrogen temperatures (125 K). Additionally, we report photoluminescence from higher-lying energy states.

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## Time-resolved microphotoluminescence study of 2D layered hybrid perovskites crystals. Correlation between the structural and optical properties.

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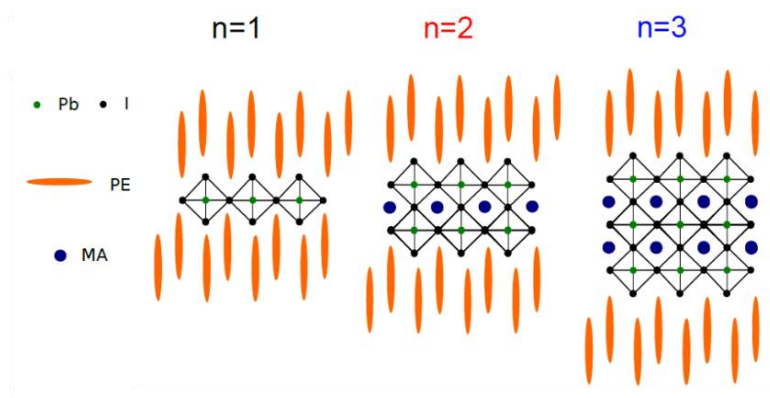
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Over the past few years, organic-inorganic halide 3D perovskites (3D-HOP) were found to present remarkable optoelectronic properties. In particular, the efficiency of perovskite solar cells rivals now with commercial silicon solar cells. However, their instability in presence of moisture and under irradiation hinders their practical applications.

There is currently a renewed interest in 2D layered hybrid perovskites (2D-HOP) due to their chemical versatility and stability. They consist in natural self-assembled quantum well where the perovskite layers are separated by bulky organic cations. Recently, solar cells based on low-dimensional perovskites have demonstrated high efficiency and improved stability. [1] However, the fundamental photophysics of 2D-HOP is not fully understood. A great attention has been paid to thin films, which present generally multiple phases and grain boundaries, as an ideal building block for PV and LED devices. Nevertheless, the study of crystals has proven necessary to unveil some of the intrinsic properties of hybrid perovskites. [2,3]



**Fig.1** Schematic representation of  $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{Pb}_n\text{I}_{3n+1}$  ( $n=1,2$  and  $3$ ) structures

In this work, we have studied the optical properties of 2D layered perovskites crystals of  $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_{n-1}\text{Pb}_n\text{I}_{3n+1}$  ( $n=1,2$  and  $3$ ) (Fig. 1) using time-resolved microphotoluminescence as function of temperature. The emission properties are correlated with the material morphology. Analysis of the fluence and temperature dependence of the photoluminescence decay provides insight into the exciton recombination dynamics in low-dimensional perovskites.

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# Nanocrystals

## Substitution du plomb dans des nanocristaux de pérovskites halogénées

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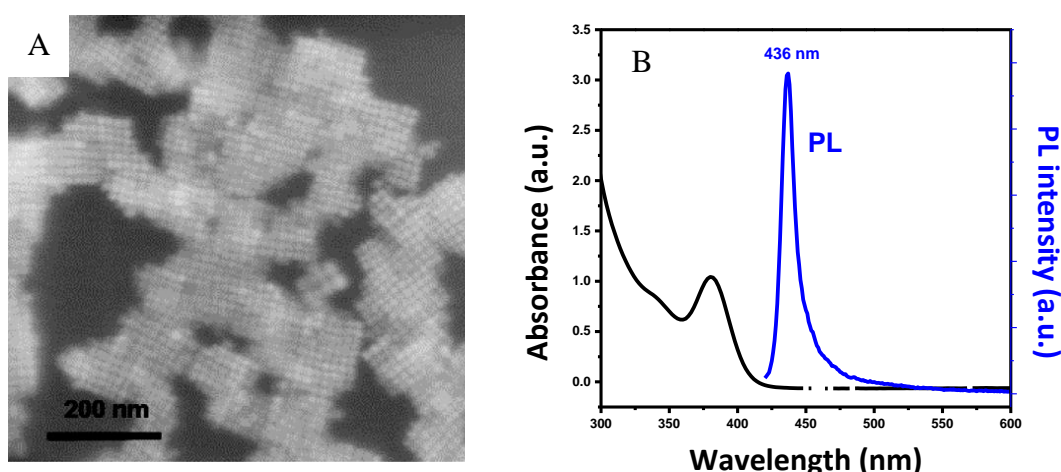
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<http://www.spram-solar.fr/> ; <http://inac.cea.fr/spram/NanoX/index.htm>

Les composés pérovskites halogénées  $ABX_3$  ( $A^+ = Cs^+$ , MA :  $[CH_3NH_3]^+$ , FA :  $[CH(NH_2)_2]^+$ ; B = Pb ;  $X^- = I^-, Br^-, Cl^-$ ) possèdent des propriétés remarquables en tant qu'absorbeur solaire dans des cellules photovoltaïques. Afin de faciliter l'intégration de ces matériaux dans des applications à plus grande échelle le remplacement du plomb par des cations moins toxiques reste un point critique. La structure pérovskite offre la possibilité de moduler facilement les propriétés des matériaux en modifiant leur composition chimique.

Nous étudions ici les propriétés des nouveaux matériaux pérovskites halogénées mixtes  $A(Pb_{1-x}M_x)Br_3$  de faibles dimensions tels que les nanocristaux qui ont récemment démontré leur grand potentiel dans des cellules solaires.<sup>1</sup> En particulier nous nous intéressons à l'influence de la substitution partielle du  $Pb^{2+}$  par des cations métalliques monovalents sur la structure et les propriétés optiques des nanocristaux pérovskites hybrides et inorganiques. La morphologie et la taille des nanocristaux hybrides  $MAPb_{1-x}M_xBr_3$  ( $M^{2+}$  = métal alcalino-terreux ou métal de transition 3d) synthétisés par méthode de réprécipitation est largement impactée malgré un faible taux de substitution (x : maximum 6 % avec  $Mg^{2+}$ ). Au contraire, dans les nanocristaux inorganiques  $CsPb_{1-x}M_xX_3$ , synthétisés par injection à chaud, jusqu'à 16 % du  $Pb^{2+}$  peuvent être remplacés par du  $Mg^{2+}$  en conservant leur taille, forme et structure avec des changements des spectres d'absorption et de photoluminescence. Pour un taux de substitution plus élevé, la formation de la structure  $A_4BX_6$  est favorisée. Dans certains cas le remplacement jusqu'à 100 % de Pb était possible.

Dans la deuxième partie, les approches permettant la fabrication de pérovskites 100% sans plomb seront discutées en focalisant sur un nouveau composé à base de bismuth ( $FA_3Bi_2Br_9$ ).



**Figure 1.** A : Image TEM de nanocristaux de  $CsPb_{0,84}Mg_{0,16}Br_3$  ( $x_{ini} = 0,50$ ) ; B : spectres optiques de NCx de  $FA_3Bi_2Br_{11}$ .

1) J. M. Luther et al., *Science*, **2016**, 354, 92–95

## Magneto-optical spectroscopy of single lead halide perovskite nanocrystals

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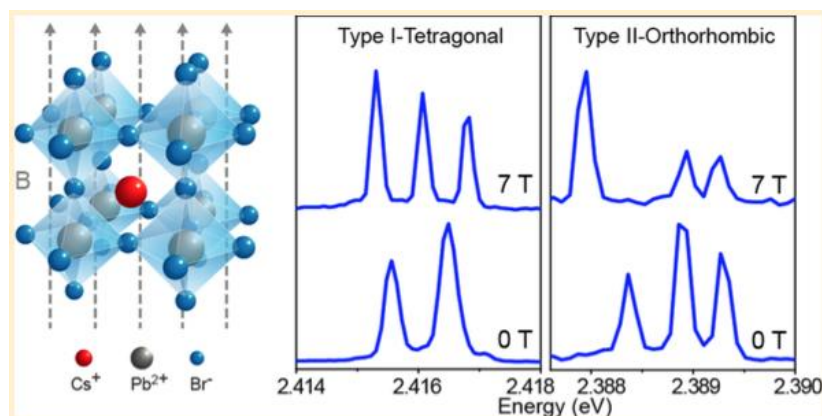
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Revealing the crystal structure of lead halide perovskite nanocrystals is essential in order to optimize the stability of these emerging materials in applications such as solar cells, photodetectors and light emitting devices. We use magneto-photoluminescence spectroscopy of individual perovskite CsPbBr<sub>3</sub> nanocrystals as a unique tool to determine their crystal structure, which imprints distinct signatures in the excitonic sublevels of charge complexes at low temperatures [1]. At zero magnetic field, the identification of two classes of photoluminescence spectra, displaying either two or three sublevels in their exciton fine structure, shows evidence for the existence of two crystalline structures, namely tetragonal  $D_{4h}$  and orthorhombic  $D_{2h}$  phases. Magnetic field shifts, splitting and coupling of the sublevels provide a determination of the diamagnetic coefficient and valuable information on the exciton  $g$ -factor and its anisotropic character. Moreover, this spectroscopic study reveals the optical properties of charged excitons and allows the extraction of the electron and hole  $g$ -factors for perovskite systems.



In the second part of the presentation, we also show that formamidinium lead iodide (FAPbI<sub>3</sub>) perovskite nanocrystals can serve as efficient single photon sources in the near-infrared (~750 nm), a photon energy domain particularly attractive for quantum communication applications. We also lead the first investigations of the photoluminescence spectrum of single FAPbI<sub>3</sub> nanocrystals at cryogenic temperatures [2], which reveal an exciton-longitudinal optical phonon coupling responsible for the homogeneous broadening of the emission line with increasing temperatures. The study of the photoluminescence decay of single FAPbI<sub>3</sub> nanocrystals with temperature shows that the photoluminescence arises from two thermally mixed fine structure states, a dark ground state and upper bright states. Strikingly, two longitudinal optical phonon modes rather than the acoustic phonon modes are involved in this thermal mixing process, which points to a weak exciton-acoustic phonon coupling and a very low acoustic vibrational density of states in these soft materials.

[1] Ming Fu, Philippe Tamarat, He Huang, Jacky Even, Andrey L. Rogach, and Brahim Lounis "Neutral and Charged Exciton Fine Structure in Single Lead Halide Perovskite Nanocrystals Revealed by Magneto-optical Spectroscopy", Nano Letters 17 (2017) 2895-2901

[2] Ming Fu et al., Submitted (2018)

## Highly luminescent colloidal nanocrystals of APbX<sub>3</sub> perovskites [A=Cs<sup>+</sup>, CH(NH<sub>2</sub>)<sub>2</sub><sup>+</sup>, X=Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>]: synthesis, spectroscopy and applications

Maksym V. Kovalenko

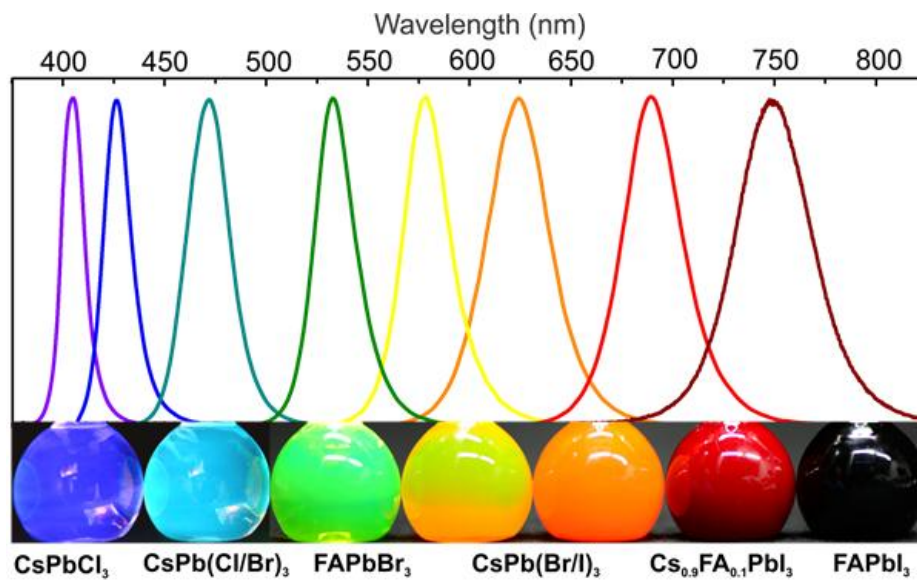
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We review the important differences that exist in the chemistry and physics of colloidal lead halide perovskite nanocrystals (APbX<sub>3</sub>, NCs, A=Cs<sup>+</sup>, FA<sup>+</sup>, FA=formamidinium; X=Cl, Br, I) as compared to conventional semiconductor NCs made of metal pnictides and chalcogenides. We survey the synthesis methods, optical properties and prospects of these NCs for optoelectronic applications [1, 2, 3].

The absorption spectral, spontaneous and stimulated emission spectra of these NCs are readily tunable over the entire visible spectral region of 400-800 nm by composition as well as by the NC size and shape [4-5]. Post-synthetic chemical transformations of colloidal NCs, such as ion-exchange reactions, provide an avenue to compositional fine tuning or to otherwise inaccessible materials and morphologies [6]. The photoluminescence of these NCs is characterized by narrow emission line-widths of <100 meV (12-45 nm from blue-to-near-infrared), wide color gamut covering up to 140% of the NTSC color standard, high quantum yields of up to 100%. Cs- and FA-based perovskite NCs are highly promising for luminescence downconversion (bright and narrow emission at 530 and 640 nm; backlighting for displays), for light-emitting diodes and as precursors/inks for perovskite solar cells.

With a new ligand capping strategy utilizing common and inexpensive long-chain zwitterionic molecules such as 3-(N,N-dimethyloctadecylammonio) propanesulfonate, a much better chemical durability can be attained [7]. In particular, this class of ligands allows for the isolation of clean NCs with high photoluminescence quantum yields of above 90% after 4 rounds of precipitation/redispersion along with much higher overall reaction yields of uniform and colloidal dispersible NCs. Densely packed films of these NCs exhibit high photoconductivity, high photoluminescence quantum yields and low thresholds for amplified spontaneous emission. In particular, high purity colloids are ideal for further engineering as needed for photochemical/photocatalytic applications. Towards these applications, a unique feature is that perovskite NCs appear to be trap-free without any electronic surface passivation, making photogenerated electrons and holes readily available for surface chemical reactions. Perovskite NCs also readily form long-range ordered assemblies known as superlattices. These assemblies exhibit accelerated coherent emission (superfluorescence), not observed before in semiconductor nanocrystal superlattices [8].



