



# 7<sup>ème</sup> Journées Pérovskite Halogénées

*Les 16, 17, et 18 mars 2022*

Amphi 3, Bâtiment W1

Ecole Centrale de Lyon

36 Avenue Guy de Collongue, Ecully 69130

Site web du colloque : <https://jph2022.sciencesconf.org>

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## PROGRAMME SCIENTIFIQUE



## Tutoriels:

- Marie Gueunier-Farret, laboratoire GeePs
- Emmanuel Drouard, Institut des Nanotechnologies de Lyon

## Exposé plénier:

- Dawei Di, Zhejiang University
- Cesare Soci, Nanyang Technological University

## Exposés invités:

- Elise Bruhat, CEA-LITEN, Département des Technologies Solaires
- Carole Diederichs, Laboratoire de Physique de l'Ecole Normale Supérieure
- Lionel Hirsch, IMS Bordeaux
- Nicolas Mercier, MOLTECH Anjou

## 16/03 (Day 1)

### OPENING:

- 13:00-13:15: Registration
- 13:15-13:30: **Opening of JPH2020**

### TUTORIAL SESSION:

- 13:30-14:30: **Tutorial** - Marie Gueunier-Farret (GeePs, Gif Sur Yvette)  
*Introduction to tandem solar cells*
- 14:30-15:30: **Tutorial** - Emmanuel Drouard (INL, Ecole Centrale de Lyon)  
*Light Management for perovskite PV cells and LEDs: a tutorial*

Coffee break: 15:45-16:15

### SESSION 1: SYNTHESIS AND FUNDAMENTAL PROPERTIES 1

- 16:15-16:45: **Invited talk** - Nicolas Mercier (University of Angers, MOLTECH-Anjou)  
*Layered perovskites for optoelectronic applications*
- 16:45-17:00: **Talk 1**- Philippe Lang (ITODYS, University of Paris Diderot)  
*Tailor-made amino-based Self-assembled monolayer grafted on  $MO_x$  layers for Perovskite solar cells*
- 17:00-17:15: **Talk 2**- Austin Hubley (ILM, ENS Lyon)  
*Inducing chirality in perovskite nanoplatelets*
- 17:15-17:30: **Talk 3**- Abdel Rahman Allouche (ISMO, Université Paris-Saclay)  
*Croissance sous-vide de couches minces de  $MAPbI_3$  : Evidence pour une phase hexagonale*
- 17:30-17:45: **Talk 4**- Davide Raffaele Ceratti (IPVF, Palaiseau)  
*The Importance of Proton Chemistry in Halide Perovskites*

**POSTER SESSION: 17:45-19:30**  
**(with welcome aperitif)**

## 17/03 (Day 2)

### SESSION 2: PEROVSKITE FOR OPTOELECTRONIC APPLICATIONS

- 09:00-09:45: **Plenary talk** – Dawei Di (Zhejiang University, China)  
*Efficient perovskite LEDs: excited-state dynamics and device design*
- 09:45-10:00: **Talk 5** - Quang Huy Do (XLIM, Université Limoges)  
*Fabrication of green light-emitting diodes with optimization of perovskite thin film growth*
- 10:00-10:15: **Talk 6** - Gabin Galnon (XLIM, Université Limoges)  
*Fabrication of inverse architecture of green light emitting diodes based on quasi-2D perovskite*
- 10:15-10:30: **Talk 7** - Julien Houel (ILM, Université Claude Bernard Lyon 1)  
*Optical properties of CdSe/CdZnS quantum dots embedded in adjustable-bandgap MAPbX<sub>3</sub> (X=Cl, Br, I) perovskite matrices*

**Coffee break:** 10:30-11:00

- 11:00-11:45: **Plenary talk** – Cesare Soci (Nanyang Technological University)  
*From Halide Perovskite Metamaterials to Metadevices*
- 11:45-12:00: **Talk 8** - Raphael Mermet-Lyaudoz (INL, Ecole Centrale de Lyon)  
*Vortex lasing emission at high oblique angle from a perovskite metasurface*
- 12:00-12:30: **Invited talk** – Carole Diederichs (LPENS, Sorbonne Université)  
*Room temperature polaritonics in all-inorganic cesium lead halide perovskite*
- 12:30-12:45: **Talk 9** - Nguyen Ha My Dang (INL, Ecole Centrale de Lyon)  
*Polaritonic topological charge at room temperature using polariton Bound States in the Continuum from perovskite metasurface*

**LUNCH:** 12:45-14:30

### SESSION 3: SYNTHESIS AND FUNDAMENTAL PROPERTIES 2

- 14:30-15:00: **Invited talk** – Lionel Hirsch (IMS Bordeaux)  
*Attempt to control the hybrid perovskites workfunction*
- 15:00-15:15: **Talk 10** - Yihui Cai (ICPEES, Université de Strasbourg)  
*Elaboration and optoelectronic properties of new hybrid perovskite@graphite composites and mixed 2D perovskites with enhanced stability via a solvent-free mechanochemical approach*
- 15:15-15:30: **Talk 11** - Thibault Lemerrier (Institut Néel, Grenoble Alpes University)  
*MAPbBr<sub>3</sub> Perovskite and Solution Surface Tensions: Looking at the Interfaces*
- 15:30-15:45: **Talk 12** - Faten Hleli (MOLTECH-Anjou, UMR 6200 CNRS, Université d'Angers)  
*Luminescence and mechanochromic luminescence of bromoplumbate perovskites*

**Coffee break:** 15:45-16:15

- 16:15-16:30: **Talk 13** – Thierry Pauporté (Chimie ParisTech, PSL Research University)  
*Controlling the formation process of Methylammonium-Free Halide Perovskite films for a homogeneous incorporation of alkali metal cations beneficial to solar cell performances*
- 16:30-16:45: **Talk 14** - Mikaël Kepenekian (ENSCR, Université de Rennes)  
*Challenges and opportunities for bismuth-based low-dimension halide perovskites*
- 16:45-17:00: **Talk 15** - Davide Raffaele Ceratti (IPVF, Palaiseau)  
*Light-Soaking, Photo-Damage and Self-Healing in Halide Perovskites*

**POSTER SESSION:** 17h00-19h00

(in parallel with CS HPERO meeting)

**GALA DINNER:** 20:30-22:30

## 18/03 (Day 3)

### SESSION 4: PEROVSKITE FOR PHOTOVOLTAICS AND SENSORING

- 09:00-09:30: **Invited talk** – Elise Bruhat (CEA Liten, University Grenoble Alpes)  
*Integration of metal halide perovskite in tandem solar cells: a new path towards manufacturable high efficiency devices*
- 09:30-09:45: **Talk 16** - Thomas Campos (IPVF, Palaiseau)  
*Study of Synthesis Parameters on the Formation and Physical Properties of 2D/3D Hybrid Halide Perovskite Heterostructures for Solar Cells*
- 09:45-10:00: **Talk 17** - Ceren Yildirim (XLIM, Université Limoges)  
*Perovskite Oxide Interface Layer in a Perovskite Solar Cell*
- 10:00-10:15: **Talk 18** - Cédric Mayer (LUMIN, ENS Paris-Saclay)  
*A new synthesis method of highly calibrated CsPbBr<sub>3</sub> nanocrystals perovskites by soft chemistry*

### Coffee break: 10:15-10:45

- 10:45-11:00: **Talk 19** - Peter Reiss (IRIG-SyMMES, University Grenoble Alpes)  
*Nickel oxide as hole-transport-layer in perovskite solar cells*
- 11:00-11:15: **Talk 20** - Cynthia Farha (LEPMI, University Grenoble Alpes)  
*Interrelated Characterizations Of Carbon-based Perovskite Solar Cells with Humidity Assisted Thermal Treatment*
- 11:15-11:30: **Talk 21** - Catherine Corbel (LSI, Ecole Polytechnique, Palaiseau)  
*Introduction and Ageing Effects of Intrinsic Defects on Radiative Recombination Properties of Quadruple Cation Organic-Inorganic Perovskite Layers*
- 11:30-11:45: **Talk 22** - Ferdinand Lédée (CEA-Leti, Grenoble)  
*2D layered perovskite micro-crystalline films for ultra-fast detection of X-rays and UV-light*
- 11:45-12:00: **Talk 23** - Javier Mayén Guillén (CEA Liten, University Grenoble Alpes)  
*MAPb(Br<sub>1-x</sub>Cl<sub>x</sub>)<sub>3</sub> perovskite materials for direct X-ray detection*

### CLOSING SESSION

- 12:00-12:30: **Award presentations**  
**Closing of JPH 2022**



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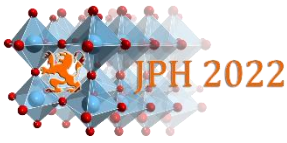
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# Résumés des Tutoriels



## **Introduction to tandem solar cells**

M.E. Gueunier-Farret, J. Connolly, S. Le Gall, J.P. Kleider

*GeePs, Gif-sur-Yvette, France*

Corresponding speaker: [marie.farret@geeps.centralesupelec.fr](mailto:marie.farret@geeps.centralesupelec.fr)

Photovoltaics has today become a mature industry and one of the main reasons of the tremendous growth in recent years is the continuous improvement in the performance and lifetime of PV modules. However, one of the main limitations in the improvement of the performance of commercialized PV devices is that the efficiency is getting closer and closer to the single-junction theoretical limit defined as the Shockley-Queisser (SQ) limit [1]. The development of new concepts to surpass the SQ limit is therefore a hot topic in PV research. Among the main candidate technologies (hot carriers, up-conversion and down-conversion, light concentration ...), multijunction devices are the only concept which have surpassed the SQ limit by a wide margin. Multijunction devices are therefore the most promising solution for industrialization in the near future, and the dominant multijunction design today is the tandem solar cell.

In this presentation, after a description of the functional advantages of multijunction solar cells, we'll review the current status of tandems. We'll compare the different types of tandem cells according to design principles, and in particular subcell materials, and discuss the challenges to upscaling tandem PV. In particular, we'll discuss recent advances in tandem cells with a Si bottom cell and examine perovskite/Si tandem cells with a recent record efficiency of 29.8% [2]. We will then present characterization techniques which allow the study of the electrical properties of tandem cells as a complete device, and of the properties of the subcells constituting the tandem.

### **References:**

- [1] W. Shockley, H.J. Queisser, Detailed Balance Limit of Efficiency of p-n Junction Solar Cells, J. Appl. Phys. 32 (1961) 510–519. <https://doi.org/10.1063/1.1736034>
- [2] [https://www.helmholtz-berlin.de/pubbin/news\\_seite?nid=23248;sprache=en;seitenid=1](https://www.helmholtz-berlin.de/pubbin/news_seite?nid=23248;sprache=en;seitenid=1)

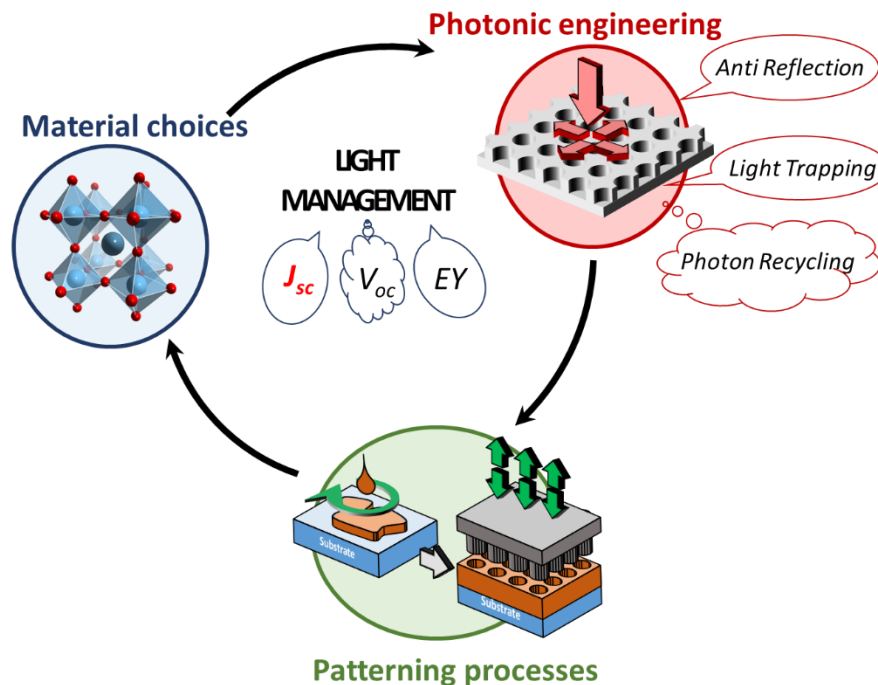
## Light Management for perovskite PV cells and LEDs: a tutorial

E. Drouard

*Université de Lyon; Institut des Nanotechnologies de Lyon INL-UMR5270, CNRS; Ecole Centrale de Lyon, Ecully, F-69134, France*

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Light Management (Fig. 1) is essential for some applications metal-halide perovskite, such as solar cells, as well as light emitting diodes, in their race for record performance. In this tutorial, criteria on materials and processes are discussed. The various possible photonic engineering mechanisms are described, illustrated through state of the art examples, and finally put into perspective, for both possible applications. Especially, it will be shown how significant light trapping [1] or out-coupling [2] effects arise from Bloch resonances in periodically corrugated perovskite layers.