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# Electron-hole exchange energy and fine structure of excitons in polymorphic CsPbBr<sub>3</sub> single nanocrystals

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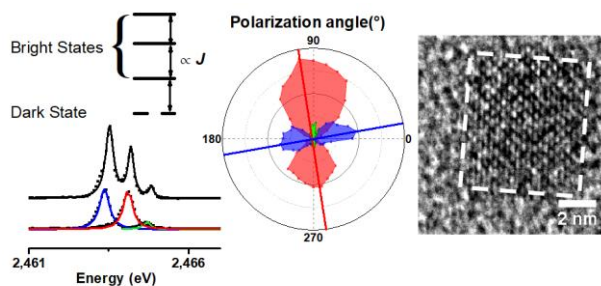
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All inorganic CsPbX<sub>3</sub> (X=Cl, Br, I) nanocrystals (NCs) belong to the novel class of confined metal-halide perovskites that currently arouses enthusiasm and stimulates a huge activity due to outstanding properties across several fields of optoelectronics [1]. A deeper knowledge of the band edge excitonic properties in those materials is thus crucial to further optimize their performances.

Here, high-resolution photoluminescence ( $\mu$ -PL) spectroscopy of single bromide based NCs reveals sharp peaks linearly polarized and grouped in doublets or triplets structures that directly mirror the adopted crystalline structure, tetragonal (D<sub>4h</sub> symmetry) or orthorhombic (D<sub>2h</sub> symmetry)[2]. The energy spacings in doublets and triplets can be expressed as a function of fundamental parameters of CsPbBr<sub>3</sub> NCs: spin-orbit splitting  $\Delta_{SO}$ , the crystal field correction with respect to the cubic crystal field of tetragonal,  $T$ , or orthorhombic terms  $|\varepsilon|$ , and the electron-hole exchange energy,  $J$  [3]. From absorption measurements performed in an ensemble of NCs which do not show confinement effects, the fundamental parameters defining the bulk band structure near the gap have been determined:  $T = -0.34 \pm 0.05$  eV and  $\Delta_{SO} = 1.20 \pm 0.06$  eV. From experimental data, at the individual object scale, fine estimations of  $|\varepsilon|$  and  $J$  are obtained. The latter parameter is proportional to the spatial overlap of the electron and hole wave-functions. A sharp enhancement of the electron-hole exchange energy due to the electronic confinement has been already demonstrated in low-dimensional systems [4]. We have obtained for NCs with sizes comparable to the exciton Bohr diameter,  $J \approx 3$  meV. This value is enhanced by confinement and is nearly constant for the studied NCs sizes.



**Fig. 1-** Left-side : scheme of the exciton fine structure of an orthorhombic crystal. Typical triplet spectrum of a single NC. In the center: the polarization diagram of the shown triplet with the same color code that in  $\mu$ -PL spectrum. Right-side TEM image of a single CsPbBr<sub>3</sub> NC.

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# Magnetoexcitons in colloidal MAPbI<sub>3</sub> nanoplatelets

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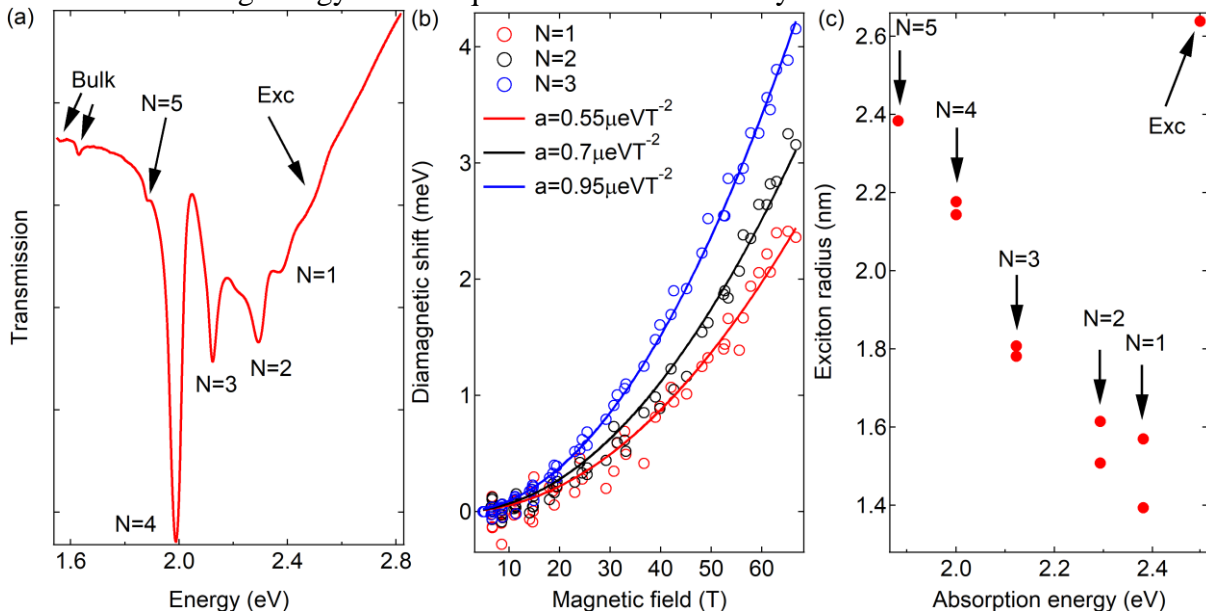
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Methylammonium (MA) lead halides form quasi-2D nanocrystals, referred to as nanoplatelets, under the right synthetic conditions [1]. Their optical properties can be readily tuned by varying controllably their thickness, taking advantage of quantum confinement effects. We investigated the excitonic properties of a dispersion of MAPbI<sub>3</sub> nanoplatelets containing nanocrystals of thicknesses  $N$  ranging from 5 to 1 PbI<sub>6</sub> octahedra planes. A typical low temperature transmission spectrum of the multidispersed solution is shown in Fig. 1(a). We attributed the low absorption features at 1.6eV to bulk MAPbI<sub>3</sub>, probably related to a residual fraction of very thick nanoplatelets. We assigned the energy dips comprised between 1.9eV and 2.4eV to the excitonic absorption of nanoplatelets of varying thickness. The highest energy absorption at 2.5eV is assigned to an excited excitonic state. We performed systematic magnetotransmission measurements up to 70T, and we observed a quadratic magnetic field dependence for all the dips related to quasi-2D nanoplatelets, which confirms the excitonic nature of their absorption. Interestingly, we observed a well-defined trend of the diamagnetic coefficient, which decreased with decreasing nanoplatelet thickness, as shown in Fig. 1(b). We estimated the exciton radius  $\langle r \rangle$  via its relationship with the diamagnetic coefficient  $a = e^2 \langle r^2 \rangle B^2 / 8\mu$ , where  $\mu$  is the exciton reduced mass,  $B$  is the applied magnetic field and  $e$  is the electron charge. These results, summarized in Fig. 1(c), demonstrate that the dip observed at 2.5eV is related to an excited excitonic state. These results can be used to estimate the exciton binding energy in these quasi two-dimensional systems.



**Figure 1 (a) Low temperature transmission spectrum of a dispersion of MAPbI<sub>3</sub> nanoplatelets. The dips correspond to absorption of nanoplatelets with the indicated thickness. (b) High magnetic dependence of the absorption energy of nanoplatelets of different thicknesses. (c) Exciton radii corresponding to nanoplatelets of different.**

1. Hintermayr et al., *Advanced Materials* 28, 9478

# Devices

## Approaches towards perovskite industrialization: efficient 4-T Tandem integration and encapsulation techniques

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Perovskite Solar Cells (PSC) have grown extraordinarily during recent years, being today one of the most interesting and promising photovoltaic technologies. In particular, their excellent electro-optical properties such as wide tunable bandgap and high diffusion lengths, in combination with a great variety of possibilities for their fabrication have converted them in interesting candidates for future commercial applications in general and for top cells in perovskite/silicon tandems in particular.

On the one hand, different encapsulation techniques consisting in ALD- $\text{Al}_2\text{O}_3$  deposition and EVA lamination respectively were demonstrated as effective methods to enlarge long-term stability of encapsulated perovskite solar cells in comparison to non-encapsulated ones.

On the one hand, we have fabricated a semitransparent PSC with the following architecture ITO/Spiro-OMeTAD/Perovskite/mp-TiO<sub>2</sub>/bl-TiO<sub>2</sub>/FTO/Glass obtaining 17% efficiency in small size ( $J_{SC}=20.34 \text{ mA cm}^{-2}$ ,  $V_{OC}=1095 \text{ mV}$ ,  $\text{FF}=76.2\%$ ,  $\text{area}=0.16 \text{ cm}^2$ ) and 16.7% in bigger devices ( $J_{SC}=21.53 \text{ mA cm}^{-2}$ ,  $V_{OC}=1065 \text{ mV}$ ,  $\text{FF}=73.0\%$ ,  $\text{area}=0.64 \text{ cm}^2$ ). It is remarkable the absence of buffer layer between Spiro-OMeTAD and magnetron sputtered ITO which was found not necessary when heating processes were carefully optimized. Then, a conventional commercially-available aluminum back surface field (Al-BSF) silicon solar cell with 19.5% efficiency (18.5% after cutting) was placed as a bottom cell of a 4T perovskite/silicon tandem giving a filtered performance of 5.7% for an overall 22.4% efficient 4-T tandem when bigger semitransparent PSCs were employed.

## Interface Energetics in Halide Perovskites

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My talk will focus on the means and developments to analyze and tailor functional interfaces in metal halide perovskite (MHP) based semiconductor devices. The topic is originally rooted in our drive to understand and control the key parameters for performance, stability and scalability of the new generation of perovskite solar cell (PSC) technology. In this regard, gaining control over the electronic properties at the nanoscale and the respective interfacial design routes is on track to generate the next big leap for renewable energies.

For the complete device, the electronic coupling between the perovskite absorber and adjacent charge extraction and transport layer is critical for maximizing the cell functionality. On the one hand, the device characteristics can be affected by the alignment of the frontier molecular orbitals of an organic charge transport layers (CTL) with the electronic transport level in the perovskite [1]. On the other hand, the doping type of the substrate underneath can template the doping type of subsequently deposited MHP films [2].

In our studies we elucidated these mechanisms by examining a selection of organic and oxide charge transport layers adjacent to the perovskite film. The choice of transparent conductive oxide layers employed ranges across functional *n*-type (e.g. TiO<sub>2</sub>), *p*-type (e.g. NiO<sub>x</sub>), high work function oxides (e.g. MoO<sub>x</sub>) and intrinsic oxides (e.g. Al<sub>2</sub>O<sub>3</sub>) [1-3]. In my talk, I will highlight the use of ultraviolet and X-ray photoemission spectroscopy (UPS/XPS) as well as inverse photoemission spectroscopy (IPES) to determine the surface energetics and electronic energy level alignment at the MHP/CTL interface while at the same time tracking the interface chemistry. This approach enables us to explain band offset in the perovskite layer by either chemical interactions or by changes in the electrostatic potential. The results not only suggest guidelines on how to integrate charge extraction layers into perovskite photovoltaic devices but also explain more generally to what extent the electronic structure of the perovskite is subject to extrinsic perturbations. The respective results then inform us on alternative interface configurations, that could for instance include conductive carbon contacts. In particular, our work on semiconducting single walled carbon nanotubes demonstrates a preferential energetic alignment which results in rapid charge carrier collection at the absorber/transport layer interface [5,6].

I will conclude my talk by giving one examples of interfacial design in the PSC device architecture, which allowed us to reach an unprecedented level of operational stability [6], and a further example, that underlines how MHP surface treatment can be employed to achieve record power conversion efficiencies in MHP-based quantum dot solar cells [7].

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## Effect of chlorine addition on intrinsic stability of Perovskite solar cell

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In the field of photovoltaics, the recent concept of perovskite solar cells has attracted great interest due to their high efficiency combined with a potential low cost and good versatility. The main remaining challenge now concerns their intrinsic stability. There is a vital need for a better understanding of the degradation mechanisms and thereby the possible mitigation strategies.

The presented work focuses on perovskite solar cells with architectures specifically optimized for large scale production on flexible substrates. The planar NIP architecture uses aluminum doped zinc oxide (AZO) as the N layer, a chlorine containing MAPbI<sub>3</sub> as active perovskite material, and regular P3HT as P layer. AZO presents the advantage of having a low processing temperature (<150°C) enabling its use with flexible substrates. P3HT is available at large scale. In addition, it acts as a barrier material and delays the degradation of the perovskite (1). The studied perovskite material is a Cl containing MAPbI<sub>3</sub> system. This system has been described in details (2), and may lead to high efficiency. Nevertheless the exact composition of the perovskite material can have a strong impact on the performance durability. We propose to thoroughly study the effect of chlorine addition on intrinsic stability of Perovskite during an ageing at 35°C under nitrogen.

In presented work, we will unravel the occurring degradation processes with a broad range of characterization methods. Thanks to chemical and microstructural characterizations such as infrared spectroscopy, Raman spectroscopy, optical microscopy and XRD, some markers of degradation (PbI<sub>2</sub>, PbCl<sub>2</sub>...) and of the different perovskite phases (MAPbI<sub>3</sub>, MAPbCl<sub>3</sub>) have been determined and these latter allow to follow the chemical composition of the perovskite material and eventually its degradation during aging. Combining the Raman and optical microscopy, it is possible to study the lateral degradation gradient. Correlating these results with UV-visible absorption, photoluminescence spectroscopy and photovoltaic characteristics enables to track the degradation processes, and their impact on performances. Using this procedure for variable chlorine ratios it was possible to understand the effect of each degradation parameter on the performances of the cells and to provide a path for improvement of the device intrinsic stability.

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## Thin film perovskite solar cells by evaporation

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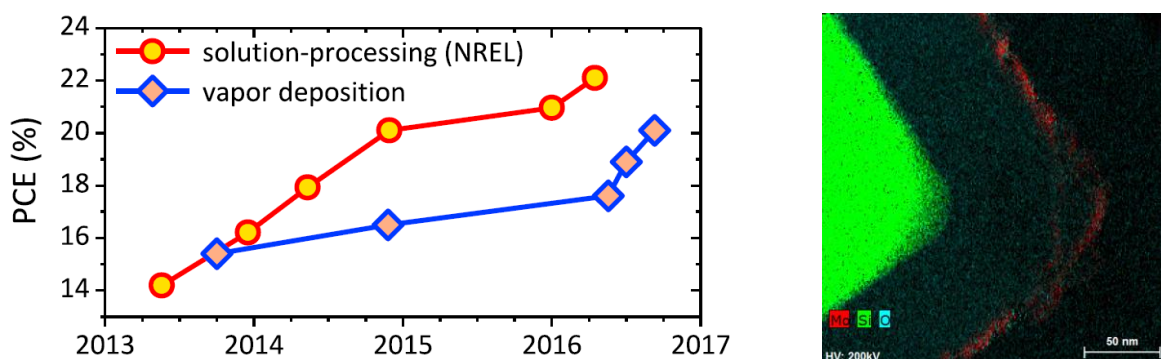
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Thin film perovskite solar cells have made an impressive breakthrough in the pool of the most promising materials for reaching high power conversion efficiencies (PCE) in a near future, with established record of 22.7% for  $\sim$ mm<sup>2</sup> cells [1]. For the ease of fabrication, these improvements have been, to a far extent, based on lab-scale solution-processing techniques. Significant progresses have been made to move to larger areas and 10% PCE have been demonstrated for 170 cm<sup>2</sup> mini-module [2]. On the other hand, vapor-based techniques have already been proven to be compatible with mass production in many sectors of the industry, notably in the semiconductor industry; for example, commercial OLEDs devices are now fabricated by fully vapor-based techniques. In the field of thin film photovoltaics, we note that leading companies have also adopted this route, being for inorganic compounds like CdTe (First Solar), CIGS (Solar Frontier) or for organic compounds (Heliatek). Last but not least, Oxford PV, the leading company for the mass production of perovskites has recently announced to build a pilot-line at former Bosch Solar CIGS thin film site with evaporation tools.

In this context, evaporated perovskites have gained a strong interest and, at the lab-scale, are in close competition with solution-processed perovskites, as illustrated in Figure 1. In this contribution, we will explain the advantages of evaporation techniques for the fabrication of high quality perovskite-based solar cells. However, it is also clear that not real large area device has been demonstrated so far on this route. A key factor to reach this goal is the control of the highly volatile CH<sub>3</sub>NH<sub>3</sub> precursor used in the standard CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite. We will briefly review the several strategies in use to overcome this point and show preliminary results of homogeneity measurements on a 100 mm diameter size obtained in a home-made dual source evaporation set-up in our lab. Modest but homogeneous efficiencies of 5% have been obtained on 16 mm<sup>2</sup> cells. Another often highlighted advantage of evaporation is its superior conformability on textured surfaces where wettability issues must be faced for solution-processing techniques. However a clear comparison between wet and dry routes has not been realized so far. We have started to investigate this point and will show preliminary results of evaporated ultrathin layers (down to 5 nm, obtained on an evaporation tool from German company Creaphys, Dresden) on textured silicon surfaces studied by high resolution transmission electron microscopy (Figure 1).



**Fig. 1** (left) comparison of PCE progress of solution-processing and vapor deposition route [3]; (right) conformability of ultrathin evaporated layers of MoOx (hole transporting material in use in perovskite solar cells) on textured silicon surfaces, studied by HRTEM.

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2) <https://solliance.eu/solliance-realizes-a-first-up-scaled-perovskite-based-pv-module-with-10-efficiency/>

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## **3D perovskites, physics**

# Unravelling fine structure splitting of the bright exciton in a bulk MAPbBr<sub>3</sub> single crystal

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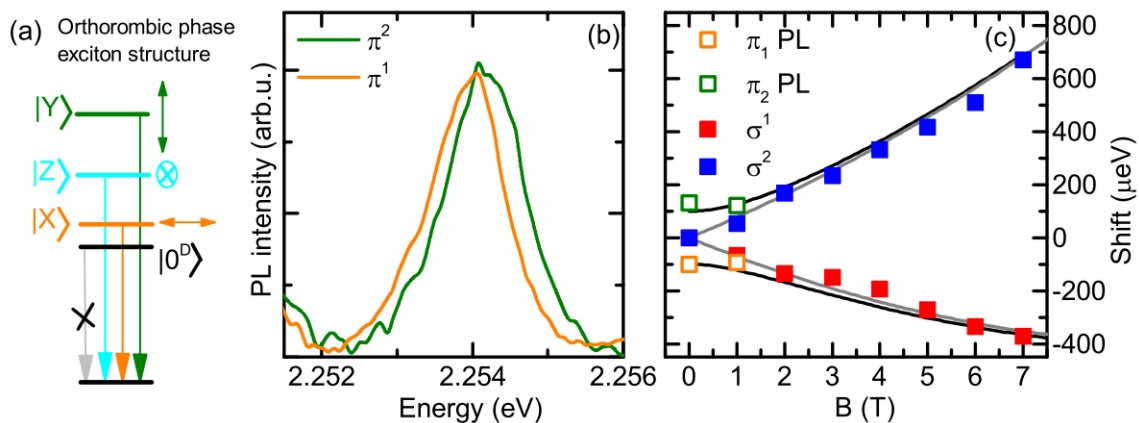
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The exchange interaction between the electron and the hole lifts the degeneracy between the dark singlet and bright triplet excitonic states. The bright states can be further split in the presence of a symmetry breaking leading to bright excitonic fine structure. To date, investigations have largely focused on semiconductor nanostructures where quantum confinement greatly enhances the exchange interaction and breaks the symmetry of the system.

To the best of our knowledge, the fine structure splitting of the bright exciton triplet state has never been observed in a bulk semiconductor. Here we report on the observation a giant FSS of the bright 1s exciton states in a bulk high quality MAPbBr<sub>3</sub> single crystal. We have performed a detailed magneto-optical investigation to reveal the FSS as large as 200 eV. Such a large FSS in bulk material indicates a strong symmetry breaking in the orthorhombic crystal lattice and/or significant Rashba enhancement of the FSS. For our bulk single crystal quantum confinement can be excluded so our results give direct insight into the FSS related solely to crystal structure of bulk MAPbBr<sub>3</sub>.



**Figure 1. (a) Scheme of exciton fine structure in orthorhombic crystal lattice phase. (b) two linear polarized components of photoluminescence. (c) dependence of PL peak position as a function on magnetic field detected at linear and circular polarization base.**

Our investigation provide valuable insight for the future understanding of the contribution of different mechanisms, such as confinement anisotropy or Rashba effect, to the FSS of excitons in perovskite based nanostructures. This represent a crucial step in the understanding of fine structure splitting in lead-halide perovskites.



## Quantum modeling of electronic transport in MAPI : role of the dipole of the organic molecule

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The electron and hole mobilities in MAPbI<sub>3</sub> are of the order of a few 10 cm<sup>2</sup>/Vs and in view of the effective mass estimated by band structure calculations, of the order of 0.2 m<sub>e</sub>, the scattering time is expected to be very short, of the order of a few femtoseconds. Recent ARPES measurements indicate also a very short scattering time [1]. This suggests that the electronic mean-free path is short, of the order of a few unit cells and that the disorder plays a central role for the electronic characteristics of charge carriers.

We consider a tight-binding model, which parameters have been determined from band structure calculations [2]. Our model takes into account the presence of disordered dipoles of the methyl ammonium molecule and of structural disorder at a level compatible with the measured mobilities. We compute the quantum diffusion by a method that we used recently to analyze the mobility of organic semi-conductors [3].

Our calculations show that the disordered dipoles alone can hardly explain the transport properties of charge carriers. We find also that semi-classical models (Bloch-Boltzmann or Drude like) cannot be applied to describe the hole and electron transport in MAPI. We show that strong localization effects due to disorder take place in these systems. We also compute the AC-conductivity in the Terahertz range. Our results compare well with recent experiments, which also suggest the existence of backscattering which is typical of quantum localization [4].

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## Emission properties of quantum dots in perovskite matrix.

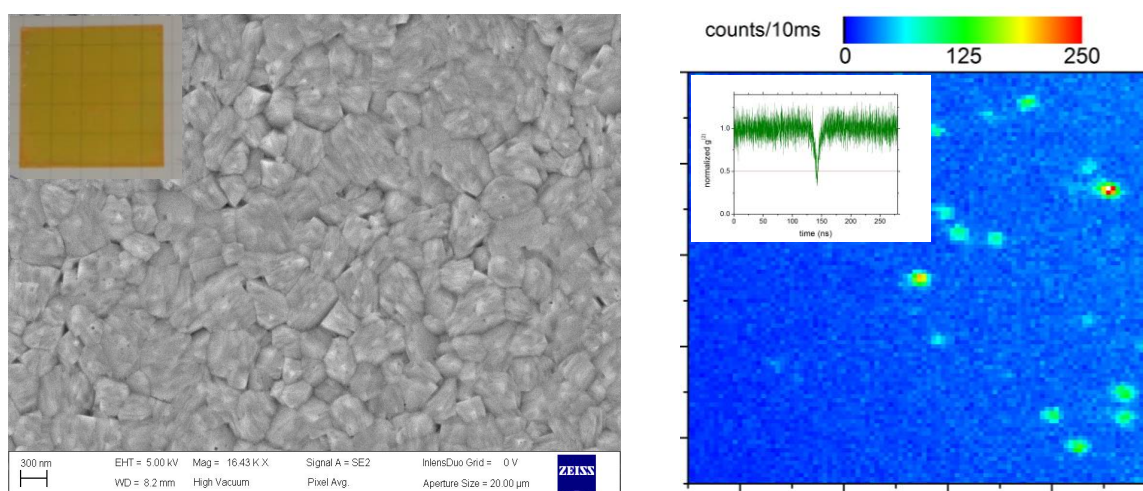
Justine Baronnier<sup>a</sup>, Benoît Mahler<sup>a</sup>, Julien Houel<sup>a</sup>, Florian Kulzer<sup>a</sup> and Christophe Dujardin<sup>a</sup>.

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Application-critical optical properties of single quantum dots, for example their emission wavelength and their fluorescence decay rate,<sup>1</sup> can be influenced by incorporation in a suitable matrix. Hybrid lead halide perovskites are promising candidates for such matrices with respect to charge control and reduction of type-A blinking of chalcogenide quantum dots. Methylammonium lead bromide perovskite (MAPbBr<sub>3</sub>) in particular not only exhibits a favorable and tunable band alignment, but furthermore a lattice parameter that is compatible with the formation of a crystalline matrix around the QD nanocrystals.

We have established an experimental protocol for producing thin films of a hybrid QDs-MAPbBr<sub>3</sub> perovskite in which the QD concentration is adjustable. To this end, we first fabricated highly luminescent core-shell QDs with a CdSe/Cd<sub>x</sub>Zn<sub>1-x</sub>S gradient shell<sup>2</sup> that are sufficiently resilient to the deleterious effects of mobile lead cations in the perovskite matrix. The second crucial step was the exchange of the organic ligands of the QDs with bromide ions<sup>3</sup> under preservation of colloidal stability so that all precursors of the film can be mixed in solution without the presence of long carbon chains that would interfere with subsequent crystal formation. Finally, a method had to be identified that allowed to prepare compact and homogeneous perovskite films to ensure the successful embedding of the QDs. For this purpose, we found that thin-film creation by chlorobenzene injection<sup>4</sup> showed the best results (Figure 1a).



**Figure 1: a) SEM image of the thin film perovskite and b) Image of QDs-perovskite sample by confocal microscopy with a QDs selective filter and antibunching graph ( $\lambda_{\text{excitation}} = 590\text{nm}$ , FB  $650 \pm 20\text{nm}$ )**

The emission of single QDs could be detected in MAPbBr<sub>3</sub> perovskite films with a low degree of doping (Figure 1b). A red shift of the emission, monoexponential fluorescence decays and fluorescence antibunching could be observed, all of which indicates that the quantum efficiency of the QDs was largely preserved during the encapsulation process. These samples thus constitute a starting point for investigating and, possibly, controlling the blinking behavior of single nanocrystals in a semiconducting matrix with favorable band structure.

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## Evidence of halide ion migration in $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ based perovskite solar cell and its effect on current-voltage hysteresis

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Hybrid perovskite solar cells (PSCs) have rapidly emerged as a promising candidate for the next generation photovoltaics with power conversion efficiencies (PCEs) up to 22%. Low temperature solution processing, low cost raw material and relative insensitivity to intrinsic point defects are some of the attractive qualities of this emerging class of devices. But one of the major obstacles for the commercialization of PSCs lies in the long-term stability of the perovskite films subjected to different environmental conditions such as temperature, humidity and illumination.

In this work, we focused on experimental evidence of halide ion migration in  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  based solar cells and its effect on current-voltage hysteresis for which various mechanisms have been proposed. The inverted planar structure adopted for the PSCs was: glass/ITO/PEDOT:PSS/perovskite/PCBM/Ag. The perovskite thin films were deposited by 1-step spin-casting process and the organic PEDOT:PSS (hole-transporting layer) and PCBM (electron-transporting layer) layers were deposited by spin-coating process.

Firstly, the PCE under 1 sun equivalent illumination reached 12.7% for the best cell of a series of 10 samples with an active area of  $0.28 \text{ cm}^2$ . The J-V hysteresis effect was small (less than 2.5%) between the reverse and the forward direction, consistent with the results reported in the literature. Secondly, using glow discharge optical emission spectrometry (GD-OES), a spectroscopic technique allowing direct determination of major and trace elements, we have shown that halide ions migrate inside the perovskite films under an applied bias during 2 minutes in both directions. Furthermore, no migration of lead and nitrogen ions was observed in the same time scale. Thirdly we observed the hysteresis of current-voltage characteristics under dark conditions (thus without any photo-generated carriers) versus voltage scanning rate and temperature. The activation energy value of 0.253 eV derived from the Nernst-Einstein relation above 264 K, for which the perovskite phase is tetragonal, indicates that the conduction is dominated by the ions (instead of electrons for conventional semiconductors) and furthermore confirms that the conduction is ascribed to the migration of anion vacancies, which is well known in the perovskite-type halides such as  $\text{CsPbCl}_3$  or  $\text{CsPbBr}_3$ . These experiments prove that there is a direct link between halide ion migrations in  $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$  based perovskite thin films and current-voltage hysteresis.

# Low temperature cation local dynamics in mono and poly cation halogenated perovskites as seen by neutron backscattering spectroscopy

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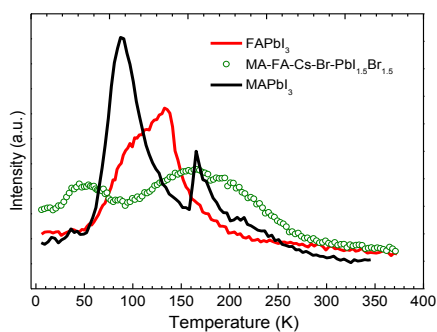
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Investigating the motion of the organic cations is crucial to understand the properties of the recently promising hybrid photovoltaic materials based on a lead triiodide anionic sublattice coupled to organic cations as methylammonium  $\text{CH}_3\text{NH}_3$  [1-3], formamidinium  $(\text{HC}(\text{NH}_2)_2)$  [4] or a mixture of both [5]. In particular in this last case, it has been shown that solar cells based on photoactive  $(\text{CH}_3\text{NH}_3)_{0.5}(\text{HC}(\text{NH}_2)_2)_{0.5}\text{Cs}_{0.05}\text{Rb}_{0.05}\text{Pb}(\text{I}_{0.5}\text{Br}_{0.5})_3$  perovskite are much more stable under light than their mono-cation counterparts [6,7]. Accordingly we decided to investigate the local motion of organic cations in these three different materials using incoherent quasi-elastic neutron scattering measurements. Here we will concentrate on the results obtained in the low temperature range  $2 < T < 180\text{K}$  by using neutron backscattering spectroscopy (figure1).