*Figure 1: The three main correlated aspects that governed Light Management.*

### References:

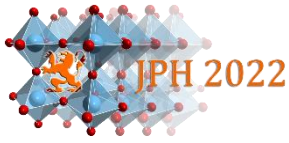
- [1] Schmager, R., Hossain, I.M., Schackmar, F., Richards, B.S., Gomard, G., Paetzold, U.W., 2019. Light coupling to quasi-guided modes in nanoimprinted perovskite solar cells. *Solar Energy Materials and Solar Cells* 201, 110080. <https://doi.org/10.1016/j.solmat.2019.110080>
- [2] Mermet-Lyautoz, R., Combeau, P., Drouard, E., Julien-Vergonjanne, A., Seassal, C., Nguyen, H.S., Sahuguède, S., 2021. Multiscale Simulation for Visible Light Communication using Perovskite Metasurface, in: 2021 17th International Symposium on Wireless Communication Systems (ISWCS). Presented at the 2021 17th International Symposium on Wireless Communication Systems (ISWCS), pp. 1–6. <https://doi.org/10.1109/ISWCS49558.2021.9562213>



# Résumés des Présentations

## Plénières





## Efficient perovskite LEDs: excited-state dynamics and device design

Dawei Di<sup>1,2</sup>

<sup>1</sup> *State Key Laboratory of Modern Optical Instrumentation, College of Optical Science and Engineering, Zhejiang University, Hangzhou, 310027, China*

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Perovskite light-emitting diodes (PeLEDs) have exceeded the 20% external quantum efficiency (EQE) milestone. For example, we have shown in our work that with careful device design, it is possible to achieve near-unity internal quantum efficiencies (IQEs) [1], demonstrating the potential of perovskite materials for extremely efficient electroluminescence. In this presentation, we discuss some design considerations behind the high IQEs, and for achieving EQEs that approach the theoretical limits [1, 2]. We discuss the lessons learned from our recent studies in high-efficiency OLEDs [3, 4], and the important role of charge-transport interfaces in the realization of this goal [5]. Transient spectroscopy experiments are carried out to illustrate how radiative and non-radiative processes play their roles in the high-efficiency devices. Besides, our recent efforts in the development of novel devices, including germanium-lead perovskite LEDs [6], and mini/micro-PeLEDs [7], will be presented.

### References:

- [1] B. Zhao, R. H. Friend\*, D. Di\* *et al*, High-efficiency perovskite-polymer bulk heterostructure light-emitting diodes, *Nature Photonics* 12, 783–789 (2018).
- [2] C. Cho, R. H. Friend, D. Di\*, F. Deschler\*, N. C. Greenham\* *et al*, The role of photon recycling in perovskite light-emitting diodes, *Nature Communications* 11, 611 (2020).
- [3] **D. Di**, A. S. Romanov, L. Yang, R. H. Friend, M. Linnolahti, M. Bochmann, D. Credgington *et al*, High-performance light-emitting diodes based on carbene-metal-amides, *Science* 356, 159-163 (2017).
- [4] L. Yang, V. Kim, Y. Lian, B. Zhao, **D. Di**\*, High-efficiency dual-dopant polymer light-emitting diodes with ultrafast inter-fluorophore energy transfer, *Joule* 3, 2381-2389 (2019).
- [5] B. Zhao, Y. Lian, D. Di\*, R. H. Friend\* *et al*, Efficient light emitting diodes from mixed dimensional perovskites on a fluoride interface, *Nature Electronics* 3, 704–710 (2020).
- [6] D. Yang\*, G. Zhang, D. Di\* *et al*, Germanium-lead perovskite light-emitting diodes, *Nature Communications* 12, 4295 (2021).
- [7] C. Hsu, S. Tian, Y. Lian, B. Zhao\*, D. Di\* *et al*, Efficient mini/micro-perovskite light-emitting diodes, *Cell Reports Physical Science* 2, 100582 (2021).

Cesare Soci

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The last decade has seen a shift in interest from metallic to dielectric metamaterials, where high refractive index semiconductors structured at the subwavelength scale are used to achieve efficient confinement of light and functional devices. After the first demonstration of a perovskite metasurface [1], halide perovskites have become a dielectric metamaterials platform of choice thanks to the unique combination of cost-effectiveness, large area processability, compositionally tunable optoelectronic properties, high luminescence quantum yield, and high refractive index [2].

The next technological challenge will be to progress from passive halide perovskite metamaterials to active metadevices for light-emitting and photovoltaic applications. Here we will discuss our recent efforts toward this goal, specifically the realization of chiral metasurfaces with large *superstructural chirality* [3], light-emitting metasurfaces with *directional chiral luminescence* [4], optically driven *tunable polarization-vortex microlasers* [5], and early demonstrations of electrically driven *light-emitting metatransistors* - with spatial and polarization control of the electroluminescence.

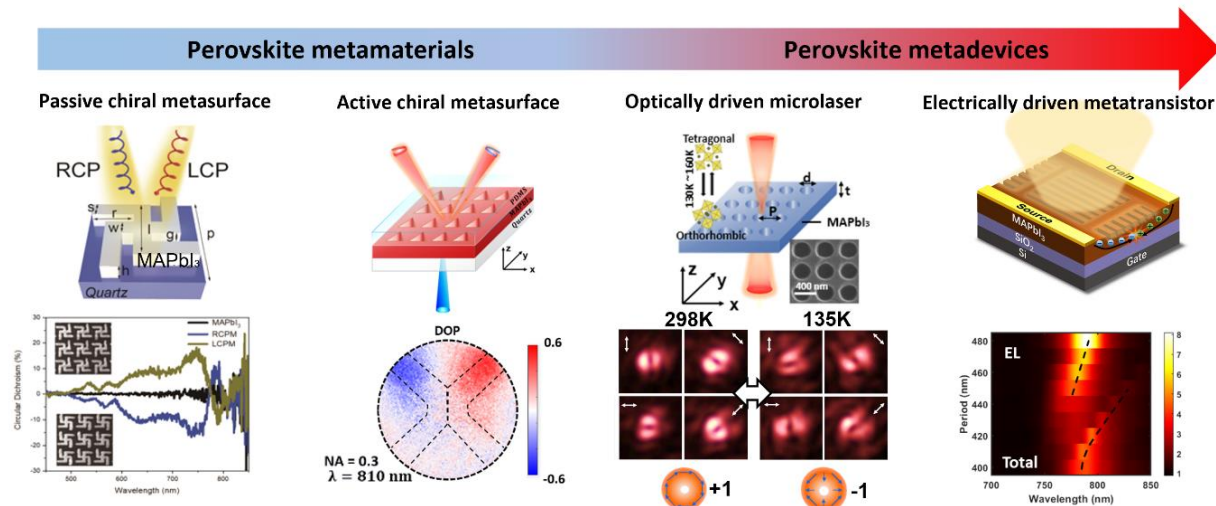


Figure 1: From halide perovskite metamaterials to metadevices.

## References:

- [1] B. Gholipour, G. Adamo, D. Cortecchia, H.N.S. Krishnamoorthy, M. D. Birowosuto, N. I. Zheludev, C. Soci, *Organometallic perovskite metasurfaces*, *Adv. Mater.* 29, 1604268 (2017).
- [2] G. Adamo, J. Tian, H.N.S. Krishnamoorthy, D. Cortecchia, G. Long, C. Soci, C., *Perovskite metamaterials and metasurfaces*, in *Halide Perovskites for Photonics*, edited by A. Vinattieri and G. Giorgi (AIP Publishing, Melville, New York, 2021), pp. 10-1–10-28.
- [3] G. Long, G. Adamo, J. Tian, M. Klein, H. N. S. Krishnamoorthy, E. Feltri, H. Wang, C. Soci, *Perovskite metasurfaces with large superstructural chirality*, *Nat. Commun.*, accepted (2022).
- [4] J. Tian, G. Adamo, H. Liu, M. Klein, S. Han, H. Liu, C. Soci, *Optical Rashba effect in a light-emitting perovskite metasurface*, *Adv. Mater.* 2109157 (2022).
- [5] J. Tian, G. Adamo, H. Liu, M. Wu, M. Klein, J. Deng, N. S. S. Ang, R. Paniagua-Domínguez, H. Liu, A. I. Kuznetsov, C. Soci, *Phase-change perovskite tunable microlaser*, arXiv:2107.05239.



# Résumés des Présentations Invitées

## Layered perovskites for optoelectronic applications

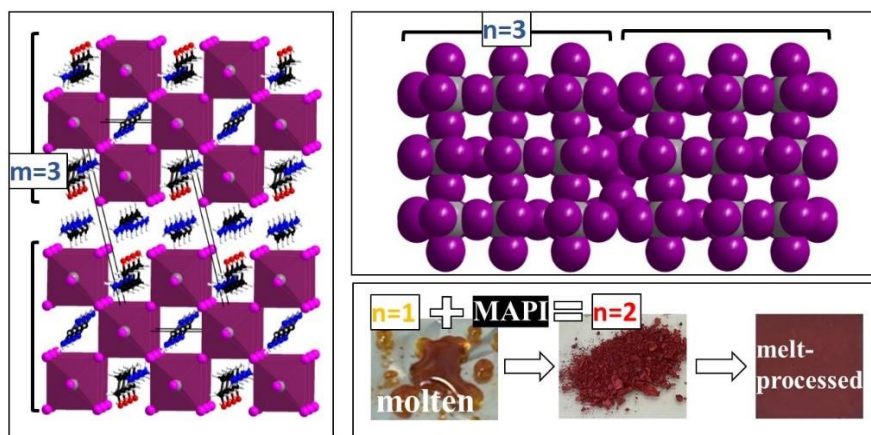
N. Mercier

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Metal-halide perovskites have recently demonstrated great potential for a wide variety of optoelectronic applications, with their layered subfamily<sup>[1]</sup> offering improved stability as compared to their 3D analogs. The subclass of  $\langle 1\ 0\ 0 \rangle$  terminated HP  $(A')_2(A)_{n-1}B_nX_{3n+1}$  or  $(A'')(A)_{n-1}B_nX_{3n+1}$  ( $A'^+$ ,  $A''^{2+}$ , organic cations) are currently dominating the field. In particular HP exhibiting inter-layer electronic coupling due to short I...I distances have shown photovoltaic efficiencies over 18%.<sup>[2]</sup> The  $\langle 1\ 1\ 0 \rangle$  subclass  $(A')_2(A)_mB_mX_{3m+2}$  is comparably much less explored, while structures often reveal short I...I interlayer contacts.<sup>[3]</sup> In this context, some recent results will be presented : *i*) the synthesis, structure, solid state NMR and electronic structure of the  $m=3$  member of the  $\langle 1\ 1\ 0 \rangle$ -oriented HP,  $(FA)_3(HEA)_2Pb_3I_{11}$  (HEA = hydroxyethylammonium,  $FA^+$  formamidinium); *ii*) Series of  $\langle 1\ 0\ 0 \rangle$  HP ( $n=1-5$ ) based on organic cations containing iodine atoms.

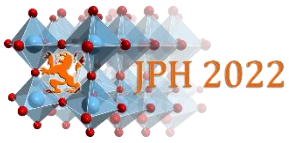
Halide perovskites are mainly prepared from solution techniques as bulk or thin films. D. Mitzi has reported several monolayered RP phases ( $n=1$ ) exhibiting a congruent melting with  $T_m$  ( $T_{\text{melting}}$ ) of 171 °C for the lower which allowed thin film preparation.<sup>[4]</sup> In this context, we will show that using a functional cation  $A'^+$ , a  $n=1$   $(A')_2PbI_4$  material exhibiting an exceptional low  $T_m$  of 126 °C has been obtained, allowing, *i*) unprecedented liquid-solid reaction involving molten  $(A')_2PbI_4$  and  $MAPbI_3$  leading to pure multilayered compounds  $(A')_2(MA)_{n-1}Pb_nI_{3n+1}$  ( $n=2, 4$ ), and *ii*) the preparation of melt-processed thin films of  $n=1$ ,  $n=2$  and  $n=4$  perovskites. This solvent-free process appears as a greener route with less waste for thin film preparation, but also open opportunities for the discovery of new materials not accessible through solution routes.



**Figure:** Structures of layered perovskites ( $m=3$ ,  $\langle 110 \rangle$  type and  $n=3$ ,  $\langle 100 \rangle$  type -organic components not shown-) and solvent-free preparation of powder and thin film of a  $n=2$  layered perovskite.

### References:

- [1] Katan, C.; Mercier, N.; Even, J. *Chem. Rev.* **2019**, *119*, 3140–3192  
 [2] Li, W. et al. *Nat. Nanotechnology* **2021**, doi.org/10.1038/s41565-021-01010-2  
 [3] Mercier, N. *Angew Chemie Int. Ed.* **2019**, *58*, 17912-17917  
 a) T. Li, W. A. Dunlap-Shohl, Q. Han, D. B. Mitzi, *Chem. Mater* **2017**, *29*, 6200-6204 ; b) T. Li, W. A. Dunlap-Shohl, E. W. Reinheimer, P. Le Magueres, D. B. Mitzi, *Chem. Sci.* **2019**, *10*, 1168-1175..



## **Room temperature polaritonics in all-inorganic cesium lead halide perovskite**

C. Diederichs<sup>1,2</sup>, R. Su<sup>3</sup>, S. Gosh<sup>3</sup>, T. C. H Liew<sup>3</sup> and Q. Xiong<sup>2,3</sup>

<sup>1</sup> *Laboratoire de Physique de l'Ecole Normale Supérieure, (LPENS), Université PSL, CNRS, Sorbonne Université, Université de Paris, F-75005 Paris, France*

<sup>2</sup> *MajuLab, CNRS-UNS-NUS-NTU International Research Laboratory, UMI 3654, Singapore,*

<sup>3</sup> *Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371*

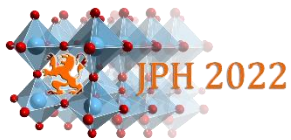
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Strong light-matter coupling in microcavities of various dimensionalities and the resulting hybrid exciton-photon quasiparticles, i.e. the exciton-polaritons, have been reported in a wide range of organic and inorganic semiconductors. While demonstrations of the polariton Bose-Einstein condensation, which is at the heart of promising applications such as polariton lasers, all-optical polaritonic circuits or polariton quantum simulators, are limited within a handful of semiconductors at both low and room temperatures. In inorganic materials, polariton condensation significantly relies on sophisticated epitaxial growth, while organic active media usually suffer from large threshold density and weaker nonlinearities. In this respect, strong efforts have been done in hybrid organic-inorganic perovskite materials, as they combine the advantages of both inorganic and organic materials. However, up to now, polariton condensation has not been observed in such materials. The all-inorganic cesium lead halide perovskites are part of a new class of materials that are drawing attention for polaritonics at room temperature. The epitaxy-free fabrication combined with their excellent optical gain properties, their tunable emission from UV to NIR, and their better optical stability under high laser flux illumination compared with hybrid perovskites, promise further important technological developments. In this seminar, I will present our first results on polariton condensation at room temperature in all-inorganic perovskite microplatelets embedded in planar microcavities [1], which opened the way to the demonstration of polariton condensates propagation in perovskite microwires [2] and polariton condensation in perovskite lattices [3] that will be also presented. These realizations in epitaxy-free wavelength-tunable materials advocates the great promise of perovskite for polaritonics applications.

### **References:**

- [1] R. Su et al., Nano Letters 17, 3982 (2017).
- [2] R. Su et al., Science advances 4, eaau0244 (2018).
- [3] R Su et al., Nature Physics 16, 301(2020).





## Attempt to control the hybrid perovskites workfunction

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Hybrid organic–inorganic perovskite (HOIP) solar cells combine the advantage of solution-phase processing technologies with high power conversion efficiency (PCE) that are in constant improvement. This class of materials has benefited from pre-existing knowledge gained from both inorganic semiconductors (band structure, photon absorption, charge transport...) and organic semiconductors (wet process, soft substrates, etc.). Nevertheless, the spread of PCEs reported in literature remains very large, suggesting that material properties and interfaces are very dependent on the quality of the fabrication process, including environmental factors.<sup>1</sup> As pointed out in the reviews by Brenner et al.<sup>2</sup> and by Fakharuddin et al.<sup>3</sup> a consensus has emerged in the literature on the critical role of surfaces / interfaces in the operation of HOIP-based devices and their stability.

Interfaces and contacts are therefore key points to achieve reliable and efficient solar cells. This is generally true for all type of solar cells. However, in most inorganic solar cells (and in silicon solar cells in particular), this difficulty is partially solved by using well-controlled doping layers. Indeed, doping allows contacting metal electrodes with highly doped semiconductor layers, removing interfaces away from the carrier collection area. Moreover, connecting semiconductor through highly doped layers also makes the cell performance insensitive to the value of the metal work function, giving more flexibility in selecting metals.

In this presentation we will present results obtain on the two options we are working on. The first option consists to graft polar molecules at the surface of perovskite layer<sup>4</sup> and the second approach lies with the doping of the perovskite layer.

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<sup>1</sup> Z. Molenda, S. Chambon, D. M. Bassani, L. Hirsch, *Eur. J. Inorg. Chem.*, **2021**, 2533 – 2538.

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## Integration of metal halide perovskite in tandem solar cells: a new path towards manufacturable high efficiency devices

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Single-junction crystalline silicon (c-Si) solar cells dominate the market, with more than 90 % of market shares. However, their record Power Conversion Efficiency (PCE) of 26.7 % [1] is very close to their theoretical limit of 29.4 % [2]. A successful approach to push c-Si cells efficiencies is to couple them with higher bandgap semiconductors, like metal halide perovskite (PK), to form tandem architectures that can achieve higher theoretical limits [3]. Such PK on c-Si devices already have PCEs reaching up to 29,80% [4] at lab scale (1 cm<sup>2</sup> devices), still the development of industry compatible processes for the fabrication of the PK subcell is needed.

CEA INES focuses on the development of manufacturable large area PK/c-Si solar cells with present record efficiency of 24,9% on PIN 9cm<sup>2</sup> devices. To achieve this goal CEA-INES' research focusses:

- Developing upscalable solvent coating solutions (slot die coating, blade coating)
- Studying vacuum-based deposition for all perovskite layers (magnetron sputtering, Atomic Layer Deposition, thermal evaporation,...)
- Assessing Intrinsic and extrinsic stability of the developed devices
- Advanced characterizations of tandem devices

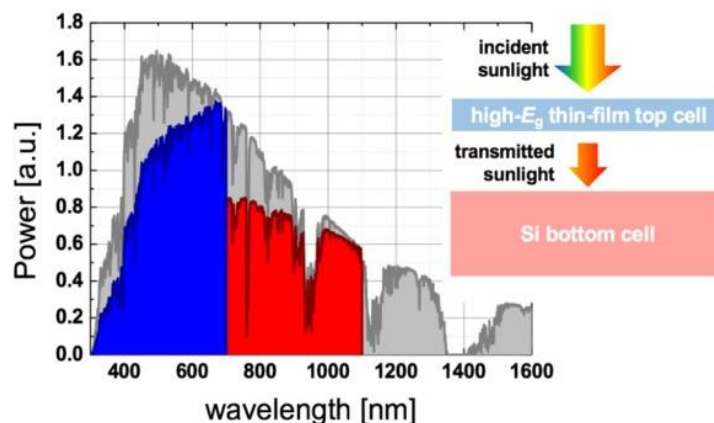


Figure 1: Solar spectrum utilizations for tandem solar cells as represented in [5].

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# Résumés des Communications Orales



## Tailor-made amino-based Self-assembled monolayer grafted on MOx layers for Perovskite solar cells

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Self-assembled monolayer (SAMs) have been grafted via a carboxylic acid function onto a both electron and hole transport layer to control the growth and structure of a hybrid perovskite  $\text{CH}_3\text{NH}_3\text{PbI}_3$  (MAPI) used as the active layer in a solar cell. Several molecules, from the SAM S made with  $\text{HO}_2\text{C-PP-NH}_2$  (PP = biphenyl), to synthesized SAMs based on  $\text{HO}_2\text{C-(CH}_2)_n\text{-PP-CH}_2\text{-NH}_3\text{Cl}$  molecules (A:  $n = 0$ ; B:  $n = 1$ ), have been used in this work. They have been tailored in order to ensure (i) rigidity/self-assembly and conductivity via the biphenyl and (ii) some flexibility via the methylene groups, to ensure bonding both to the solid MOx layer and to the methylammonium lead Iodide (MAPI) layer. The amino group was chosen to create an efficient 2D sub-layer for the growth of the methylammonium-based perovskite. The organization and orientation of the SAMs have been analyzed by IR spectroscopy (PM-IRRAS). Then we studied and compared the influence of such SAMs on the structure of MAPbI3 perovskite film .

The deposition of SAMs on the metal oxide layers improves device stability and the efficiency of perovskite solar cells (PSCs). The SAMs enhance the long-term stability of PSCs in ambient air atmosphere.

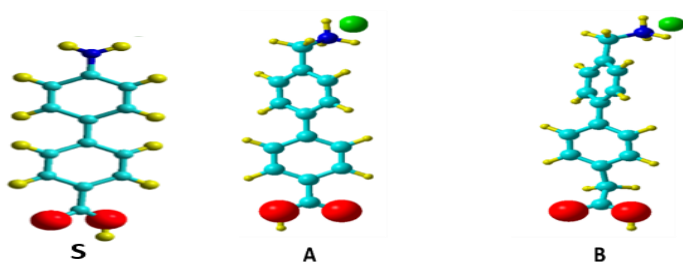


Fig.1 : structure of the molecules used in the SAMs :  $\text{HO}_2\text{C-PP-NH}_2$  (S),  $\text{HO}_2\text{C-PP-CH}_2\text{-NH}_3\text{Cl}$  (A) and  $\text{HO}_2\text{C-CH}_2\text{-PP-CH}_2\text{-NH}_3\text{Cl}$  (B); red :O blue C; dark blue N; green: Cl; yellow :H

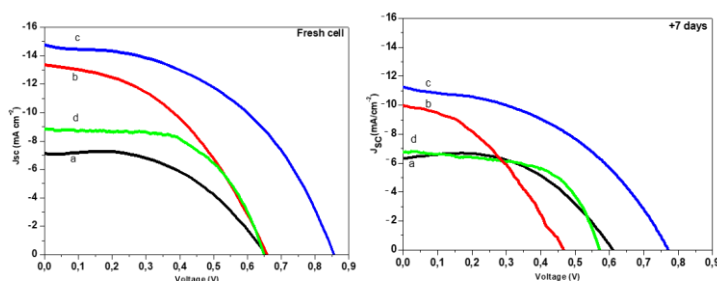
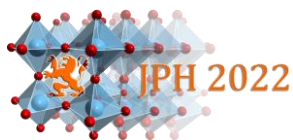


Fig.2 The photocurrent density–voltage ( $J$ – $V$ ) curves of the Perovskite cells under illumination a, b, c, d for bare ZnO, ZnO treated with SAM A, SAM B and SAM S respectively at  $t=0$  (fresh cell) and after 7 days ageing

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[1] H.Kouki, S.Pitié, A. Torkhani, F. Mamèche, P. Decorse M.Seydou, F. Kouki, P. Lang *ACS Appl. Energy Mater.* 2022, January 27, 2022 <https://doi.org/10.1021/acsaem.1c03050>



## Inducing chirality in perovskite nanoplatelets

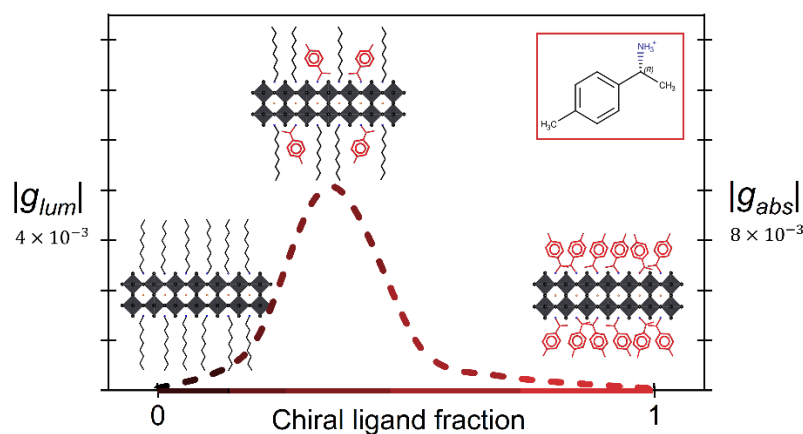
Austin HUBLEY<sup>1,2</sup>, Amina BENSALAH-LEDOUX<sup>1</sup>, Bruno BAGUENARD<sup>1</sup>, Stephan GUY<sup>1</sup>, Benjamin ABÉCASSIS<sup>2</sup>, and Benoit MAHLER<sup>1</sup>

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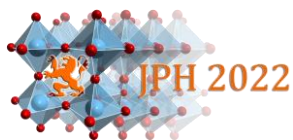
Chiral halide perovskite nanocrystals have many applications in next-generation optoelectronic devices due to their interaction with circularly polarized light. Through the careful selection of chiral organic surface ligands, control over the circular dichroism (CD) and circularly polarized luminescence (CPL) of these materials can be achieved. However, while recent developments of CD-active perovskites have seen significant advances, effective CPL remains a challenge. Here, we synthesize colloidal perovskite nanoplatelets exhibiting room temperature CPL with dissymmetry factors up to  $g_{lum}=4.3\times 10^{-3}$  and  $g_{abs}=8.4\times 10^{-3}$ . Methylammonium lead bromide nanoplatelets are synthesized with a mixture of chiral dimethyl benzyl ammonium ligands and achiral octylammonium ligands, the precise ratio of which is shown to be critical to achieving high g-factors. We investigate the competitive binding of these surface ligands using <sup>1</sup>H NMR, and use an equilibrium model to demonstrate the ligand affinity. The magnitude of CPL and CD is quantitatively shown to exhibit a linear correlation, such that  $g_{lum}=0.4\times g_{abs}$ . Lastly, by screening several amines with close structures, we show that subtle differences in ligand structure have significant impact on the resulting CD signal of the nanoplatelets. Our findings provide new insights for the effective design of perovskites exhibiting CPL and can facilitate the development of high-performance devices based on circularly polarized luminescence.