**Fig. 1:** Inelastic Fixed Window Scans of the three studied compounds as recorded on the backscattering spectrometer IN16B (ILL).

First, we will show the results concerning the motion in the low-temperature phase of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  using both experimental and theoretical methods, with a particular focus on the activation energy. Inelastic and quasi-elastic neutron scattering measurements result in an activation energy of 48 meV. We attribute this activation energy to the rotation of  $\text{CH}_3$  rotors only, with the  $\text{NH}_3$  rotors not involved in the dynamics. First-principles (density-functional-theory) calculations shows that the rotation of a  $\text{CH}_3$  rotor does not induce the motion of  $\text{NH}_3$  and the surrounding inorganic atoms. Including the nuclear quantum effects, path integral molecular dynamics results in an activation energy of 42 meV for the  $\text{CH}_3$  rotation, agreeing well with the neutron scattering experiments. For the rotation of an  $\text{NH}_3$  rotor which is bound to the inorganic cage via strong hydrogen bonding, density-functional-theory modeling indicates an energy barrier of 120 meV thus it is unlikely to occur at low temperatures [8].

Concerning  $(\text{HC}(\text{NH}_2)_2)\text{PbI}_3$ , we found a clear motion of protons with an activation energy of 40,9 meV below the cubic I – tetragonal structural transition at 135K. When approaching the structural transition at 135K, at least two different regimes of local motions of cations could be revealed, one with a 45 meV activation energy and a second one with a lower 25 meV activation energy, suggesting the existence of two unequivalent populations of cations when the system undergoes the structural transition. Finally, concerning the phase with mixed cationic and mixed halogen sublattices, we will show that the local motion of cations at low temperatures can not be described the same way as it is in the mono-cation systems. As a consequence of possible thermally activated soft octahedral rotations in the formamidinium based system [9], this mixed compound keeps in average the same structural type through the whole explored temperature range. This structure accommodates both MA and FA cations. As a consequence we will show that our measurements suggest the coexistence of a large number of motions types for the two cations. This situation is then misleading for estimating a unique energy activation for the local motions of protons [10]. We will show that it is more correct to describe this dynamics in terms of at least six stochastic components to reproduce the experimental data and we will discuss this result.

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- 10) D. Djurado et al., oral talk given for JPH2017 in Angers will be accordingly reconsidered.

## Low-frequency Raman spectroscopy and elastic softness of hybrid lead halide perovskites

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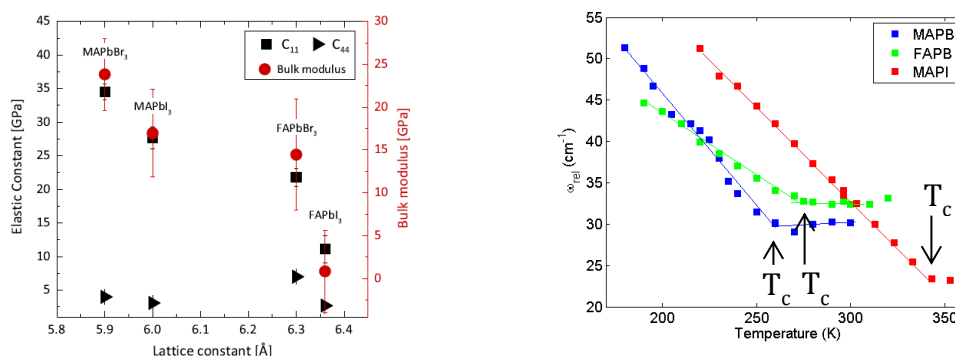
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<http://www.coulomb.univ-montp2.fr/Presentation-131->

Hybrid organic-inorganic perovskites are intensively studied as promising materials for various applications, taking advantage of their low cost and easy processing. Although much recent attention has been devoted towards unraveling their microscopic optoelectronic properties, the low frequency dynamics (*e.g.* their softness) is currently still lacking a comprehensive understanding as compared to that already reached for classic semiconductors.

Here we investigate the low frequency dynamics in four different hybrid perovskite single crystals: MAPbBr<sub>3</sub>, FAPbBr<sub>3</sub>, MAPbI<sub>3</sub> and  $\alpha$ -FAPbI<sub>3</sub>. Using coherent inelastic neutron scattering spectroscopy and Brillouin light scattering, we investigate the low frequency acoustic phonons [1,2]. A very small shear C<sub>44</sub> elastic constant is found for all the compounds as well as sizeable elastic anisotropy. The extremely low bulk modulus and negative C<sub>12</sub> in  $\alpha$ -FAPbI<sub>3</sub> substantiates its very unstable nature and in FAPbBr<sub>3</sub>, a tendency towards an incipient ferroelastic transition, is interpreted as further evidence of the influence of plasticity in hybrid perovskites. We observe a systematic lower sound group velocity in the technologically important iodide-based compounds compared to the bromide-based ones [2]. The findings suggest that low thermal conductivity and hot phonon bottleneck phenomena are expected to be enhanced by low elastic stiffness, particularly in the case of the ultrasoft  $\alpha$ -FAPbI<sub>3</sub> (Fig. 1a).

The low-frequency dynamics is further investigated by Raman spectroscopy. The scattering from the low-frequency optical phonons has been collected across the cubic to tetragonal transition. With the resolution and contrast available by our experiment ( $\sim 4\text{-}5\text{ cm}^{-1}$  at the bottom of the elastic line) we do not observe the divergence of a central peak. However, the lowest frequency vibration, almost temperature independent in the cubic phase, hardens on cooling in the tetragonal phase. These conclusions apply in three of the four samples (analysis in  $\alpha$ -FAPbI<sub>3</sub> still in progress) suggesting a common framework for the analysis of the low-frequency vibrational dynamics of this family compounds (Fig. 1b). In CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> the Raman spectroscopy across the full set of phase transitions down to 20 K will also be discussed.



**Fig. 1 (a)** Elastic constants C<sub>11</sub> and C<sub>44</sub> and bulk modulus in the cubic phase as a function of the changing of lattice constant between compounds (neutrons). **(b)** Temperature dependence of the relaxational frequency  $\omega_{rel} = \omega_0^2/\Gamma$  of the lowest frequency phonon (Raman).

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# Poster session

## Cristallogénèse et caractérisations de monocristaux de $\text{CH}_3\text{NH}_3\text{PbBr}_3$

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Les pérovskites hybrides constituent une famille de matériaux aux propriétés prometteuses pour les applications optoélectroniques. Leur mise en œuvre par voie liquide et sous forme de couches minces polycristallines, permet de les intégrer dans plusieurs types de dispositifs comme les cellules solaires, les diodes électroluminescentes, ou les photodétecteurs. D'autre part, les composés faisant intervenir des cations organiques à chaînes carbonées courtes présentent des structures tridimensionnelles favorables à l'élaboration de monocristaux (Figure 1). Ces derniers bénéficient d'un double intérêt, ils servent d'une part de matériaux modèles pour l'étude des propriétés intrinsèques des pérovskites hybrides [1], et d'autre part, permettent d'ouvrir de nouvelles perspectives d'applications grâce leurs caractéristiques singulières [2].



Figure 1 : Image de monocristaux de  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  fabriqués par la méthode de croissance cristalline par montée en température

Nous nous attacherons à présenter les développements récents menés en partenariat entre le CEA LITEN, le CEA LETI, et l'Institut Néel du CNRS, autour de la croissance en solution de monocristaux de  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  et de leurs caractérisations. La méthode de croissance cristalline par montée en température a été choisie car elle permet de faire croître des cristaux millimétriques en seulement quelques heures [3]. Nous exposerons nos derniers résultats concernant cette cristallogénèse, et discuterons de l'effet de plusieurs paramètres clés pour la maîtrise de la sursaturation en solution et de la qualité cristalline des monocristaux obtenus. Nous montrerons également les propriétés structurales, optiques, et optoélectroniques de ces cristaux. L'objectif à court terme sera de mesurer les propriétés électroniques et optoélectroniques des monocristaux de  $\text{CH}_3\text{NH}_3\text{PbBr}_3$  pour compléter les données actuellement disponibles dans la littérature et les positionner par rapport aux autres familles de semi-conducteurs.

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## TiO<sub>2</sub>/graphene-based nanocomposites for perovskites solar cells: synthesis and properties

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<http://www.xlim.fr/recherche/pole-electronique/rf-elite/elite>

Since 2012, hybrid solar cells based on perovskite materials demonstrated several significant advances, with power conversion efficiencies now over 22%, attracting strong interest within the scientific community [1][2]. Still, efforts remain to be performed to improve photo-current extraction, especially concerning the development of efficient and reliable charge transporting electrodes and selective contacts. Titanium dioxide mesoporous layer, while remaining an important component for perovskite structuration and electron transport in high efficiency devices, can however still promote charge trapping and recombination. To reduce these phenomena and improve electron collection, our strategy consists in using the excellent conductivity properties of graphene materials through its incorporation within the TiO<sub>2</sub> electrode.

Here, we combine specific know-hows on both perovskite solar cells processing and production of nano-scaled materials by laser pyrolysis. Our aim is to develop high quality TiO<sub>2</sub>/graphene nanocomposites with well-controlled physical properties for an optimal energy conversion.

We pay particular attention to material characterizations such as morphological and structural analysis as well as physical properties evaluation of the nanocomposites and their role and effects within solar cells. Our first results show a better electron injection efficiency with graphene, observed through steady-state photoluminescence spectroscopy. This tendency has been reinforced by devices performance that show larger photocurrents and smaller series resistance under standard illumination. More generally an increase in power conversion efficiency from 14.1 % to 15.1 % is reached for perovskite solar cells containing graphene in the mesoporous layer, demonstrating the benefit of the laser pyrolysis process for the production of high quality electron transport layer.

[1] [www.nrel.gov/ncpv/](http://www.nrel.gov/ncpv/)

[2] H. Zhou et al., *Science* **2014**, vol 345, page 542-546



## The finer points of lead halide perovskites: atomic-scale characterization through solid-state NMR

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Lead halide perovskites are leading the research scene because of their wide ranging applications in photovoltaics, detectors, light emission, and thermoelectricity. A lot of work is being put into the characterization of these materials finding band gap, phase composition and segregation (if any), and cation dynamics, using conventional means (UV-Visible spectroscopy, calorimetry, thermogravimetric analysis, XRD, TEM etc.). Solid-state NMR has recently proved to be a particularly useful technique for the purpose because it can study specific nuclei, short-range order, and dynamic components. It has recently been used to analyse systems with varying cationic and halogen moieties by studying nuclei like  $^{207}\text{Pb}$ ,  $^{133}\text{Cs}$ ,  $^{87}\text{Rb}$ ,  $^{39}\text{K}$ ,  $^{13}\text{C}$ ,  $^1\text{H}$ , and measuring organic cation dynamics using quadrupolar  $^2\text{H}$  and  $^{14}\text{N}$  NMR. We have performed variable temperature (100 to 300 K)  $^1\text{H}$  and  $^{13}\text{C}$  NMR experiments on CsFAPbI<sub>3</sub>, a highly promising photovoltaic material. As the temperature is elevated, the  $^1\text{H}$  longitudinal relaxation rate becomes slower, a characteristic of lead halide perovskites, uncommon for  $^1\text{H}$  nuclei in general, which indicates faster motion of cations in perovskite materials with increasing temperatures. From  $^{13}\text{C}$  NMR experiments we can attribute peaks belonging to black FAPI and also, notably, remaining DMF from the synthesis procedure. Upon performing  $^1\text{H}$  homonuclear correlation experiments we found interactions between the protons from FA and DMF, indicating incorporation of DMF into the perovskite material. Further investigations will involve studying other NMR active nuclei present in various substituted-perovskite systems, providing rich information about the phase and dynamics of the materials.

# Combining Solid-State NMR and Molecular Dynamics Simulations to investigate hybrid halide perovskites

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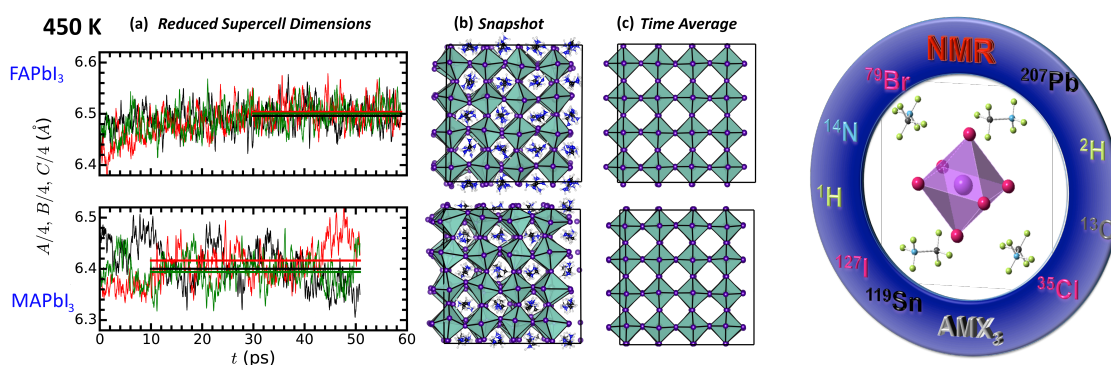
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The dynamical behavior of the organic cations in hybrid halide perovskites has triggered a wealth of experimental and theoretical investigations in the recent years. The intrinsic dynamical and electrical (dipolar) properties of the organic part were suggested to be responsible of some of the most noticeable features of these materials. A complex dynamic picture has progressively emerged for  $AMX_3$  (A is organic cation, M is metal, X is halogen) bulk materials, which combine highly anharmonic lattice vibrations and stochastic molecular reorientations, at high temperature [1-5]. These properties significantly influence the opto- electronic and thermal properties. Solid-state NMR is a tool that has the ability to probe the local structure and the dynamics in the solid state in several ranges of frequency. Interpretation of experimental NMR data frequently relies on input from atomic scale simulations such as those performed using density functional theory (DFT). Recently, it has been shown that static theoretical calculations of quadrupolar parameters ( $^2H$ ) in the orthorhombic phase of deuterated-MAPbBr<sub>3</sub> (MA = CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>), lead to significant overestimation of the linewidth broadening [6]. This was rationalized in terms of thermally activated internal rotational dynamics of the molecular cations. Herein, we further inspect the dynamics of APbX<sub>3</sub> solids by a joint experimental and theoretical effort with low temperature solid-state NMR measurements (< 25K). Starting from extensive DFT molecular dynamics trajectories performed on large (4x4x4) supercells for both the tetragonal and orthorhombic phases [5], we use a specifically designed procedure to account for the effect of the thermally activated cation dynamics in the calculated NMR parameters, which includes the quadrupolar lineshapes of the NMR spectra.