**Figure 1:** Surface chemistry of perovskite nanoplatelets exhibiting circularly polarized luminescence.

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[1] Hubley A, Bensalah-Ledoux A, Bagueard B, Guy S, Abécassis B, Mahler B. Surface chemistry of perovskite nanoplatelets exhibiting circularly polarized luminescence. ChemRxiv. Cambridge: Cambridge Open Engage; 2022; 10.26434/chemrxiv-2022-kt5wn



## Croissance sous-vide de couches minces de MAPbI<sub>3</sub> : évidence pour une phase hexagonale

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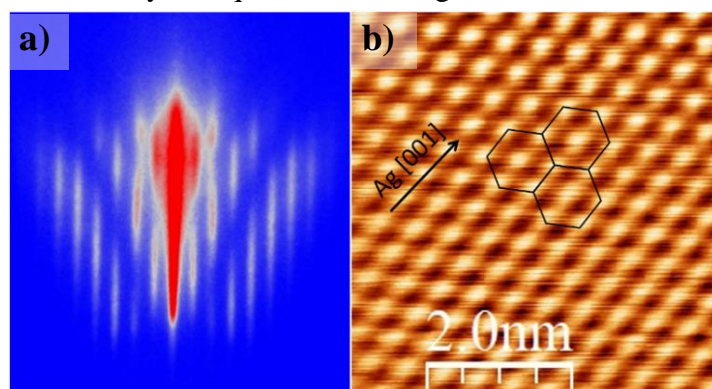
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Les couches minces de pérovskites hybrides suscitent un très large intérêt pour leurs propriétés optoélectroniques remarquables. Cependant, leur exploitation pour des applications à grande échelle se heurte à deux problèmes majeurs : (i) leur dégradation rapide par interaction avec l'environnement (lumière, humidité, etc.) ainsi que (ii) la difficulté de fabrication de grandes surfaces par la méthode de spin-coating très largement utilisée pour fabriquer ces couches. Le dépôt par évaporation sous vide, compatible avec de grandes surfaces, permet aussi un meilleur contrôle de la croissance et pourrait potentiellement aider à mieux comprendre l'origine de l'instabilité de ces couches [1].

Pour atteindre un niveau de contrôle inégalé du processus de croissance, nous utilisons la technique GIFAD (Grazing Incidence Fast Atom Diffraction). Cette technique, sensible et non destructive, permet de suivre en temps réel la dynamique d'organisation des atomes de surface, d'identifier et quantifier la structure cristalline ainsi que les transitions de phase [2].

Les premiers résultats obtenus sur une couche ultra-mince de MAPbI<sub>3</sub>, déposée sur Ag(100), montrent une phase hexagonale jamais observée auparavant, bien que l'existence de structures de même symétrie ait déjà été prédite par une étude théorique [3]. Des analyses complémentaires par LEED et STM confirment ces observations. La qualité structurale dépend de manière très sensible des flux relatifs de CH<sub>3</sub>NH<sub>3</sub>I et PbI<sub>2</sub>, ces derniers pouvant être ajustés en temps réel. Cette approche, qui permet de contrôler la croissance couche par couche et qui combine plusieurs outils d'analyse spécifiquement sensibles à la surface, devrait permettre de produire des couches à la morphologie contrôlée et *in fine* aider à mieux comprendre le rôle de la thermodynamique dans leur dégradation.



**Figure 1:** (a) : combinaison (rocking-curve) de diagrammes de diffraction GIFAD d'une couche ultra-mince de MAPbI<sub>3</sub>, mesurés avec des atomes d'hélium de 800 eV. (b) : image STM montrant la structure hexagonale et son orientation relativement au substrat d'argent.

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## The Importance of Proton Chemistry in Halide Perovskites

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The widely used Methylammonium ( $\text{MA}^+$ ) and Formamidinium ( $\text{FA}^+$ ) cations are relatively acidic compounds, with the potential to dissociate in the halide perovskites, giving a proton ( $\text{H}^+$ ) and the corresponding ammine. Despite the fact that they were considered not to do so, I will bring new evidence that the dissociation does happen and that  $\text{H}^+$  can migrate, associate with eventual water molecules internalized in the perovskite, be absorbed by basic hole transporting layers and other related phenomena. I will also comment on the chemistry of  $\text{H}^+$  in solution and show how it influences the final state of a perovskite layer after the coating. As it happens in general, in the perovskites the chemistry of protons is reversible and is characterized by chemical equilibria, which are modified by a large number of factors. I will provide indications on how temperature, illumination intensity, electronic doping of the perovskite material and the presence of other molecules pushes the acid-base equilibrium towards the dissociation or the association. The complexity of these equilibria is at the base of a series of phenomena that have been observed in halide perovskites like fast ion-migration, light-soaking and reversible damage repair (self-healing). In this talk, I will provide proof of the migration of protons in the perovskites as obtained by exchange of  $\text{H}^+$  with deuterons ( $\text{D}^+$ ) and discuss their diffusion coefficient in halide perovskite single crystals. Through optical microscopy (confocal, hyperspectral, fluorescence lifetime imaging spectroscopy), I will also provide proof on how the proton chemistry influences the photoluminescence of the perovskites showing how proton deficient perovskites have better optoelectronic properties. In particular, I will analyze how the positive effects of methylamine treatment in the perovskites can be related to proton chemistry and how light might locally originate methylamine causing the effect of light soaking in the perovskites. I will also show that  $\text{H}^+$  acts as an oxidizer when the perovskite is put into contact with metals and its influence should be considered when depositing contacts directly on the perovskite material. I will also analyze the chemistry of protons in the perovskite precursor solutions showing how their presence influences which particular lead complexes are actually in solution during crystallization. I will show how the electrochemical potential of the precursor solution (and therefore of the perovskite material) is partially determined by the presence of protons with consequences on the quality and quantity of defects in the perovskite materials. To conclude, the aim of this talk is to provide the listener a wide view on proton chemistry in halide perovskites providing the theoretical tools to understand the influences that proton chemistry has on the optoelectronic properties and the stability of the perovskites. This talk will be rich in chemical knowledge but it will be adapted to an audience working on halide perovskite devices with more engineering or physics background.





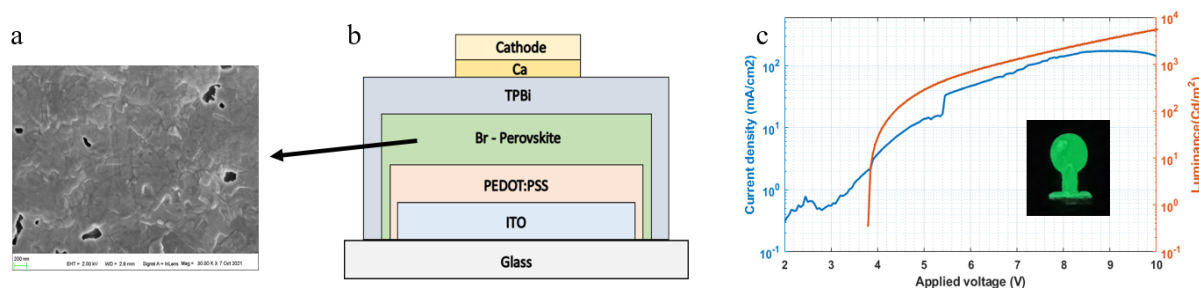
## Fabrication of green light-emitting diodes with optimization of perovskite thin film growth

Quang-Huy DO, Rémi ANTONY, Johann BOUCLÉ and Bernard RATIER

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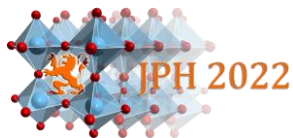
Lead halide perovskites has emerged rapidly as a promising alternative to organic emitters in lighting technology thanks to their color purity, controllable emission spectrum and high luminescence quantum yield. Recent researches have shown that the energy funneling kinetics in quasi-2D perovskites is essential for effective radiative recombination in light-emitting diodes [1], enabling devices with better performance and stability than those of conventional 3D perovskites [2]. Here, we report bright green PeLEDs with optimization of the low-dimensional perovskite thin films via compositional engineering and antisolvent treatment. First, by mixing of phenylethyl ammonium bromide (PEABr), methyl ammonium bromide (MABr) and lead bromide ( $\text{PbBr}_2$ ) at different stoichiometry ratios, perovskite thin films with different distributions of 3D and quasi-2D phases were synthesized. The influences of composition on the optical property of the thin films were then investigated using photoluminescence measurement. In addition, we studied the effects of the antisolvent treatment on the crystallization of our quasi-2D perovskites. Surprisingly, our toluene-antisolvent-treated thin films showed no clear difference in optical properties than the non-treated case, which suggests that merely adding the large organic cation might be sufficient for surface passivation [3].



**Figure 1:** a) SEM image of the quasi-2D perovskites thin film deposited on PEDOT:PSS layer, b) Cross-section view of the LED design and c) J-L-V curves of the PeLEDs based on quasi-2D perovskites.

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## Fabrication of inverse architecture of green light emitting diodes based on quasi-2D perovskite

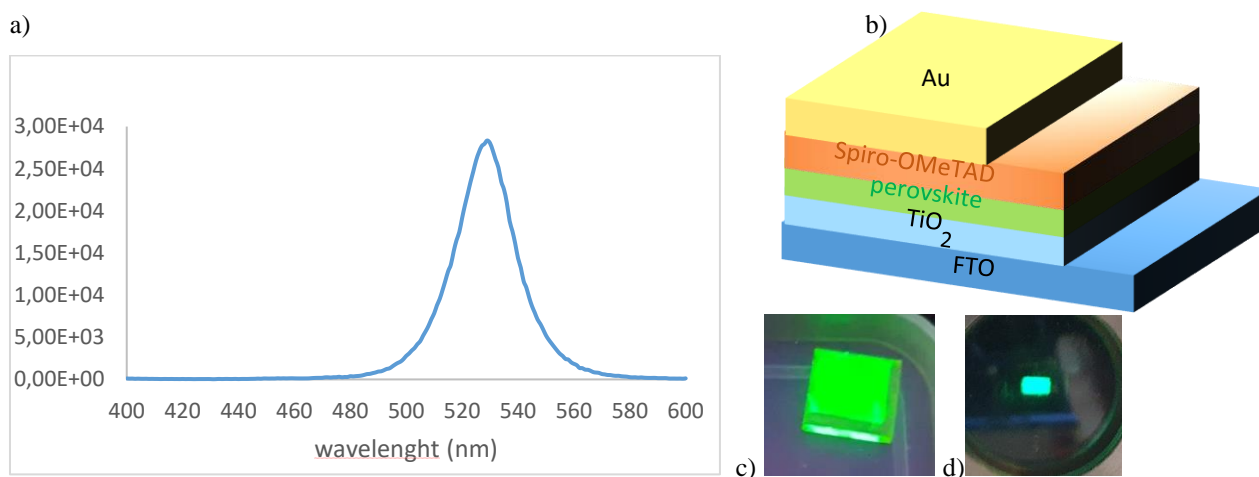
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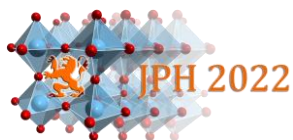
Gabin Galnon: [gabin.galnon@xlim.fr](mailto:gabin.galnon@xlim.fr)

Quasi-2D perovskites are well known for high efficiency and high semiconducting properties. In this study, we demonstrate bright perovskite light-emitting diodes (PeLED) in an inverse structure, FTO-TiO<sub>2</sub>-perovskite-spiro-OMeTAD-Au. Phenyl ethyl ammonium bromide (PEABr), methyl ammonium bromide (MABr) and lead bromide (PbBr<sub>2</sub>) have been mixed leading to the synthesis of our quasi-2D bromide perovskite.

Here, different quasi-2D perovskites with various stoichiometry ratio of PEABr have been synthesized and optically characterized (PL, UV-Vis absorption...) and then used in inverse PeLED devices.



**Figure 1:** a) Photoluminescence spectra of PEABr-MABr-PbBr<sub>2</sub> quasi-2D perovskite excited at 360 nm, b) representation of PeLED design and c) picture of quasi-2D thin film under UV lamp excited at 365 nm, d) working quasi-2d PeLED.



## Optical properties of CdSe/CdZnS quantum dots embedded in adjustable-bandgap MAPbX<sub>3</sub> (X=Cl, Br, I) perovskite matrices

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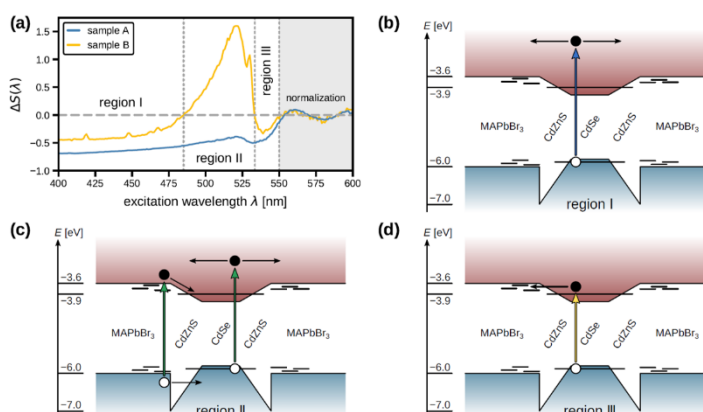
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We report on the optical properties of crystalline methylammonium lead chloride/bromide/iodide perovskite thin-films doped with high fluorescence quantum-yield CdSe/CdZnS core/shell quantum dots (QDs) [1].

The QDs are embedded in a 100 nm MAPbBr<sub>3</sub> thin film after an inorganic ligand-exchange with halide ions [2]. Ensemble photoluminescence (PL) confirms emission of the QDs after incorporation into MAPbBr<sub>3</sub>.

PL excitation (PLE) exhibits different types of wavelength-dependent couplings: from MAPbBr<sub>3</sub> to QDs, and from QDs to shallow defects in MAPbBr<sub>3</sub>, Figure 1. The amplification of the QD signal can reach up to 150 %.



**Figure 1 :** (a) PLE signal difference for two MAPbBr<sub>3</sub> samples (orange and blue lines) with an uncoupled model as a reference. Signal above 0 means amplification, 1 means 100%. (b)-(d) Tentative charge-transfer model to describe the behavior in (a).

Fluorescence lifetime imaging microscopy reveals a lengthening of the MAPbBr<sub>3</sub> emission lifetime at the QD locations combined with higher emission intensity, which might suggest that QDs act as local crystallization seeds.

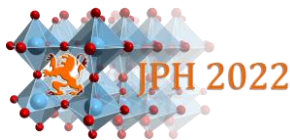
We demonstrate single photon emission from a single QD-in-perovskite hybrid via antibunching measurements.

We have furthermore created QD-in-perovskite hybrids that are bandgap-adjustable over most of the spectrum covered by the MAPbX<sub>3</sub> compounds by means of substituting Br ions with either Cl or I. Preliminary results show that QD PL is conserved during the procedure.

At high CdSe/CdZnS QD doping levels, this work opens the route to hybrid solar concentrator for visible-light harnessing and scintillators, while low-doping content could lead to hybrid single-photon sources in field-effect devices for single charge control.

### References :

- [1] J. Baronnier *et al.*, arXiv:2110.12886 (2021)  
 [2] J. Baronnier *et al.*, Phys. Chem. Chem. Phys. **23**, 22750-22759 (2021)



## Vortex lasing emission at high oblique angle from a perovskite metasurface

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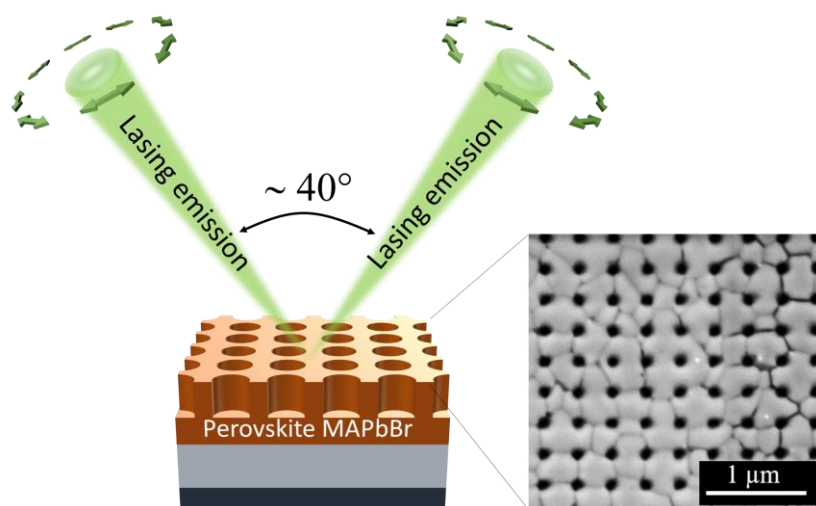
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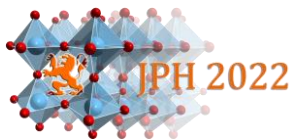
Hybrid organic-inorganic halide perovskites have experienced considerable popularity over the past decade and have become key materials for optoelectronics. Having both a direct band gap, easily adjustable properties according to the composition, and allowing low-cost production processes, they enable to envisage new generations of light emitters such as LED, lasers, or even polaritonic devices. Here we report on an original perovskite micro-laser that exhibits both highly directional emission at oblique angles and polarization vortex in momentum space. Such novel coherent emission is obtained by engineering Friedrich-Wintgen interference between multiple Bloch resonances of a subwavelength scale perovskite metasurface. Our results pave the way to make steerable coherent emission with novel polarization pattern for applications in optical communication/manipulation in free-space, high-resolution imaging /focusing and data storage.



**Figure 1:** Left: Sketch of vortex lasing emission from a perovskite metasurface. Right: Scanning Electron Microscope image of the perovskite metasurface.

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## Polaritonic topological charge at room temperature using polariton Bound States in the Continuum from perovskite metasurface

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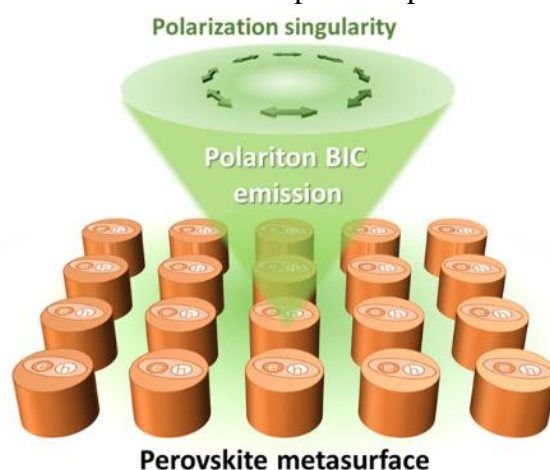
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We investigate experimentally the formation of exciton-polaritons arising from the strong coupling regime at room temperature between hybrid inorganic-organic perovskite excitons and an optical Bound state In a Continuum (BIC) of a subwavelength-scale metasurface. These polaritonic eigenmodes, hereby called polariton BICs (pol-BICs) are revealed in both reflectivity, resonant scattering, and photoluminescence measurements. Although pol-BICs only exhibit a finite quality factor that is bounded by the non-radiative losses of the excitonic component, they fully inherit BIC peculiar features: a full uncoupling from the radiative continuum in the vertical direction, which is associated with a locally vanishing far-field radiation in momentum space. Most importantly, our experimental results confirm that the topological nature of the photonic BIC is perfectly transferred to the pol-BIC. This is evidenced by the observation of a polarization vortex in the far-field of polaritonic emission. Our results pave the way to engineer BIC physics of interacting bosons, as well as novel room temperature polaritonic devices.

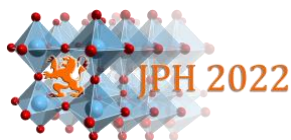


**Figure 1:** Emission of polariton BIC from perovskite metasurface.

### References:

- [1] N. H. M. Dang *et al.*, **Advanced Optical Materials** 2102386 (2022)





## **Elaboration and optoelectronic properties of new hybrid perovskite@graphite composites and mixed 2D perovskites with enhanced stability via a solvent-free mechanochemical approach**

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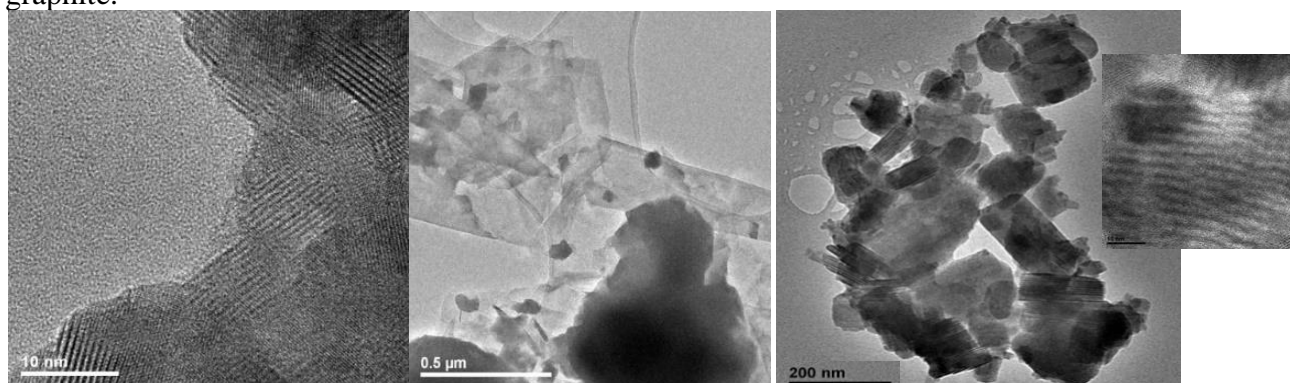
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3D hybrid perovskites (HP) are considered as a vastly potential material for high-efficiency solar cell and other light based applications. However, their industrial development is hampered because they suffer from chemical (air) and thermal instabilities. A HP powder approach, instead of direct chemical film formation, was proposed to easily produce high-performance HP with a better stability in large quantity. In that context, we have developed a mechanosynthesis based strategy, which is an environmentally friendly, solvent-free and energy-efficient process. To further enhance the HP stability, different strategies have emerged, one of them being the incorporation of triple/quadruple cations within the A-site and other being the development of lower dimensional HP. Thus, we have mechanosynthesized mixed 2D/3D HP to combine both 2D and 3D HP advantages, namely the outstanding optoelectronic properties of the 3D HP and the high robustness and stability of the 2D Ruddlesden–Popper phase. By partially replacing methylammonium cation with long chains ammonium or amine such as hexylammonium and octadecylamine, mixed 2D/3D HP were successfully synthesized. The layered structure was evidenced by TEM (Figure 1) and the optical and PL properties of 2D, 3D and mixed 2D/3D HP powders compared highlighting the effect of the layered structures.

We have also combined HP with graphite by mechanosynthesis as graphite may protect HP from moisture and improves the device efficiency. HP/graphite composites with different amounts of graphite were elaborated and graphene sheets coated with HP were observed to form only with HP containing alkyl chains. The presence of MAPbI<sub>3</sub> was shown to induce the creation of defects in graphite structure when graphite milled alone displays fewer defects. The presence of graphite protects MAPbI<sub>3</sub> from chemical degradation by comparison with MAPbI<sub>3</sub> alone. The evolution of PL spectra as a function of graphite content illustrates that the PL intensity of MAPbI<sub>3</sub> peaks decreases with an increase of the amount of graphite. It is in agreement with the graphite's role, which is to favor charge separation or transfer and it confirms also a good mixing/interaction between MAPbI<sub>3</sub> and graphite.



**Figure 1:** from left to right: TEM images of nanostructured MAPbI<sub>3</sub>, MAPbI<sub>3</sub>@Graphite and 2D/3D MAPbI<sub>3</sub>/octadecylamine nanosheets





## MAPbBr<sub>3</sub> Perovskite and Solution Surface Tensions: Looking at the Interfaces

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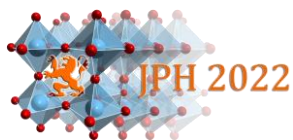
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Due to their unique properties, hybrid perovskite materials have attracted huge attention as semiconductors for various applications such as photovoltaics, light-emitting diodes, photo-detectors or X-ray detectors. Regarding the latter application, much thicker perovskite layers are required to absorb most of the X-rays so the desired thickness is in the order of magnitude of a millimeter. Reaching such thickness by crystallization from solution cannot be done by nucleation of grains alone but puts an emphasis on their growth at the later stages of the elaboration process. This requires a good control of the nucleation and growth processes in order to get perovskite layers with high orientation, compactness and surface coverage, hence a good knowledge of the various interfaces: solution/substrate, solution/perovskite, perovskite/substrate. In addition, thick layers (hundreds of micrometers) may bring extra difficulties when compared to the corresponding thin film (hundreds of nanometers). For example a high layer/substrate adhesion is particularly desired to withstand the accumulation of the layer internal strains and/or differences in thermal expansion coefficients with the substrate. So, a good knowledge of all the interfaces involved is of particular interest. However, very few data are available regarding the surface tension of perovskites and their solutions.

That is why we have recently undertaken a fundamental study of surface tension through contact angle and hanging drop measurements in the system MAPbBr<sub>3</sub> (DMF, DMSO) and different substrates. This gives us fundamental data involved in many aspects of perovskite devices elaboration: substrate wettability, grains size and number (nucleation/growth balance through the nucleation rate), estimation of the work of adhesion of the layer on a substrate, *etc.* It highlights also that adjusting the surface tension of the substrate to promote the affinity between the *in situ* grown solid perovskite and the beneath layer could be a way for improving this interface and enhancing then its properties (*e.g.*, mechanical resistance, charge transfer).