**Fig. 1 a-c** DFT molecular dynamics [5] with **a**, time evolution of the reduced supercell edges for the hybrid perovskites at 450 K (horizontal lines represent the mean values over the production fraction of the trajectories); **b**, snapshots displaying the instantaneous deformation of the inorganic lattice and the random orientation of the organic cations; **c**, time average of the inorganic lattice displaying a simple cubic structure. **d**, Multinuclear NMR as a tool for studying the local order and the dynamics in lead-halide hybrid perovskites [6].

- 1) J. Even, *J. Phys. Chem. Lett.* 6, 2238, **2015**
- 2) D. H. Fabiani et al., *J. Phys. Chem. Lett.* 7, 376, **2016**
- 3) M. A. Carignano et al., *Phys. Chem. Chem. Phys.* 18, 27109, **2016**
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- 5) M. A. Carignano et al., *J. Phys. Chem. C* 121, 20729, **2017**
- 6) C. Roiland et al., *Phys. Chem. Chem. Phys.* 18, 27133, **2016**

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# Ingénierie Nanophotonique pour cellule solaire tandem pérovskite/silicium

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Une des perspectives pour améliorer le rendement des cellules solaires en silicium est de combiner le silicium cristallin avec un autre matériau dans une structure en tandem afin d'obtenir une cellule d'efficacité supérieure à 30% [1]. Pour cela, la pérovskite est un matériau prometteur, en effet, elle possède un meilleur coefficient d'absorption dans le visible que le silicium, les deux matériaux peuvent se compléter pour former une cellule solaire tandem. Mais, que ce soit dans une cellule tandem de 2 terminaux, ou une cellule de 4 terminaux, un problème de pertes se pose. En effet, pour une cellule 2 terminaux, le courant de sortie est limité par la cellule de plus faible courant de court-circuit. Pour une cellule 4 terminaux, l'absorption des photons à haute énergie n'est pas totale dans la cellule pérovskite tandis qu'une partie des photons à faible énergie s'échappent à cause des réflexions à l'interface entre deux sous-cellules. Pour remédier à ça, nous envisageons d'insérer une structure nano-photonique entre les cellules. En fonction de la configuration (2 terminaux ou 4 terminaux), le design de cette structure nano-photonique sera optimisé pour : i) répartir la lumière dans le cas d'une cellule 2 terminaux afin d'obtenir un courant de court-circuit identique et maximisé dans chaque cellule ; ii) piéger les photons de haute énergie (i.e.  $\lambda < 800\text{nm}$ ) dans la cellule de pérovskite, et maximiser la transmission de photons de faible énergie (i.e.  $\lambda > 800\text{nm}$ ) vers la cellule de silicium dans le cas d'une cellule 4 terminaux (figure 1).

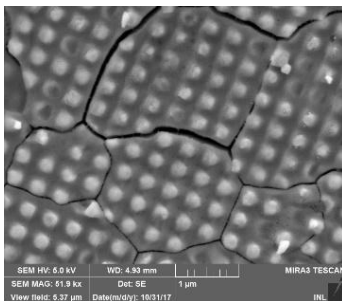


Image 1 : Image MEB de pérovskite structurée

Pour ce projet, le focus est établi sur la cellule pérovskite et la structure nano-photonique. La structure nano-photonique sera constituée de cristaux photoniques, et doit permettre, grâce aux couplages résonants entre la lumière incidente et les modes de Bloch lents du cristal photonique, de contrôler la réflectivité, l'absorption et la transmission de lumière [2]. Pour ce faire, nous envisageons de créer directement les cristaux photoniques dans la couche de pérovskite. En effet, il semble plus contrôlable, et reproductible de structurer la pérovskite au lieu de déposer la pérovskite sur une structure déjà conçue. Le choix de structuration s'est donc porté sur la nano-implosion de la pérovskite. Le principe de cette technique est d'appliquer un moule, avec une pression, sur la pérovskite durant son recuit. Cette dernière, va alors cristalliser en prenant la forme du moule. Les premiers résultats sont montrés image 1. Les résultats complets en termes de structure et de propriétés optiques seront présentés

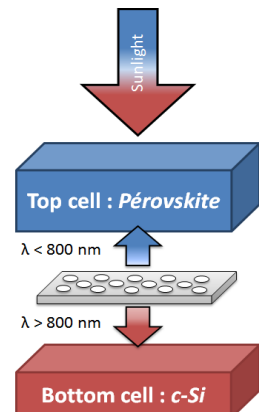


Fig. 1 : Structure de la cellule tandem avec cristaux nanophotoniques dans le cas d'une cellule 4 terminaux

- 1) N. N. Lal, T. P. White, and K. R. Catchpole, "Optics and Light Trapping for Tandem," *IEEE Journal of Photovoltaics*, **2014**, vol. 4, no. 6, pp. 1380–1386.
- 2) X. Letartre, et al., "Switching Devices With Spatial and Spectral Resolution Combining Photonic Crystal and MOEMS Structures," *Journal of Lightwave Technology*, **Jul 2003**, vol. 21, no. 7, pp. 1691–1698.

# Cathodoluminescence mapping of perovskite materials for photovoltaics

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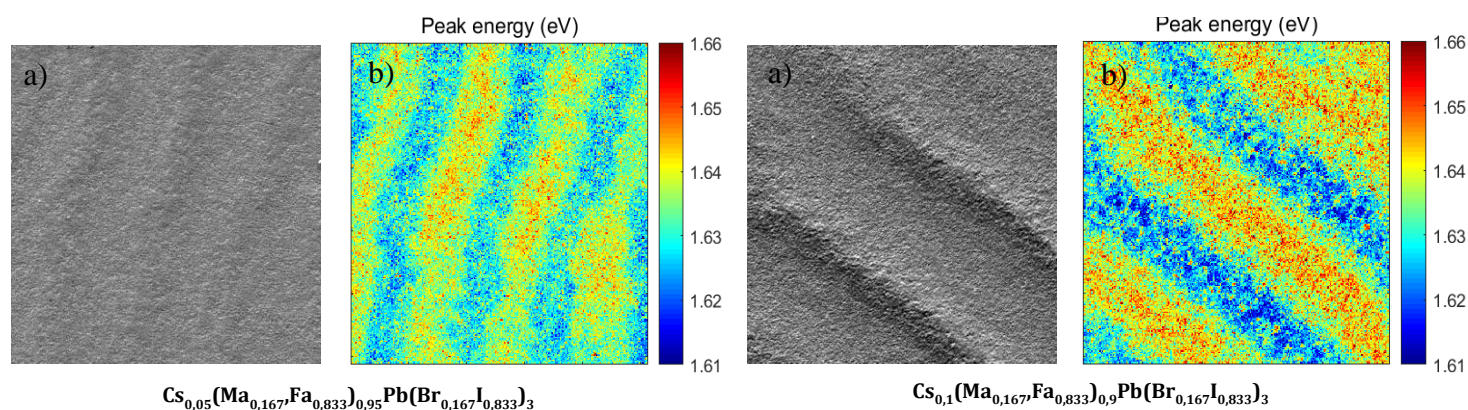
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Mixed-halide perovskites are promising materials for photovoltaic applications. However, their properties depend on their grain structures (boundaries, intra-grain properties,...) and phase segregation phenomena that require characterization techniques at the nanoscale<sup>[1-3]</sup>. Here, we present our first results on cathodoluminescence (CL) mapping of mixed halide mixed cation perovskite layers. The CL setup installed at C2N has a spatial resolution down to 10 nm thanks to the electron gun excitation source. It is able to acquire SEM, CL and EBIC maps simultaneously.

First experiments have been devoted to the study of electron-beam-induced damage of perovskite layers<sup>[4]</sup>. At this point, excitation conditions (low current, 3kV acceleration voltage) were defined to ensure low damage and reproducible results.

Then, (Cs,MA,FA)Pb(Br,I) perovskite materials with various compositions have been investigated. Morphological analysis by SEM exhibited wrinkles on the surface of the samples with widths and heights varying with its composition. Localized luminescence peaks at ~500nm were observed and attributed to PbI<sub>2</sub> clusters. For composition varying from 0% 5% and 10% of Cs, we observe a spectral shift of the luminescence peak across wrinkles (width 10-20µm). It is attributed to the presence of Cs-rich phases. This interpretation is also supported by the variation of the density of PbI<sub>2</sub> peaks. Several perovskite phases are also observed at the grain scale in (MA,FA)Pb(Br,I) layers (no Cs). CL maps were carefully analyzed by numerical filtering and fitting, and compared to PL and EDX mapping.



**Fig. 1:** a) 53x53 µm Top view Scanning Electron Microscopy (SEM) image and b) energy of the maximum luminescence peakpoint of each spectra from each point of the map for two different (Cs,MA,FA)Pb(I,Br) samples.

[1] X. Tang et al., Local observation of phase-segregation in mixed-halide perovskite, *Nano Letters*, **2018**.

[2] D.W. deQuilettes et al., Impact of microstructure on local carrier lifetime in perovskite solar cells, *Science*, **2015**, 348, 683–686.

[3] D. J. Slotcavage et al., Light-induced Phase Segregation in Halide-perovskite Absorbers, *ACS Energy Lett.*, 2018, 3 (1), 204–213.

[4] C. Xiao et al., Mechanisms of Electron-Beam-Induced Damage in Perovskite Thin Films Revealed by Cathodoluminescence Spectroscopy, *J. of Phys. Chem. C*, **2015**, 119, 26904-26911

## Halide perovskite polaritons and lasers

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Since 2012, the hybrid organic-inorganic perovskite  $\text{CH}_3\text{NH}_3\text{PbI}_3$  and its derivatives represent a material breakthrough for photovoltaics: the efficiency of perovskite-based solar cells has reached 22.7% today, which is at the same order of magnitude as the silicon-based solar cells. Since 2014, it appears that the properties of the hybrid halide perovskites are very interesting, not only for photovoltaic cells but also for light emitting devices paving the way to hybrid perovskites-based lasers and even to electrically injected lasers due to the good transport properties of this material. Additionally, it is possible to tune the bandgap of the hybrid perovskites in order to reach the green range which will allow addressing the problem of the green gap of the laser sources (the green gap refers to the fact that the laser diodes emitting directly green light are rare and not performing).

This poster will present the work on perovskite-based microcavities in the prospect of a perovskite-based laser working in the strong coupling regime. The strong coupling regime between the photonic mode and the perovskite's exciton has been observed at low-density pumping regime. Non-linear effects have occurred at high-density pumping. The nature of this non-linearity will be discussed.

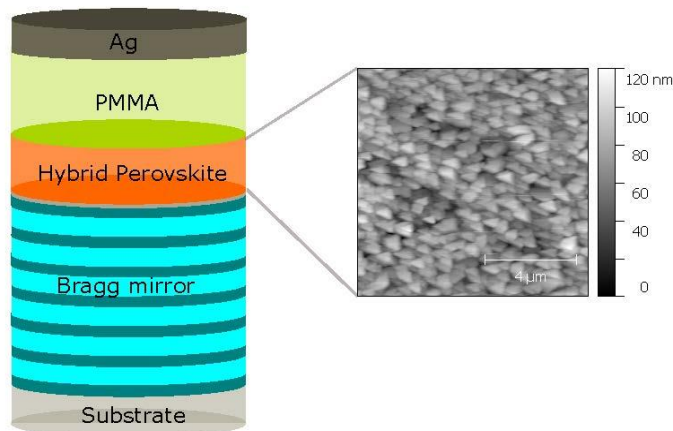


Figure 1 – Sketch of the microcavity structure.

A thin film of hybrid perovskite is deposited onto a commercial Bragg mirror (Layertec®) on which is deposited a thin layer of PMMA (poly(methyl methacrylate)) and a thin layer of silver constituting the second mirror. The perovskite and



## Temperature-dependent exciton linewidth of a single CsPbBr<sub>3</sub> nanocrystal

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Goubet Nicolas<sup>a</sup>, Frédéric Bernardot<sup>a</sup>, Christophe Testelin<sup>a</sup>, Emmanuel Lhuillier<sup>a</sup>, Alberto Bramati<sup>b</sup>,  
Maria Chamarro<sup>a</sup>

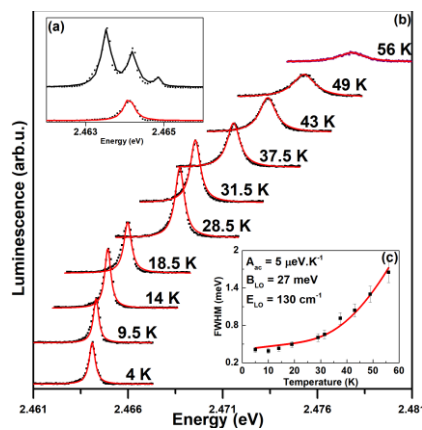
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All-inorganic halide perovskite nanocrystals present very attractive optoelectronic properties. Since their first synthesis in 2015 [1], they have been the center of a big quantity of studies exploring fundamental aspects and applications of these materials. Here, we address the electron-phonon interaction in a single CsPbBr<sub>3</sub> nanocrystal (NC). This interaction is of prime importance to determine performances of this material in optoelectronic devices as lasers and LED emitters, since this interaction governs the band-edge emission broadening.

We have performed micro-photoluminescence ( $\mu$ -PL) measurements on a single CsPbBr<sub>3</sub> NC with a size comparable to the Bohr diameter (7 nm) [2]. When the NC has an orthorhombic crystal symmetry, we observe an exciton fine structure composed of three peaks linearly polarized [3]. We took advantage of the polarization properties of  $\mu$ -PL to monitor in situ both the energy and linewidth of individual peaks when increasing temperature above 5K. We have found that two regimes exist, one at low temperature, dominated by interaction with acoustic phonons and another at high temperature for which interaction is dominated by longitudinal optical phonons. The acoustic contribution does not change when the energy of the excitonic transition varies in the range of 2.46–2.62 eV, i.e., with NC sizes corresponding to this range. Further investigations are required to explain the residual broadening contribution at 5K which is measured around 400  $\mu$ eV. Finally, by extrapolating our single NC measurements until room temperature, we obtain that the emission linewidth of CsPbBr<sub>3</sub> NCs would be in the order of 10 meV. This value sets a lower limit to the spectral width of the gain curve that can be achieved in lasers based on CsPbBr<sub>3</sub> NCs.