## Luminescence and mechanochromic luminescence of bromoplumbate perovskites

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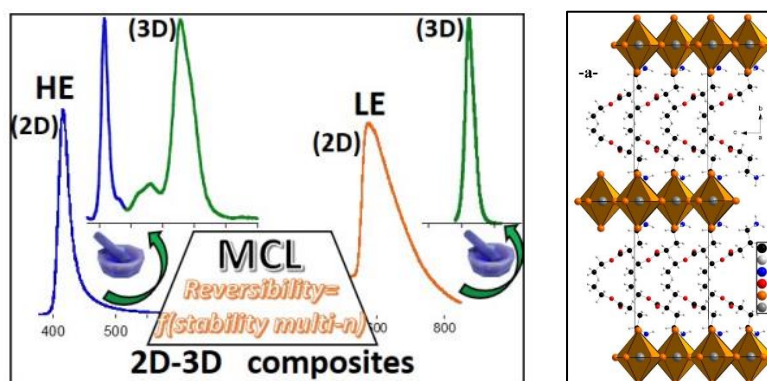
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In recent years, halide perovskites have been attracting intense attention as novel materials for optoelectronic applications. In particular, a breakthrough in the field of hybrid perovskites was the discovery of broadband emission at room temperature throughout the visible range, mainly for hybrids based on bromo- or chloroplumbate lattices, which makes these materials serious candidates for applications as white light phosphors [1] [2].

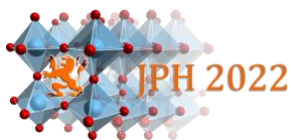
In a first part, the mechanochromic luminescence (MCL) properties of crystallized powders of composites based on the 3D perovskite MAPbBr<sub>3</sub> and one layered (2D) halide perovskite (HP) will be presented. Following our previous result [3], we have selected 2D HPs for their distinct emission properties: (PEA)<sub>2</sub>PbBr<sub>4</sub> (narrow emission (HE)), (EDBE)PbBr<sub>4</sub> (broad band emission (LE)) and (BA)<sub>2</sub>PbBr<sub>4</sub> (dual emission (HE and LE)). All composites exhibit sensitive MCL due to the activation of the 3D component emission through energy transfer from multi-layered perovskites formed at the interface. While the excitonic HE band is less affected by the mechanical treatment, LE is quenched in crushed composites, suggesting that it rather originates from the crystal edge/surfaces. The reversibility of the MCL process depends on the stability of multi-layered phases formed at the interface [4]. In a second part, we report on a new <100> PbBr<sub>4</sub> layered perovskite based on the ethyl-butyrate-ammonium cation (C4-E<sup>+</sup>), (C4-E)<sub>2</sub>PbBr<sub>4</sub>. Interestingly, this acentric compound which exhibit dual HE and LE emission at room temperature and a strong SHG signal, undergoes a structural transition at 45 °C and a rare congruent melting at 170°C.



**Figure 1:** Mechanochromic luminescence properties of 2D-3D composites (2D HP: narrow (HE) or broad band (LE) emission) (left) and acentric structure of the broad band emission (C4-E)<sub>2</sub>PbBr<sub>4</sub> HP (right)

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## Controlling the formation process of Methylammonium-Free Halide Perovskite films for a homogeneous incorporation of alkali metal cations beneficial to solar cell performances

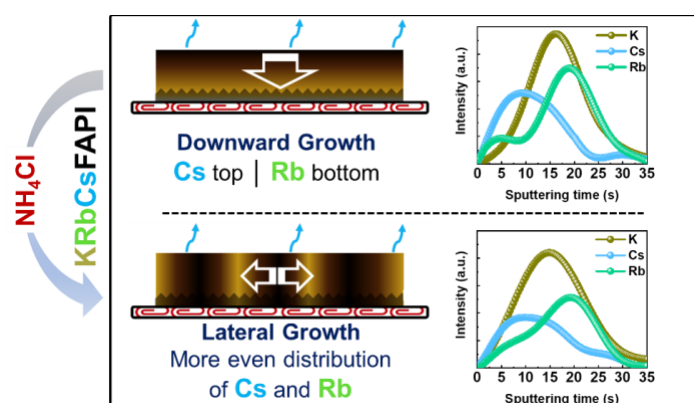
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Incorporating multiple cations of the IA alkali metal column of the periodic table ( $K^+/Rb^+/Cs^+$ ) to prepare perovskite films is promising for boosting the photovoltaic properties. However, contrary to  $K^+$ , both  $Cs^+$  and  $Rb^+$  suffer from non-uniformity at the origin of performance and stability losses. In our recent work, Ammonium chloride ( $NH_4Cl$ ) additive is shown to address this concern. First, we highlight the action of  $NH_4Cl$  additive on the spin-coating and the anti-solvent dripping processes. Then, we investigate the annealing process, showing the increased grain size, improved crystallinity and  $PbI_2$  suppression by adding  $NH_4Cl$ . Moreover, inspired by our previous work, [1-3] by introducing depth profile evolution monitoring by the glow discharge optical emission spectroscopy (GD-OES) technique, the real-time distribution changes of multi-alkali metal cations (m-AMCs) in the film upon annealing at  $155^\circ C$  is visualized. [4] We show that  $NH_4Cl$  can slow down the movement of m-AMCs so that they are better evenly distributed into the perovskite layer (Figure 1). Moreover, it changes the growth direction of the perovskite film, making the overall crystallization quality improved and the distribution more uniform. It results in perovskite films with large monolithic grains, permitting a high stabilized power conversion efficiency (PCE) over 21%. Finally, by combining AC additive and film surface treatment with n-propylammonium iodide (PAI), the performance was further upgraded at a stabilized PCE of 22.04%.



**Figure 1:** The addition of  $NH_4Cl$  changes the growth direction of perovskite film while making the distribution of alkali metal cations in perovskite layer more uniform.

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- [1] D. Zheng, T. Pauporté, *J. Mater. Chem. A* 2021, 9, 17801-17811.
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## Challenges and opportunities for bismuth-based low-dimension halide perovskites

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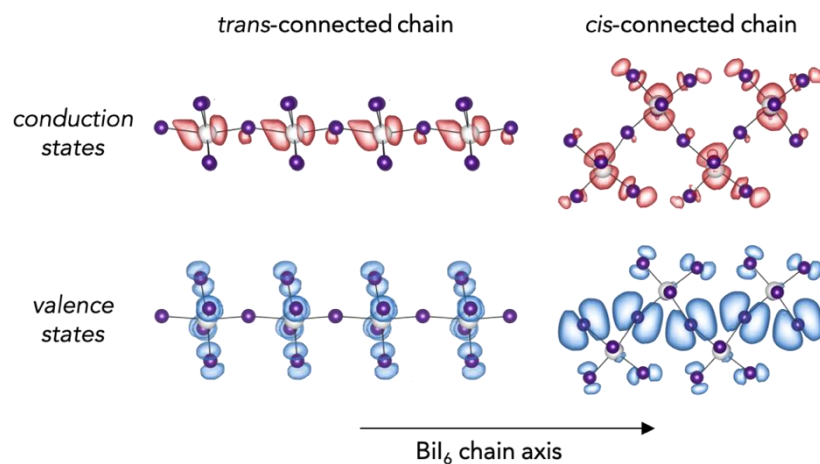
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The impressive flexibility exhibited by halide perovskites [1] offers many opportunities for chemists to design application driven materials [2,3]. Among the challenges still to be overcome is the replacement of toxic lead in materials for optoelectronic devices. If bismuth seems to be an ideal candidate owing to its low toxicity and natural abundancy, the performances of 3-dimensional (3D) Bi-based materials in solar cells remain far from their Pb-based competition [4]. However, the low-dimension side of the family (2D and 1D) still holds promises.

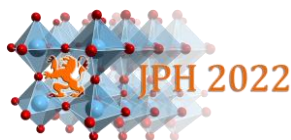
Here, we focus on 2D and 1D Bi-based halide perovskites thanks to joint experimental characterization and computational investigations. By highlighting, among others, the key aspects of connectivity between octahedra (see Figure), we will describe the challenges of designing efficient lead-free materials, as well as the opportunities offered by this not yet fully explored territory [5,6].



**Figure:** Valence (blue) and conduction (red) states for 1D Bi-based halide perovskites with trans and cis connectivity. Trans-connected chains exhibit overlapping Bi(6p)-orbitals leading to efficient electron transport, while the valence state is detrimental to the transport of holes. The situation is different for the cis-connected chain with worsen electron effective mass but order of magnitude better hole effective mass [6].

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## Light-Soaking, Photo-Damage and Self-Healing in Halide Perovskites

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Light-soaking, photo-damage and self-healing are intriguing phenomena widely reported in halide perovskites. Yet, their origin is still not understood even if they strongly influence the stability of the material. We discussed recently which could be the chemical origin of various phenomena connected to these effects revealing how the stability of the interstitial Br defects (associated with photodamage) in MAPbBr<sub>3</sub>, FAPbBr<sub>3</sub>, CsPbBr<sub>3</sub> is inversely related to the kinetic of self-healing of photodamage after intense illumination. In this talk, I will extend the description of the effects of intense illumination to MAPbI<sub>3</sub> showing how this material can also self-heal from photodamage with kinetics in the order of (several) minutes. I will reveal the presence of multiple (chemical) pathways activated by intense illumination some of which cause an increase of the photoluminescence (light soaking) and some of which decreasing it (photodamage). All of these are, at least partially, reversible and proceed from what can be called the “high entropy” of the halide perovskites. I will also show how water, even in conditions that do not cause the degradation of the material, strongly influences all the mentioned processes actually “protecting” MAPbI<sub>3</sub> from photodamage but also substantially impeding light-soaking. This causes the measurements performed over a short time in an inert atmosphere to provide better results because of transient light-soaking effects which, eventually, disappear over time in both humid and inert atmospheres. I will provide a panoramic over the literature of the reported effect trying to identify any other critical experimental condition inducing variations on the photodamage and light soaking effect or the kinetics and extent of self-healing. I will also provide additional information on the activation energies involved in the mentioned processes as obtained studying the temperature dependence of these in MAPbBr<sub>3</sub>, FAPbBr<sub>3</sub> and CsPbBr<sub>3</sub>.

The talk will conclude with an analysis of the diagram of stability of the halide perovskites trying to relate the analyzed self-healing properties with the possible equilibria between halide and their components or products of decomposition. In particular, I will show how self-healing causes the material to reach the thermodynamic equilibrium with its defects determined by the surrounding chemical environment. This process will possibly allow the perovskites to have an extremely long-lasting stability.



## **Study of Synthesis Parameters on the Formation and Physical Properties of 2D/3D Hybrid Halide Perovskite Heterostructures for Solar Cells**

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Perovskite-based solar cells, using three-dimensional (3D) perovskites, have reached power conversion efficiencies (PCE) of 25.5% <sup>[1]</sup>, close to silicon technology. However, it is still limited for commercialization by the instability of the 3D perovskites when exposed to light, temperature, oxygen, and moisture. Meanwhile, two-dimensional (2D) perovskites have shown higher stability and versatility, with a current PCE record of 17.8% <sup>[2]</sup>. Taking the advantages of 2D and 3D perovskites by merging them in a 2D/3D heterostructure seems a promising way to get more stable and efficient perovskite solar cells. <sup>[3]</sup>

This work focuses on synthesizing a 2D/3D perovskite heterostructure by depositing a solution containing a 4-Fluorophenylethylammonium (4-FPEA) cation salt on the annealed 3D perovskite layer, followed by subsequent annealing. This leads to forming a thin layer of 2D perovskite crystallized on top of the 3D bulk perovskite layer.

We applied a large panel of characterizations, from the analysis of extreme surface (XPS) and morphology (SEM) to the characterization of the bulk (PL, XRD), to understand the formation mechanisms of the 2D perovskite and the phenomena occurring at the 2D/3D interface. We showed that the concentration of the 2D cation solution is the most efficient parameter to control the 2D perovskite layer properties. Forming a pure 2D phase layer below 10nm thick using a low solution concentration seems the best way to have a smooth 2D/3D interface morphology without deteriorating the 3D bulk, with improved performances on small-scale solar cell devices, leading to best PCE over 18%.

These studies pave the route to a better understanding of the properties of the 2D/3D perovskites stack, which is crucial to improve perovskite-based solar cells efficiency and stability.

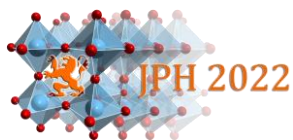
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10.1038/ncomms15684.



## Perovskite Oxide Interface Layer in a Perovskite Solar Cell

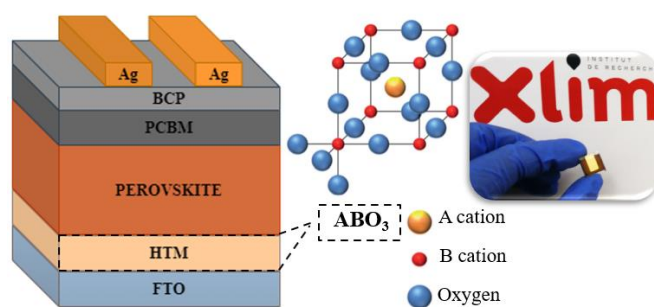
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Perovskite solar cells (PSCs) show a strong potential in the field of photovoltaic technologies thanks to several advantages such as suitable optoelectronic properties, low material costs, low temperature processing and high performance [1]. However, they are still facing some drawbacks towards their commercialization on a wide scale, such as poor resistance to fracture, stability issues and fast degradation mainly associated with the material instability itself and to defects associated with interlayer materials and interfaces [2]. In this context, these challenges can be tackled by a proper interlayer optimization, stable material preference and developing elimination process of defect problems in the interfacial layers. In p-i-n device architectures, PEDOT: PSS is one of the most widely used hole transport materials (HTMs) due to its ability to form uniform and smooth films via simple solution-processing, its low cost, high mechanical flexibility, and high electrical conductivity [3,4]. However, PEDOT: PSS degrades naturally since PSS chain contains the sulfonic acid group [5]. The purpose of this work is to develop alternative interfacial layers for efficient and stable PSC using perovskite oxide materials as an alternative HTM to PEDOT: PSS in p-i-n architectures. Perovskite oxides are known to present a very stable structure, and also highly tunable electrical and optical characteristics through stoichiometry [6]. Like in this study, the examples of perovskite oxide optoelectronic applications become available in the literature [7]. In this work, SrTi<sub>0.7</sub>Fe<sub>0.3</sub>O<sub>3-δ</sub> composition of perovskite oxide thin film is deposited by pulsed laser deposition (KrF= 248 nm, 10 Hz) from solid-state target in a high vacuum with oxygen. The deposition is carried out at low temperature which is quite new process for oxide perovskites deposition. This oxide thin film is integrated into PSC as shown in Fig. 1 and also the differences are investigated between two PSCs which were deposited with the oxide and PEDOT: PSS.



**Figure 1:** The perovskite oxide integrated PSC structure

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## A new synthesis method of highly calibrated CsPbBr<sub>3</sub> nanocrystals perovskites by soft chemistry.

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Our current period has highlighted electronic semiconductors components. This class of material is still mostly used but recent technological developments in various application areas such as smartphones, TV, or flexible screens, reveal their limitations. Therefore, the community has moved towards alternative technologies which also take into account the availability of the materials.<sup>1</sup> Among the candidates, organic electronics is a suitable way to achieve new devices, particularly for optoelectronic components. However, the all-organic approach does not provide the same performance as purely inorganic semiconductors. It is in this context that perovskite nanocrystals (NCs) respond to this technological need, of easily exploitable semiconductors, as conformable as the all-organic, with performances equivalent to classical semiconductors.<sup>2,3</sup> CsPbBr<sub>3</sub> is one of the most powerful perovskites (PVK) in terms of optoelectronic properties.<sup>4,5,6</sup> But to address the technological needs in terms of optoelectronic performances and conformabilities, it is essential to obtain the most homogeneous NCs in shape and size on macroscopic volumes.

In this oral communication, we showed a new synthesis method of highly calibrated on large scales of CsPbBr<sub>3</sub> Nanocrystals perovskites, by soft Chemistry, is described and analyzed by High-Resolution Scanning Transmission Electron Microscopy. Such large-scale monodisperse nanocrystals provide new opportunities for the deposit of homogeneous film of perovskite nanocrystals for the next generation of optoelectronic devices.

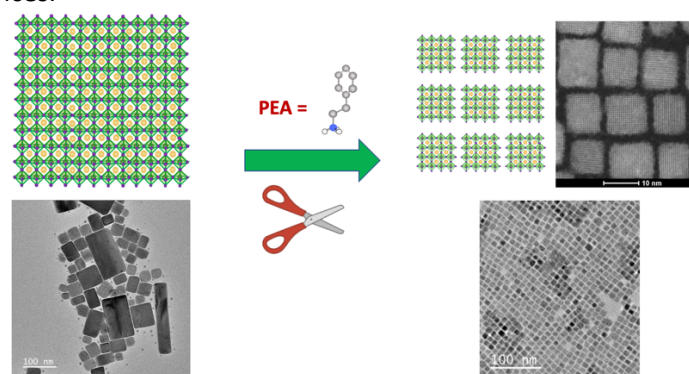
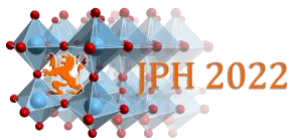


Fig. 1: schematic route of design high calibrated NCs PVK.

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## Nickel Oxide as Hole-Transport-Layer in Perovskite Solar Cells

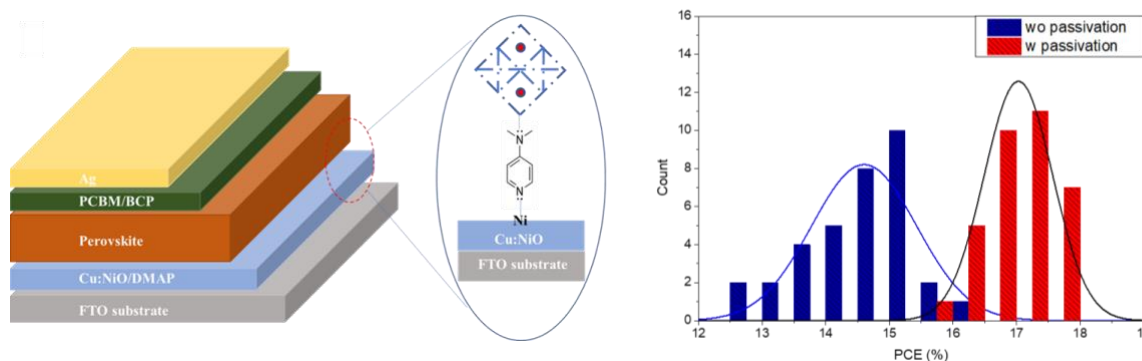
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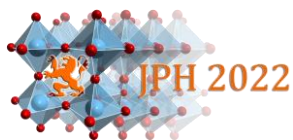
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Nickel oxide ( $\text{NiO}_x$ ) is an emerging hole transport layer (HTL) material in halide perovskite solar cells, combining high hole mobility, transparency and stability. Current limitations of the device performance are attributed to the inefficient hole extraction caused by contact problems between  $\text{NiO}_x$  and the perovskite layer. Based on its potential strong interaction with both the  $\text{NiO}_x$  surface and the perovskite layer, we selected dimethylamino(4-)pyridine (DMAP) as a molecular passivation agent for the HTL. As demonstrated by photoelectron spectroscopy and photophysical studies, DMAP passivation leads to a more favorable band alignment at the  $\text{NiO}_x$  /perovskite interface resulting in decreased carrier recombination near the interface. Moreover, X-ray diffraction reveals reduced strain and improved crystallinity in perovskite layers grown on DMAP-passivated  $\text{NiO}_x$ , induced by a different distribution of excess  $\text{PbI}_2$ . By consequence, planar perovskite solar cells (Fig. 1) with the DMAP-modified HTL demonstrate strongly increased  $FF$  and  $J_{sc}$ , resulting in a power conversion efficiency approaching 18%, while showing negligible hysteresis and enhanced stability compared to devices with an untreated HTL (max. PCE: 15.7). Finally, the development of low-temperature processable  $\text{NiO}_x$  nanoparticles is presented, opening novel perspectives for the use of  $\text{NiO}$  in flexible and tandem devices.



**Figure 1:** Planar *p-i-n* device architecture used in this study (left); distribution of PCE values for solar cells with or without DMAP passivation of the Cu-doped  $\text{NiO}_x$  HTL (right).



## Interrelated Characterizations Of Carbon-based Perovskite Solar Cells with Humidity Assisted Thermal Treatment

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Recently, organometallic hybrid perovskite materials are experiencing a real progress for solar cell applications. Due to particularly interesting properties: adaptable band gap, high crystallinity, high charge transport capacity and high thin film efficiency, these materials have the potential to exceed the performance limits of current technologies. Among alternative device structures, carbon-based perovskite solar cells (C-PSCs, see Figure 1) look highly promising due to their low cost and abundantly available materials (TiO<sub>2</sub>, ZrO<sub>2</sub>, carbon black and graphite powders), cost-efficient scalable fabrication methods and the inherent high stability. A one step (CH<sub>3</sub>NH<sub>3</sub>)<sub>1-x</sub>(5-AVA)<sub>x</sub>PbI<sub>3</sub> perovskite solution (with AVA= ammonium valeric acid additive) was pipetted to infiltrate mp-TiO<sub>2</sub>/mp-ZrO<sub>2</sub> through a thick porous carbon layer [doi: 10.1039/c7ta04132b][doi: 10.1002/ente.201800572]. To further investigate their stability, aging campaigns at 85°C/85%RH have been conducted during 1000 h. The macroscopic observations show an inhomogeneous degradation of the perovskite layer, the interfaces and the electrodes, mainly located at the edges. This inhomogeneity probably results from the pipetting process used to infiltrate the perovskite. This was confirmed by the variation of PV parameters during aging, which showed an important decrease in performance close to 50% after 1000 h of aging. In this study, a basic encapsulated system based on glass and a surlyn gasket was used, enabling the humidity permeation up to solar cells and inducing probably an accelerated degradation of devices. Thanks to dedicated characterization techniques, such as laser beam induced current (LBIC) measurements and photoluminescence imaging, the local performances have been correlated to the degradation inhomogeneity. The modifications of the perovskite layer have been evaluated with others more common techniques (X-Ray diffraction, UV-visible absorption and photoluminescence spectroscopy). Thanks to this multiscale approach, a degradation mechanism could be proposed highlighting the role playing by the prior maturation step. Today, others technological solutions are tested such as the inkjet printing for the perovskite infiltration and more advanced encapsulation systems, to improve the stability of these PV devices.

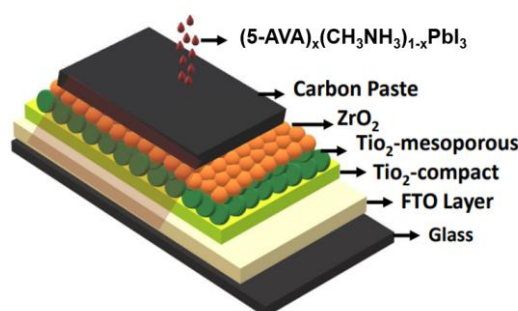


Figure 1: Schematic representation of the different layers constituting our C-PSCs



## Introduction and Ageing Effects of Intrinsic Defects on Radiative Recombination Properties of Quadruple Cation Organic-Inorganic Perovskite Layers

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Understanding the role of defects in Hybrid Organic Inorganic Perovskites (HOIPs) is critically important to engineer the stability and performance of photovoltaic devices based on HOIPs. Recent reports on multi-cation compositions of general formula  $(A^1, A^2, A^3, A^4)Pb(X^1, X^2, X^3)_3$ , where the A sites can be occupied by a distribution of 2-4 metallic/organic cations and X sites with halide anions have shown stabilization effects against the well-known methyl ammonium lead triiodide ( $CH_3NH_3PbI_3$ ). The quadruple cation perovskite  $GA_{0.015}Cs_{0.046}MA_{0.152}FA_{0.787}Pb(I_{0.815}Br_{0.185})_3$ <sup>[1]</sup> showed that the inclusion of guanidinium ( $C(NH_2)_3^+$ ), led to power conversion efficiencies above 20%.

To gain insight on the role of intrinsic defects, electron irradiation was used for introducing point defects in a controlled way in the quadruple-cation HOIPs<sup>[2]</sup>. Our results show that the engineered defects in perovskites strongly influenced the absorption, photoluminescence, and time-resolved photoluminescence of these materials, probably due to introduction of additional energy levels that modify electronic and light emitting properties of the material. Furthermore, the irradiation-induced defects were found to strongly affect the ageing behavior of HOIPs and modify their radiative recombination properties. The roles of the introduced intrinsic defects are discussed.

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## 2D layered perovskite micro-crystalline films for ultra-fast detection of X-rays and UV-light

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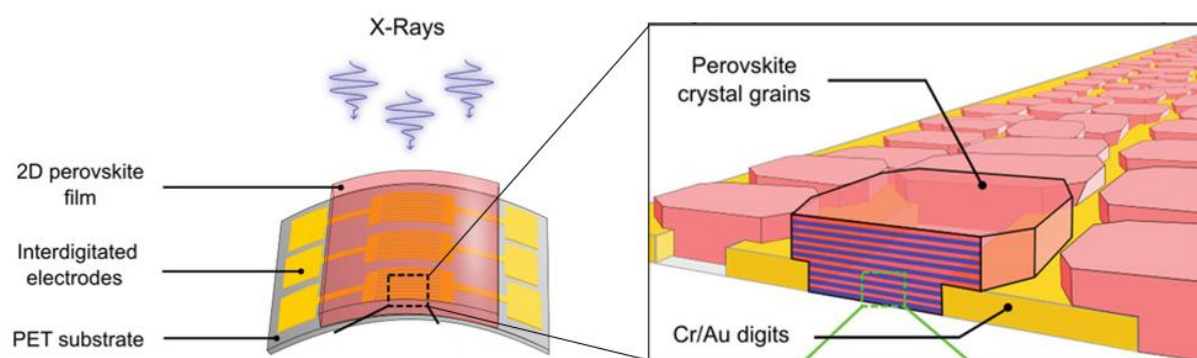
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Halide perovskites such as  $\text{CH}_3\text{NH}_3\text{PbI}_3$  and  $\text{CsPbBr}_3$  have shown promising results for the direct detection of high-energy ionizing radiation (X- and Gamma-rays), with strong absorption, high charge carrier mobility and long lifetime.[1] Their large-scale commercialization is however hindered by their large dark current drift, commonly attributed to the migration of ionic species under electric field.[2] Recently, 2D layered hybrid halide perovskites  $(\text{R-NH}_3)_2\text{PbX}_4$  (R = organic chain, X = Cl, Br, I) have been expressed increasing interest in the fields of solar cells and UV-Vis photodetectors.[3] This sub-class of perovskite crystallizes in a natural, self-assembled quantum well structure and possess several interesting features, among which better environmental stability than their 3D counterparts.