**Fig. 1.**-(a) (Black color)  $\mu$ -PL spectrum obtain at 5K in a orthorhombic CsPbBr<sub>3</sub> NC after excitation at 475 nm with an average excitation power of 2.5  $\mu$ W and a confocal-like microscope with NA= 0.6 to excite and measure the  $\mu$ -PL. (Red color) linealy polrized  $\mu$ -PL spectrum of the same NC. Solid lines represent fits to 3 or 1 lorentzien lines, respectively. (b) Evolution of the selected line with temperature. Experimental data (black dots) were fitted with a Lorentzian profile. (c) Evolution of the linewidth with temperature. Solid line represents a fit to the expresion  $\gamma(T) = \gamma_0 + A_{ac}T + B_{LO}n_{LO}(T)$ , where  $\gamma_0$  is a residual homogeneous linewidth including spectral diffusion supposed to be temperature independent. The second and third terms are homogeneous broadening terms resulting from acoustic and LO phonons (Fröhlich) scattering with charge-phonons coupling constants  $A_{ac}$  and  $B_{LO}$ , respectively.

- 1) L. Protesescu, *et al*, Nano Lett. **15**, 3692 (2015).
- 2) J. Ramade, *et al*, App. Phys.Lett, **112**, 072104 (2018).
- 3) M. Fu, *et al*. Nano Letters, **17**, 2895, (2017).

# Observation of strong coupling with hybrid perovskite in photonic crystal

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Cavity polaritons are quasi-particles arising from the strong coupling regime between excitons of quantum wells and photons of micro-cavities. The hybrid light/matter nature of polaritons makes the quasi-particles behave like ultra-nonlinear photons – which are particularly attractive for optical switching and logic elements. Indeed, thanks to the photonic component, such platform exhibits naturally all advantages of photonic integrated circuits towards traditional electronic counter-parts. Moreover, the giant nonlinearity of polaritons - inherited from the excitonic - makes it possible to greatly reduce the energy consumption required for switching or amplifying photonic information. However, most of proof-of-concept polariton-based devices suffer from one practical limitation in that they require cryogenic temperatures ( $\sim 10\text{K}$ ) to function. Polariton-based technology has taken its first steps with GaAs and CdTe systems in which excitons have comparatively low binding energy ( $\sim 5\text{ meV}$ ). The quest for polaritonic devices operating at room temperature is orienting current research trends towards materials with higher binding energies such as GaN, ZnO, organic semiconductors and, more recently, monolayers of transition metal dichalcogenides (TMDCs).

One class of materials that shows particular promise for room temperature polaritonic devices are hybrid organic-inorganic perovskites (HOP). HOPs took the optoelectronics community by storm in 2013, on account of their startling ability to harvest light for photovoltaics. They have since been put to use as a gain medium for light-emitting diodes and lasers. Thin two dimensional (2D) HOPs composed of alternating inorganic/organic monolayers are crystalline multi-quantum well structures presenting robust binding energies for excitons, typically in the hundreds of meV. 2D HOPs give rise to delocalized Wannier excitons, and thus present much higher nonlinearity than Frenkel excitons in organic materials, exhibiting a behavior similar to exciton nonlinearity in GaAs quantum wells. High quality crystal growth of HOPs can be achieved via solution-based processes, exfoliation or vapor deposition, which makes it possible to sidestep challenges in growing ZnO or GaN epitaxially.

In this work, we report on demonstration of perovskite-based polaritons at room temperature in photonic crystal structures. 2D HOP is deposited via spin-coating onto photonic crystal backbone of hole-lattice and forms a pillar-lattice of high refractive index. The strong coupling regime between HOP excitons and Bloch photons is evidenced by the observation of anti-crossing effect in photoluminescence and reflectivity measurements. Compared to conventional design with Fabry Perrot cavity, our approach makes it possible to optimize separately the active material and the photonic backbone. Indeed, we show that it would be possible to engineer the polaritonic dispersion from Dirac cones to flatband by simply depositing 2D HOP onto well-designed photonic crystal structures. Our results open the way for polaritonic devices at room temperature with fragile materials such as HOP and TMDCs.

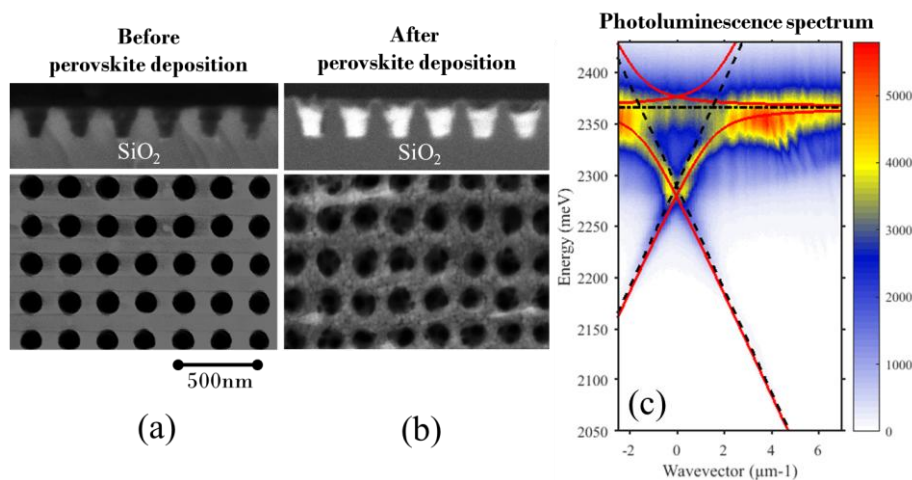


Figure 1. Scanning electron microscope images of the sample before (a) and after (b) the deposition of HOP. (c) Angular resolved photoluminescence spectrum at room temperature

1) N-H-M. Dang *et al.*, (in preparation)

## Probing diffusion of electron-hole pairs in crystalline hybrid perovskite using micro-photoluminescence and cathodoluminescence

**Fabrice Donatini<sup>a</sup>, Gilles Nogues<sup>a</sup>, Nguyen van Cao<sup>b</sup>, Hisao Yanagi<sup>b</sup> and Le Si Dang<sup>a</sup>**

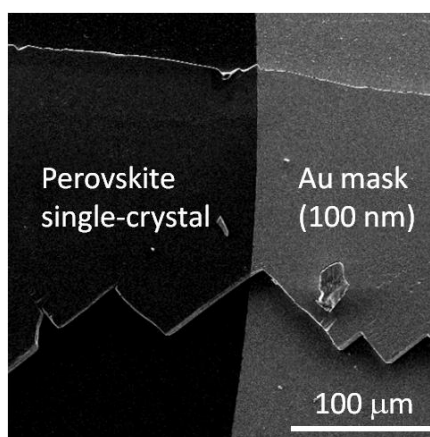
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The diffusion coefficient of charge carriers is a key parameter in many applications such as light emitting diode, solar cell, etc. Its determination can be achieved using a combination of high spatial and temporal experiments. For electron-hole pairs, both micro-photoluminescence and cathodoluminescence experiments are relevant techniques when dealing with sub micrometric diffusion length (using a classical masking technique illustrated in figure 1) and sub nanosecond carrier life time. However, the energy of the beam used to generate the carriers can deeply impact the results [2]. Therefore, we report on the comparison of micro-photoluminescence and cathodoluminescence experiments for the determination of the diffusion coefficient in single-crystal CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> perovskite prepared by cast-capping method [3].



**Fig. 1** SEM image of the single-crystal perovskite covered partly with a 100nm thick Au mask.

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- 2) D. Mayou and A. Lacroix, Institut Néel, private communication.
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## Pérovskites hybrides : quelques résultats récents

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Le groupe rennais associant les équipes des UMR FOTON (OHM) et ISCR (CTI) a poursuivi récemment son travail en 2017-2018, en explorant différents aspects associés aux propriétés optoélectroniques des matériaux pérovskites 3D et 2D en collaboration avec des laboratoires étrangers. Cette contribution décrira quelques résultats récents obtenus sur des nouveaux matériaux en couches<sup>1</sup>, l'étude de leurs propriétés optoélectroniques<sup>2</sup>, la croissance et les propriétés des matériaux 3D<sup>3</sup> ou les effets de gaz de porteurs chauds<sup>4</sup>.

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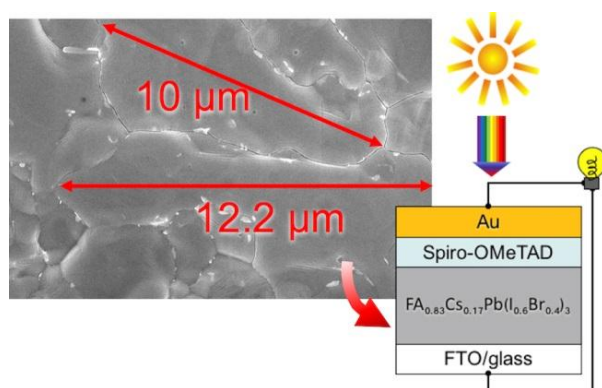
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## Compact Layer Free Mixed-Cation Lead Mixed-Halide Perovskite Solar Cells

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Mixed-cation lead mixed-halide perovskites based on  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$  (FA = formamidinium [ $\text{HC}(\text{NH}_2)_2$ ]) is currently of particular interest due to its suitable band gap allowing its immediate application on silicon solar cells by a tandem strategy. So far, solar cells based on  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$  typically involve the use of two layers of electron transporting materials. Despite the high photovoltaic performance achieved, more simplified device structure is desirable towards large-scale and low-cost fabrication. In this work, by controlling the concentration of the perovskite precursor we achieve thickness-tunable compact  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$  perovskite thin films on fluorine doped tin oxide (FTO) substrates with a large lateral grain size up to 12 microns. They are then employed to fabricate solar cells with a simplified planar structure without the use of electron-transport (ETL) layers. Functional ETL-free  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$  perovskite solar cells are obtained exhibiting a power conversion efficiency (PCE) of 13.80% with limited hysteresis and prolonged stability, which is highly encouraging for the future large-scale fabrication of  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ -based solar cells.



**Fig. 1** Scanning electron microscopy (SEM) image of the  $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$  perovskite thin films deposited on FTO substrate and the schematic diagram of the device architecture.

# Numerical investigation of the effect of interface conditions in HTM-free, printable WO<sub>x</sub> based and inverted perovskite solar cells

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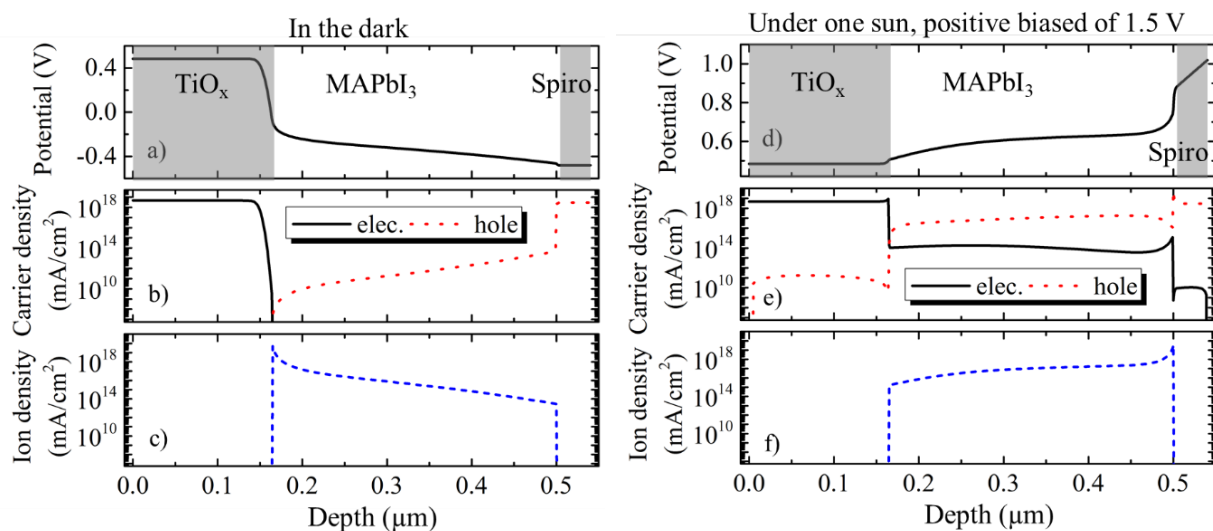
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One of the remaining issues, impeding the commercialization of the low cost and high-efficiency perovskite solar cells (PSCs) is whether the halide perovskite materials have sufficient stability. Two considerable instabilities are the light-induced degradation<sup>1</sup> and the scan-dependent performance, namely the hysteresis effect<sup>2</sup>. Using experimental parameters and parameters obtained from atomistic modelling, the perovskite/Au, perovskite/TiO<sub>x</sub>, perovskite/WO<sub>x</sub> and perovskite/PCBM interfaces are numerically investigated and compared to the experimental current-voltage (J-V) and capacitance-voltage (C-V) characteristics<sup>3</sup>. Besides interface states, the effect of mobile ions is considered in the drift-diffusion approach for more realistic modelling. As a result, the experimental built-in potential ( $V_{bi}$ ) variation, open circuit voltage ( $V_{OC}$ ) loss, hysteresis effects and photocurrent degradation/recovery can be explained. The interplay between interface traps and mobile ions is assumed to lead the anomalous hysteresis, while local trap states are considered as the main cause of performance degradation as a function of time. Furthermore, a new approach<sup>4</sup> is proposed for the modelling of Kelvin Probe Force Microscopy (KPFM) of heterostructures in dark and under illumination. The KPFM measurement of silicon PN junctions is experimentally and theoretically investigated.



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## High quality NiO blocking layers for p-i-n perovskite solar cells

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Hybrid organic/inorganic perovskite solar cells have been rapidly evolving with spectacular success in recent years. Inverted p-i-n perovskite devices incorporating inorganic hole-transporters exhibit negligible small hysteresis and enhanced stability. In particular, NiO tends to be a very promising candidate as inorganic hole-transporter due to its high transmittance, suitable work function and low-lying valence band. The most common method used to prepare NiO films is through spin-coating. However, low temperature solution processing often produces NiO films with defects (e.g. pinholes) and uncontrolled impurities, which degrade its optical transmittance and carrier transport properties. These problems can be overcome by employing a more advanced deposition method such as electrostatic spray deposition (ESD). This technique not only allows growing NiO films with fewer defects but also facilitates the introduction of appropriate dopants. Furthermore, it enables the precise control of the film thickness, which is significant for light transmittance (Fig. 1).

In this work, solution-processed and ESD grown NiO:Cu films have been compared as hole-transporter layers in perovskite solar cells. Copper has been added as a dopant to enhance the charge extraction efficiency and promote perovskite crystallization. For the light absorber, conventional single-step deposited MAPbI<sub>3</sub> has been used as a reference and has been compared to MAPbI<sub>3-x</sub>Cl<sub>x</sub> and to two-steps sequentially deposited MAPbI<sub>3</sub>. The power conversion efficiency of solar cells with MAPbI<sub>3-x</sub>Cl<sub>x</sub> has reached values up to 9.23% on an ESD grown NiO:Cu film. Two-steps sequentially deposited MAPbI<sub>3</sub> yielded a PCE of 7.08% followed by conventional MAPbI<sub>3</sub> with PCE of 6.07%. In all cases higher open circuit voltages and fill factors were obtained for cells using ESD NiO:Cu films as compared to solution-processed NiO:Cu. Furthermore, the cells using Cu-doped NiO showed better performances than those fabricated with undoped NiO. Conductivity and XRD measurements showed that the main influence of the Cu dopant is related to a modification of the perovskite crystallization.

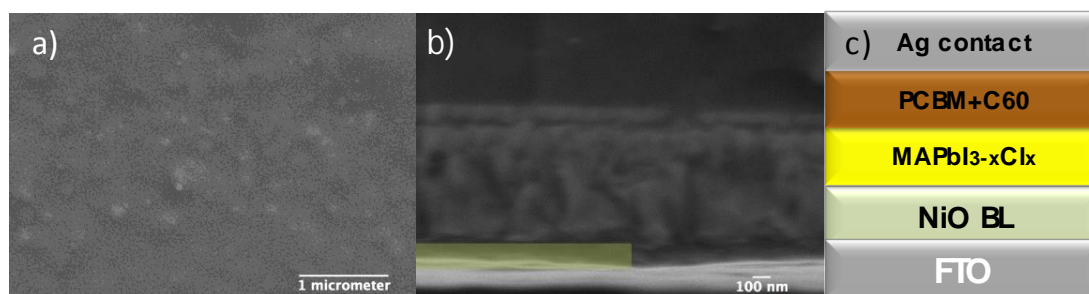


Fig. 1: a) SEM top-view; b) cross-section view of the NiO:Cu layer (indicated with green color) deposited on FTO using ESD. c) Device structure of the prepared p-i-n solar cells.

## Behaviour of Perovskite-based Solar Cells and Modules under Low Light Conditions for Indoor Applications

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The Internet of Things (IoT) is the network of physical objects—devices, vehicles, buildings and other items—embedded with electronics, software, sensors, and network connectivity that enables these objects to collect and exchange data. The number of applications in the fields of industrial and environmental monitoring, energy management, building and home automation is growing exponentially. The powering of all these objects is then a major concern, their autonomy is a requirement. The solutions to get these objects autonomous is closely linked to the energy harvesting from the surroundings.

Photovoltaic is one of this energy harvesting method from light. Moreover, the Perovskite based PV is an emerging technology with the promise of very efficient devices with high performances well over 20% under 1 SUN illumination, already demonstrated for small area lab-scale devices (ca 10 mm<sup>2</sup> or below).

Here, we are going to investigate the performances of Perovskite Solar Cells (PSCs) and modules in indoor environments, typically in the range of 200 to 1000 lux with artificial lightings. The PSCs (surface of 0.30 cm<sup>2</sup>) and modules (5x5 cm<sup>2</sup> with Geometrical Fill Factor GFF > 90%) have NIP planar architectures on glass. They are made with a processing route (wet process and structuration by laser ablation) compatible with large scale production and present performances > 10% under one SUN.

Their behavior will be studied with different lighting sources and with the variable illumination measurement method (VIM irradiance around 0,001 W/m<sup>2</sup> to more than 5 suns). The results will be discuss in function of the lighting conditions (irradiance and lighting source) and the impact of the passage from cells to module will be studied. Preliminary results obtained on PSCs of 0.30 cm<sup>2</sup> under artificial light at 200 lux (Neon tube) in air without encapsulation of are very promising with power densities over 40 μW.cm<sup>-2</sup>, exceeding the performances of amorphous silicon cells, recognized technology for indoor applications.

# ***Development of transparent electrode for semitransparent perovskite solar cells***

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My PhD's topic is on perovskite solar cells (PSCs), and two main ways of research can be distinguished: development of semitransparent PSCs for building integration and tandem application.

The first part of the presented work will focus on the development of a semitransparent PSCs on glass substrate with research efforts on charges extraction/transport layers for optimizing cell performances. As the fabrication of the solar cell uses a wet method (spin-coating) for the perovskite layer and the charges extraction layers, a large section will be devoted to solvent engineering, as well as the characterization of their effects. Moreover, two different cell architectures for PSCs, n-i-p and p-i-n, will be explored. For this research, the first identified materials of interest for electrons and holes extraction layers are respectively SnO<sub>2</sub>, PCBM and CuSCN, PTAA.

The second main part of the developed research is about tandem cells in which the previous semitransparent perovskite solar cell will be monolithically deposited on a silicon heterojunction (SHJ) cell. This second work will be particularly dedicated on the development of transparent electrodes. The aim is to have PSCs designed for top illumination (i.e. from electrode side) by using, for instance, ITO deposited by sputtering and silver nanowires. ITO deposition is already initiated and still need optimizations of the recipe to enhance performance gain. Meanwhile, silver nanowires deposition is entirely to develop: the first planned deposition process is a transfer method; other deposition ways will also be tested.

The final objective is to adjust the top perovskite cell process on an optimized silicon cell. Along with this objective, several optical characterizations and optical modeling will also be realized in order to obtain the current matching, an important monolithic tandems' feature. This tremendous work will be carried in collaboration between two research divisions inside the National Institute of Solar Energy (INES), experienced in both PSCs (LMOPS and LMPO) and SHJ cells (LHET).

## Processing of Large area Perovskite-based Solar Modules

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Over the last few years perovskite solar cells (PSCs) have attracted a considerable amount of research and record efficiency has then been quickly increasing. Performance well over 20% are now achieved, but yet, a number of challenges are still to be met to ensure a bright industrial future for PSCs. Significantly improving device active area while maintaining similar power conversion efficiency is probably one of the most important.

The main focus of this work is to provide new processing routes towards the large scale fabrication of efficient and stable solar modules.

When going from cells to modules there are a variety of challenges one has to consider to build efficient devices: the serial association of the multiple cells (and hence the presence of so-called “interconnection or dead” areas that do not actually contribute to the power conversion); the resistive power losses associated with the geometrical design ; the layers homogeneity of the stack over larger areas (encompassing processing & drying / curing issues).

Building up on a process enabling single cells with efficiencies greater than 15%, we propose to present our current advances in development of laser structured modules with stabilized efficiency greater than 13%. Different laser-patterned structures, materials and coating processes were investigated. Opportunities, challenges, issues and performances will be discussed with the support of different electrical and optical characterization techniques such as contact resistance measurements, microscopies and power losses calculations.

## Stability study of Perovskite solar cell with NIP structure

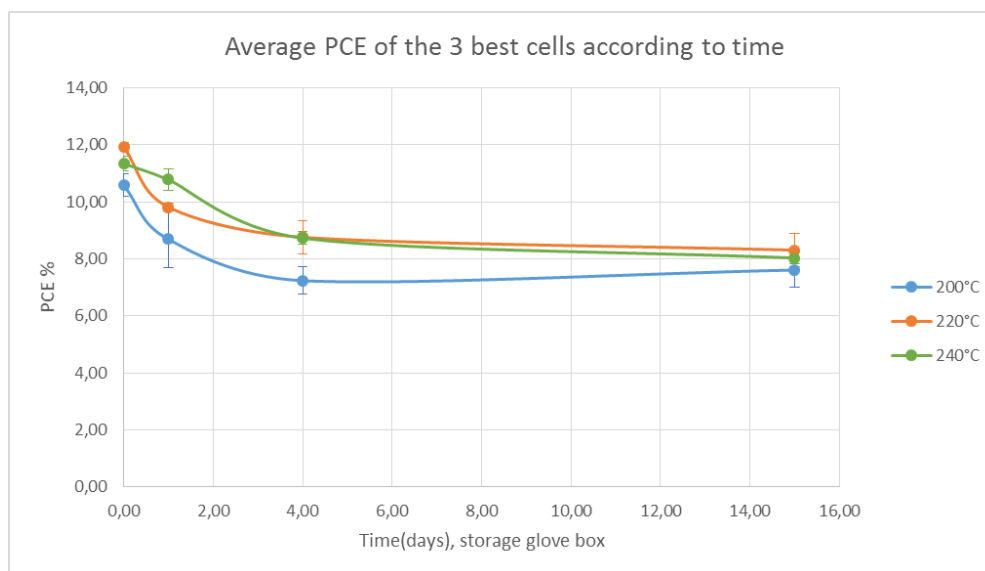
Hanadi MEHDI<sup>a</sup>, Stephane CROS<sup>a</sup>, Assia M'HAMDI<sup>b</sup>, Solenn BERSON<sup>a</sup>, Abdelaziz BOUAZIZI<sup>b</sup>

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Recently, organic-inorganic hybrid perovskite solar cells have attracted a big attention due to their excellent photovoltaic efficiencies, which led to record breaking efficiencies that have been updated from 3.8% to 22,1%. Unfortunately, these high PCE values have often been obstructed by bad stability, which is due to both the perovskite material and charge transport layer that prevent up to now the manufacture of devices that can withstand prolonged operation under normal condition. In this work, photovoltaic structures: Glass/ITO/SnO<sub>2</sub>/MAPbBr<sub>3</sub>-xCl<sub>x</sub>/HTL/Au are elaborated using the "spin-coating" technique. Here, we studied both the intrinsic stability, i. e. the effect of the annealing temperature of the both perovskite layer and the ETL layer (SnO<sub>2</sub>) on the stability in glove box (storage), and the extrinsic stability, i. e. the impact of the encapsulation procedure on the stability in damp heat conditions. It was found that the increasing of the annealing time of the perovskite layer can led to decrease in the PCE. It has been proved that the annealing of the ETL layer can affect on the perovskite solar cell stability Furthermore, it was proved that the nature of the HTM layer can affect also the stability of our cells. At the other hand, we demonstrated the importance of the choice of the encapsulation materials and procedure in order to not have a drop of performances after encapsulation and sufficient protection in damp heat testing.



**Fig. 1** Effect of annealing temperature of SnO<sub>2</sub> On the performance stability of the perovskite solar cells.



# Investigating the cubic/tetragonal phase coexistence in oriented MAPI thin films

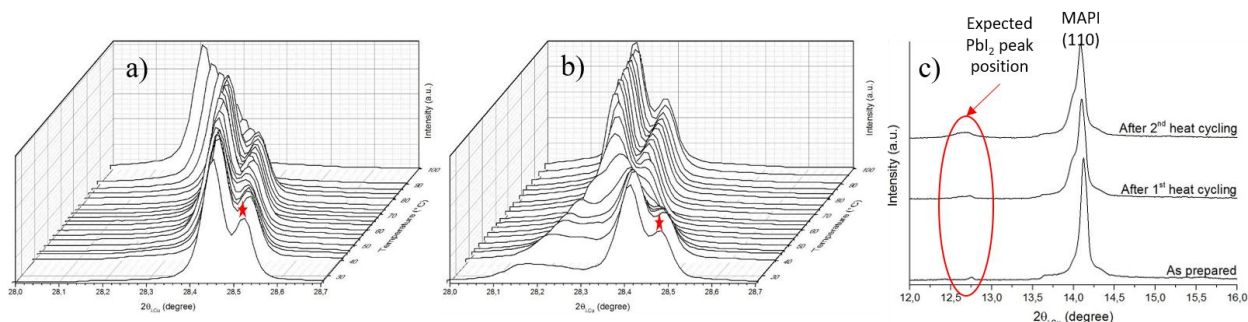
Asma Medjahed<sup>1</sup>, Tao Zhou<sup>2</sup>, Mathilde Bouchard<sup>1</sup>, Stéphanie Pouget<sup>3</sup>, David Djurado<sup>1</sup>, Dmitry Aldakov<sup>1</sup>, Peter Reiss<sup>1</sup>

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Efficiencies of perovskite solar cells are strongly related to the crystallinity and the microstructure of the perovskite layer. Several methods have been employed to improve the crystalline quality and surface coverage. One of the strategies takes advantage of the beneficial effect of chlorine addition to  $\text{CH}_3\text{NH}_3\text{PbI}_3$  (MAPI). Chlorine, which is not incorporated into the perovskite structure (noted MAPICl in the following) because of its small ionic radius, leads to bigger and preferentially oriented perovskite grains [1]. The grains align along the tetragonal [110] direction; however, X-ray diffraction (XRD) measurements often exhibit the presence of a secondary phase whose nature is still under debate. Several hypotheses concerning the origin of this phase have been proposed: double orientation along the tetragonal [110] and [002] directions, mixed-halide phase or cubic/tetragonal phase coexistence. Around 330K, MAPI undergoes a phase transition from cubic Pm-3m to tetragonal I4/mcm structures. Several studies have addressed the order of this transition but reached different conclusions [2]. Here we evidence, by combining laboratory XRD and synchrotron full field diffraction X-ray microscopy (FFDXM) measurements, the coexistence at room temperature of cubic and tetragonal phases in oriented MAPI thin layers thus demonstrating that we are dealing with a first order phase transition. We heated stepwise our MAPI thin films (300 nm thickness) spin coated on FTO/TiO<sub>2</sub> above the cubic/tetragonal phase transition while periodically recording XRD patterns. Various behaviours were observed: samples presenting initially the two phases have turned into pure tetragonal MAPI of enhanced crystallinity after heat treatment. Other samples, where only the oriented tetragonal phase was first observed, demonstrated the coexistence of the two populations after heat treatment. To get more insight into these phenomena, we used FFDXM at ESRF, which allows to image, in the direct space, the grains according to their crystallographic orientation. Using this technique, we could observe that grains corresponding to the cubic phase transform into grains of tetragonal MAPI under synchrotron illumination. These results evidence the metastable character of the cubic phase at room temperature. Furthermore, this phase coexistence has not been observed on MAPI layers free of chlorine, revealing that the effect of chlorine addition not only resides in the crystalline orientation of the grains but also in the stabilization of the cubic MAPI phase at room temperature.



**Fig. 1** a & b) XRD pattern of the same sample during heat treatment, showing a) only pure tetragonal phase at the beginning (the red star shows the  $\lambda_{K\alpha 2}$  diffraction peaks) b) the cubic/tetragonal phases coexistence after the the first cycle. c) XRD pattern of the same sample, showing negligible degradation after heat treatment.

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## Investigating the effects of incorporating p and n type dopants in perovskite thin films

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The fabrication of crystalline hybrid organic inorganic perovskite thin film on transparent conducting oxide (TCO) substrates has enormous potential in the area of photoelectrochemical research owing to the unique optical and electrical properties of these devices. Besides solar photovoltaics, perovskite-based thin film devices have potential for light emitting diodes, field effect transistors *etc.* In order to further improve the crystallinity and carrier dynamics of perovskite thin films, and to shift the Fermi level to adjust material polarity, controlled impurity ion doping is required. In this contribution, we report how incorporation of p and n type doping in  $\text{CH}_3\text{NH}_3\text{PbI}_3$  perovskite affects the crystallinity and optoelectronic properties of thin film. We chose trivalent  $\text{La}^{3+}$  and monovalent  $\text{Ag}^+$  to substitute divalent  $\text{Pb}^{2+}$  in  $\text{CH}_3\text{NH}_3\text{PbI}_3$  crystal. The presence of  $\text{La}^{3+}$  was confirmed from X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDX) analysis. The crystallinity and luminescence behavior of the perovskite films improved with incorporation of  $\text{La}^{3+}$  as evidenced from the increase in diffraction and photoluminescence intensity of the as-doped films. From ultraviolet photoelectron spectroscopy (UPS) and atmospheric Kelvin-probe microscopy (KPM) measurement, it was observed that the work function of the  $\text{La}^{3+}$ -doped perovskite increased up to 1 mol % doping and then decreased with higher dopant concentrations. Our study revealed the possibility to enhance the optoelectronic properties of perovskite thin films by  $\text{La}^{3+}$  doping. Further studies will be done to investigate the stability and power conversion efficiency of the doped perovskite thin films.

# Mechanosynthesis of organolead perovskites for photovoltaics. Road from MAPbI<sub>3</sub> to Guanidine-doped perovskites.

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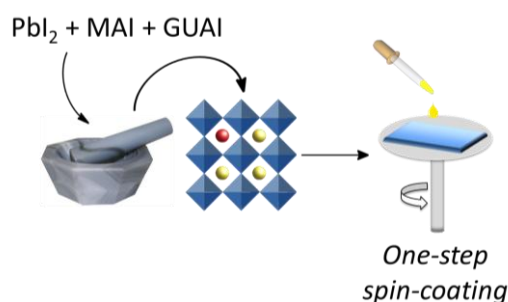
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<http://lewin.ch.pw.edu.pl>

Methylammonium (MA)- and formamidinium (FA)-based organic-inorganic lead halide perovskites provide outstanding performance as photovoltaic materials, due to their versatility of fabrication and their power conversion efficiencies reaching over 22%. The proposition of guanidinium (GUA)-doped perovskite materials generated considerable interest due to their potential to increase carrier lifetimes and open-circuit voltages as compared to pure MAPbI<sub>3</sub>. However, simple size considerations based on the Goldschmidt tolerance factor suggest that guanidinium is too big to completely replace methylammonium as an A cation in the APbI<sub>3</sub> perovskite lattice, and its effect was thus ascribed to passivation of surface trap states at grain boundaries. As guanidinium was not thought to incorporate into the MAPbI<sub>3</sub> lattice, interest waned since it appeared unlikely that it could be used to modify the intrinsic perovskite properties. Here, using solid-state NMR, we provide for the first time atomic-level evidence that GUA is directly incorporated into the MAPbI<sub>3</sub> and FAPbI<sub>3</sub> lattices, forming pure GUA<sub>x</sub>MA<sub>1-x</sub>PbI<sub>3</sub> or GUA<sub>x</sub>FA<sub>1-x</sub>PbI<sub>3</sub> phases, and that it reorients on the picosecond time scale within the perovskite lattice, which explains its superior charge carrier stabilization capacity. Our findings establish a fundamental link between charge carrier lifetimes observed in photovoltaic perovskites and the A cation structure in ABX<sub>3</sub>-type metal halide perovskites.

We present a facile mechanochemical route for the preparation of organolead halide perovskites, where the chemical reactions are forced by high energy ball mill. Advantages of this method include fast reaction time, high product purity and avoiding toxic organic solvents (producing less waste). Powder X-ray diffraction measurements demonstrate that mechanochemical synthesis is a suitable strategy to produce a highly crystalline material showing no detectable amounts of the starting substrates. The protopest material MAPbI<sub>3</sub> exhibit some features lowering its potential application. Here we report a facile mechanochemical route for: (a) preparation of MAPbI<sub>3</sub> and other two component materials (b) the stabilization of a structurally stable  $\alpha$ -FAPbI<sub>3</sub> perovskite by fine and controllable stoichiometry modification in mixed-cation (MA)<sub>x</sub>(FA)<sub>1-x</sub>PbI<sub>3</sub> perovskites, (c) the first time atomic-level evidence that guanidine cation is directly incorporated into the MAPbI<sub>3</sub> and FAPbI<sub>3</sub> lattices, forming pure GUA<sub>x</sub>MA<sub>1-x</sub>PbI<sub>3</sub> or GUA<sub>x</sub>FA<sub>1-x</sub>PbI<sub>3</sub> phases. The following materials were used to manufacture perovskite solar cells with extraordinary efficiencies reaching 20%.



**Fig. 1** Schematic presentation of mechanochemical procedure for preparation of solar cells.

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# Composite approach for layered hybrid perovskites: band alignment, quantum and dielectric confinements

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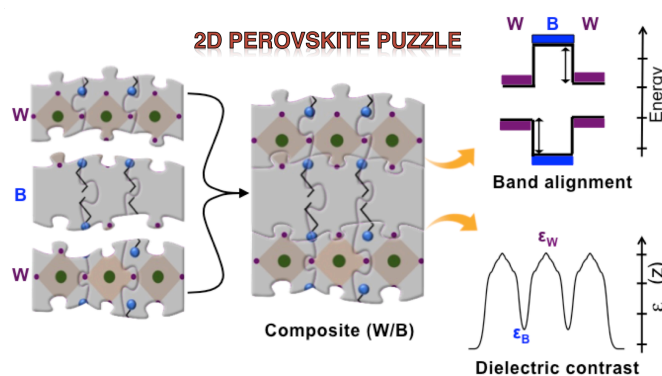
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Layered hybrid perovskites have recently re-emerged as potential technological viable solutions for photovoltaic and optoelectronic applications. Their environmental stability and immunity to moisture coupled to their exciting optoelectronic properties, have given them a new opportunity in the search of efficient solar cell and light emitting devices [1,2]. Understanding their fundamental optical and electronic properties will be important for optimization. To this aim, we present a systematic theoretical method that considers layered perovskites as composite materials in which band alignment between the perovskite and organic layers becomes affordable [3,4]. Such an alignment is an important performance criterion in the operation of optoelectronic devices. We investigate effects such as the thickness of the perovskite well, its chemical composition and the length of the organic barrier on the confinement potentials [4]. Moreover, we extend the method to inspect dielectric profiles with the salient feature of allowing the clear identification of the contributions of the perovskite and organic layers to the total dielectric profile [4]. Finally, with the insight gained from the different effects on band alignments, we propose design guidelines with the aim of achieving efficient optoelectronic devices. Hence, using the composite approach, we establish alternative theoretical methods to investigate the properties of layered perovskites and forecast that the approach will be relevant to inspect other 2D materials.



**Fig. 1** Schematics of the composite approach: W is the perovskite well and B the organic barrier.

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# Ultrafast Multi-excitonic Dynamics in Colloidal Perovskites Nanocrystals

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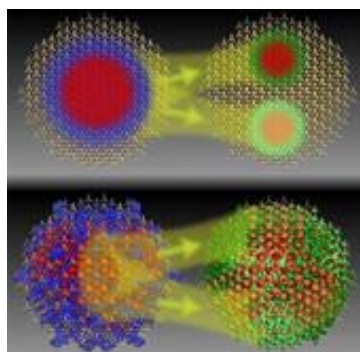
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Solar energy conversion into electricity is an old but still intense current research topic. Despite silicon solar cells are dominating the solar cell market, several non-conventional energy conversion strategies are continuously proposed to overcome the Shockley-Queisser (SQ) limit (maximum power conversion efficiency (PCE) = 33.7 % in single-junction solar cell). However, decreasing the fabrication cost remains a major challenge for these newest generation solar cells. [1]

Novel less expensive materials employed in Dye-Sensitized Solar Cells (DSSC), Organic Solar Cells (OPVs), Quantum Dot-Sensitized Solar Cells (QDSC) and more recently Perovskite Solar Cells (PSC) are the focus of considerable research development. Among them, the hybrid organic/inorganic perovskite solar cells are probably one the most promising candidates as their PCE has quickly risen from 3.8% to 22.1% over the past seven years. [2]

One strategy to overcome SQ limit is to go beyond the "one photon gives one electron". For instance, in QDSC, multiple exciton generation (MEG) process involves the conversion of a single high energy photon into multiple excitons or electron-hole pairs and so the overall cell current is increased. The PCE is estimated to over 44% in MEG based devices because the excess energy is not lost through heat (carrier cooling). MEG process was only observed in confined systems with a reduced efficiency and always indirectly, i.e., through the observation of the resulting Auger recombination occurring at much longer time scale (100s of ps). The implications for third generation photovoltaics requires a greater understanding of the underlying factors that govern MEG efficiency which so far remain unclear. [3]



**Fig. 1** illustration of multiple-exciton generation (MEG). The left side shows an electron promoted to a high energy state (blue) plus the "hole" vacated by the electron (red). The right side shows the original exciton (now dark green/red) and a new exciton (light green/orange) after MEG.

Advanced time-resolved spectroscopic techniques with high temporal resolution should play an important role in the mechanism elucidation of ultrafast processes in real time, before the system has time to relax. Accordingly, the aim of this PhD project is to study ultrafast excitonic dynamics in hybrid halide perovskites nanostructures with different compositions, sizes and morphologies as colloidal quantum dots (0D) and nanoplatelets (2D). We use a combination of transient absorption spectroscopy with high sensitivity and temporal resolution (< 100 fs, with a time range up to few ns) [4], two-dimensional electronic spectroscopy with a resolution of about 10 fs [5] and fluorescence up-conversion technique. [6]

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## Control of the structure and stability of perovskite films by modification of the metal oxide layers by bifunctional self-assembled monolayers

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The insertion of the self-assembled monolayers (SAMs) between the conductive electrodes (FTO/ITO, Metals) and the active layer in HOPV presents a promising solution for improving the performance of corresponding solar cells. In this work, we deposited semiconductor metal oxides MO<sub>x</sub> (ZnO, TiO<sub>2</sub>, WO<sub>3</sub> ...) on top of the anodic FTO layer then we proceeded to the functionalized by dipolar self-assembled monolayers COOH-R-Y (R= aromatic spacer SAMs). The SAM molecules are equipped via Y with a permanent dipole moment standing perpendicular to the surface and a specific surface energy. The resulting dipolar layer may efficiently contribute to both exciton dissociation mechanism and favoring the passage of the charge carriers at the interfaces. But the SAM functionalization contributes also to the structuring of the active layer and the improvement of the performances of our devices.

The grafting and orientation of the SAM on the MO layers were analyzed by IR spectroscopy and XRD. The photovoltaic performances of the studied structures FTO/MO/MAPI /PEDOT:PSS/Au and FTO/MO+SAM/MAPI/PEDOT:PSS/Au were obtained by electrical characteristics (I-V) in the dark and under illumination. The presence of Y=NH<sub>2</sub> and Y=NH<sub>2</sub>-HI SAMs on the oxide layers modify the growth, the electronic structure leading to better performance and slower aging of the MAPI photovoltaic cells.

## Simply designed carbazole-based hole transporting materials for efficient perovskite solar cells

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Solar cells have become one of the most important sources of renewable energies. In recent years, several emerging photovoltaic technologies showed growing interests in terms of light weight, cheap process and flexibility. Among them, hybrid solar cell using perovskite structures as sensitizer became very promising. In 2009, T.Miyasaka and his team were the first to use the perovskites for replacing the classical dyes in solid state DSSCs and obtained a conversion efficiency of 3.8%<sup>1</sup>. Nowadays, the last record is around 22.2%<sup>2</sup>. The use of perovskites is usually combined with a hole transporting material (HTM) in order to achieve high efficiency. However, spiro-OMeTAD is the only HTM available on the market and is costly for large-scale applications. That is why, the development of high-performance, simple and low cost molecular glasses present a challenge.

Herein, the properties of a simple carbazole-based hole transporting materials and its fluorinated analogue are investigated in perovskite solar cells for the first time<sup>3</sup>. After calculating the cost of such single molecules and showing the interest for industry, the electronic and thermal properties are discussed and compared to Spiro-OMeTAD reference. The fluorine atom substitution enhances hole mobility while both energy levels remain comparable. Using a conventional perovskite (MAPbI<sub>3</sub>) in planar structure photovoltaic devices, it is also demonstrated that both carbazole-based HTM have similar photovoltaic performances to the spiro-OMeTAD. Steady-state and time-resolved photoluminescence have been used to study the performances of the devices.

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# Microscopic Evidence of Upconversion-Induced Near-Infrared Light Harvest in Hybrid Perovskite Solar Cells

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Photon upconversion represents a promising avenue to reduce the spectral mismatch losses limiting the efficiency of solar cells. On solution-processed solar cells, while the application of upconversion materials have been demonstrated, their application position so far is limited on the front side of the solar cell (before the illumination reaches the semiconducting layer) which can render the mechanistic study complex due to the influence of multiple factors such as structural modification of the absorber and optical scattering by the upconversion nanoparticles (NPs). Here we studied in detail macroscopically and microscopically the impact of inserting Yb<sup>3+</sup> and Er<sup>3+</sup> co-doped KY<sub>7</sub>F<sub>22</sub> upconversion NPs into the different interfaces of a functional solar cell based on solution-processed mixed-cation lead mixed-halide perovskite. On solar cells with only half of their interface decorated by upconversion NPs fabricated on purpose, the correlation between fluorescence, upconversion-contributed photocurrent, and the morphology of the solar cell is analyzed in detailed by the light-beam induced current (LBIC)/fluorescence mapping technique.



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