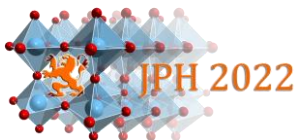
We will present in this work the first ionizing radiation detectors solely based on a pure 2D layered hybrid perovskite  $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{-NH}_3)_2\text{PbBr}_4$  (PEPBr).[4] Coplanar 2-terminal pixelated devices were fabricated using simple 1-step solution-based deposition directly onto plastic substrates with interdigitated electrodes (Figure 1). The micro-crystalline PEPBr films display crystal-like properties, as witnessed by their ultra-fast detection (sub-microsecond) under UV-Laser and negligible dark current drift which provides long-term stable operation under electric field. We demonstrate the effective detection of hard X-Rays with Sensitivity up to  $757 \mu\text{C.Gy}^{-1}.\text{cm}^{-2}$  and Limit of Detection (LoD) as low as  $8 \text{nGy.s}^{-1}$ , thus combining excellent values for two relevant figures of merit for radiation detectors. In addition, our devices show unexpectedly high photocurrent even in unfavourable excitation conditions, which we propose to attribute to photon diffusion through the PEPBr crystal grains via photo recycling processes.



**Figure 1:** Graphical representation of the coplanar 2D perovskite-based detectors.

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## MAPb(Br<sub>1-x</sub>Cl<sub>x</sub>)<sub>3</sub> perovskite materials for direct X-ray detection

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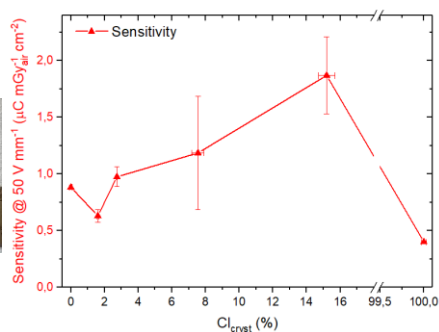
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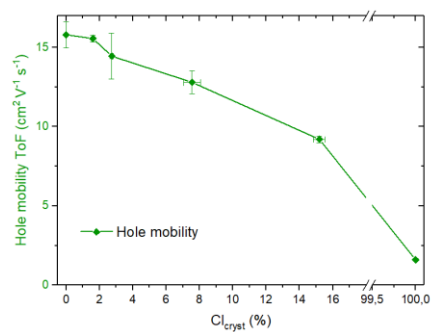
Halide based perovskite materials have generated strong and growing attention in the last years for being hopeful candidates for optoelectronic device applications. With their defect tolerance nature [1]–[3], sufficient mobility–lifetime product, and simple crystal growth from solution [4], organic-inorganic (hybrid) halide perovskite materials bring an unprecedented opportunity for radiation detection in direct mode. They show good X-ray absorption, thanks to the presence of heavy elements [2], [5], [6]. Additionally, single-crystalline halide perovskites exhibit no grain boundaries and possess low trap densities [1]–[3], [7], [8]. We optimized the growth of methylammonium lead tribromide (MAPbBr<sub>3</sub>) single crystals (SC) in dimethylformamide (DMF) [9] for X-ray radiation detection [10]. SCs were grown via Modified Inverse Temperature Crystallization (MITC). Their optoelectronic properties were evaluated under X-ray illumination showing good sensitivity but large dark current. To overcome this problem, anion engineering was employed: bromine was partially substituted by chlorine in MAPbBr<sub>3</sub> leading to SCs of general formula MAPb(Br<sub>1-x</sub>Cl<sub>x</sub>)<sub>3</sub>. Crystals were grown from solutions with different Cl contents (%Cl<sub>sol</sub>). Their respective optical band gaps E<sub>g</sub> via UV-visible spectroscopy and photoluminescence peaks were determined as a function of Cl content. Their study by energy dispersive X-Ray analysis (EDX) via field emission scanning electron microscopy (FESEM), and X-ray powder diffraction (XRD) allowed determining the Cl content inside the crystal lattice (%Cl<sub>cryst</sub>, x in the general formula above), and cell parameters *a* via LeBail refinement, indicating a typical solid solution behavior. After crystal polishing and Cr electrodes deposition, the optoelectronic performance of 3 to 4 SC devices per composition were tested via J-V sweeps, laser time of flight (ToF) and response under X-ray radiation, hinting at the existence of a potential optimal composition for MAPb(Br<sub>0.85</sub>Cl<sub>0.15</sub>)<sub>3</sub> at 50 V/mm. A decrease in hole mobility and potential rise in charge carriers lifetime were also observed, potentially linked to an improvement of mobility-lifetime product for both charge carriers and trap passivation in the material [11], [12].



**Figure 1:** MAPb(Br<sub>1-x</sub>Cl<sub>x</sub>)<sub>3</sub> SCs with %Cl<sub>cryst</sub> going from 0% (left) to 100% (right)



**Figure 2:** Sensitivity as a function of Cl content showing potential optimum at %Cl<sub>cryst</sub> = 0.15



**Figure 3:** Hole mobility as a function of Cl content showing a decrease with increasing %Cl<sub>cryst</sub>



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# Résumés des Communications par Affiche



## A family of push-pull dyes for 2D hybrid perovskites

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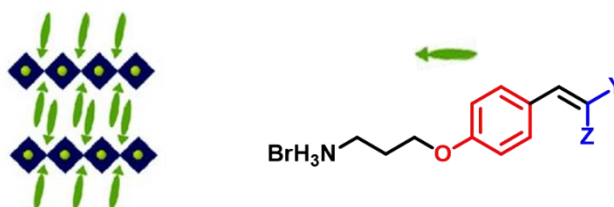
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In the last decade, the interest in lead halide perovskites has been growing exponentially due to their outstanding optical properties resulting in important breakthroughs in many opto-electronic applications such as LED, lasers, solar cells, ... [1] Inside the family of the organic-inorganic lead halide perovskites, 2D perovskites (2DHPERO) are very interesting due to their superior stability compared to their 3D counterparts (ABX<sub>3</sub> with A = Cs<sup>+</sup>, Methyl ammonium, ...; B = Pb<sup>2+</sup>; X = Halide) and due to their chemical versatility, allowing chemical engineering of the organic part. 2DHPERO are obtained by switching the small A cation of the 3D perovskites with a larger organic cation, creating auto-assembled structures with sheets of inorganic octahedral layers surrounded by 2 layers of organic cations in a sandwich configuration (Fig 1.) To tune the optical properties of 2DHPERO according to the desired application, organic semiconductors have very recently started to be used as organic cation, resulting in electron or energy transfer between the organic semiconductors and the inorganic exciton. [2][3]



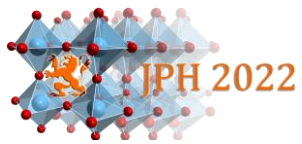
**Figure 1:** structure of 2D hybrid perovskites (left) and general structure of the push-pull dyes (right).

In this context, we designed a family of organic push-pull chromophores with various optical properties for incorporation in 2DHPERO. The push-pull dyes (D- $\pi$ -A) are composed of an electron withdrawing group connected to an electron donating group through a  $\pi$ -bridge as well as a primary ammonium group connected to the  $\pi$ -system through a C2 or C3 alkyl linker. After presenting the optical properties of the chromophores, we will show the influence of the linker length and of the  $\pi$ -system on the optical properties of the Dye<sub>2</sub>PbBr<sub>4</sub> 2DHPERO.

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## Bismuth based perovskite nanocrystals for photoelectrocatalytic CO<sub>2</sub> reduction

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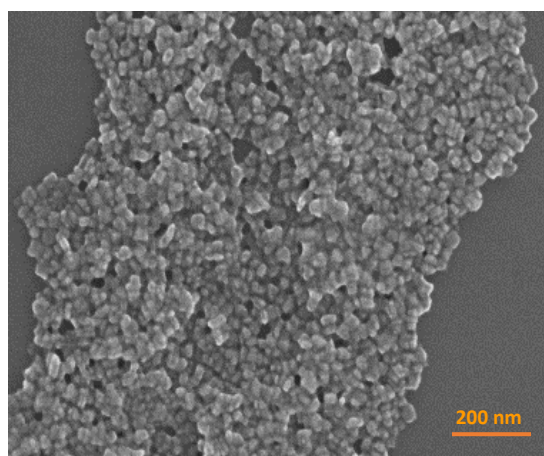
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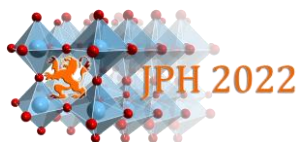
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Closing the carbon cycle is an important challenge in the context of the global warming. Valorization of the CO<sub>2</sub> produced by the industry by its transformation into useful products or fuels by using visible solar light as a driver is a promising, efficient and sustainable means to address this challenge. Bio-inspired photoelectrocatalysis can be used for the CO<sub>2</sub> conversion using only environment friendly compounds. The solar light not being sufficient alone to break the C=O bond in CO<sub>2</sub>, an external photosensitizer (PS) coupled to co-catalyst will be used in this process. The PSs used presently are often hard to synthesize, toxic and have low stability and light absorption. Semiconductor nanocrystals (NCs) have strong light absorption and stability; in addition, their properties can be easily optimized. In this project, we propose to use halogenated perovskite NCs as PSs for the photoelectrocatalysis. The perovskites have been recently very successfully used for the photovoltaics; however, most of them are based on lead, a highly toxic element. We propose to synthesize alternative perovskites based on bismuth, A<sub>3</sub>Bi<sub>2</sub>X<sub>9</sub> (A=cation; X=Br, I).<sup>1</sup> These much less toxic NCs have optoelectronic properties well adapted for the CO<sub>2</sub> photoreduction.<sup>2</sup> Later, they will be coupled to a metal co-catalyst, which is efficient for the CO<sub>2</sub> reduction into green fuels and then deposited on NiO electrodes to fabricate efficient photoelectrocatalytic devices.

The combination of Cs<sup>+</sup>, Bi<sup>3+</sup>, and halide anions (Br, I) can give rise to several different crystalline materials with varying structural and compositional modifications.<sup>3</sup> In our synthesis of layered 2D bismuth-based perovskites, we focus on two solution-based methods, hot-injection and LARP.<sup>4</sup> By optimizing synthesis protocols, we managed to obtain stable Cs<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> NCs with the size of 13±2 nm and bandgaps in the range of 2.12-2.48 eV, as well as luminescent Cs<sub>3</sub>Bi<sub>2</sub>Br<sub>9</sub> nanoplatelets. Synthesis details, structural and optoelectronic properties will be discussed as well as their perspectives for the photoelectrocatalytic CO<sub>2</sub> reduction applications.



**Figure 1:** SEM image of Cs<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> perovskite NCs synthesized by hot-injection method.



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## Hole transporting materials for perovskite solar cells: molecular design, synthesis and photovoltaic properties

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Designing organic molecules efficient for charge extraction and transport when integrated in optoelectronic devices remains a great challenge for many advanced applications. In perovskite solar cells (PSCs), the hole extraction/transport and the device stability are strongly dependent on the molecular structure of the hole transporting material (HTM). The development of new HTMs alternative to Spiro-OMeTAD and the understanding of the role of doping and interfacial agents on these layers are also important research axes in the field. Herein we present several series of carbazole<sup>[1-5]</sup> and triphenylamine<sup>[6-10]</sup> based HTMs developed for perovskite photovoltaic devices, which cover both small molecules and polymeric materials. We have investigated the relationship between the chemical structure of the HTM and both the photovoltaic efficiency and the device stability.

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## Investigation of a photoactive lead free gold perovskite material

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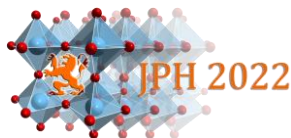
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Lead based perovskites have proven to be remarkable semiconductors in term of processability and optoelectronic properties. To circumvent the presence of lead, the photovoltaics community has started to study a variety of Lead-free halide perovskites (HaPs). Among these candidates, the gold perovskite family (AAuX<sub>3</sub>, with monovalent cation A<sup>+</sup> and halide anion X<sup>-</sup>) is under consideration, both from the theoretical<sup>1,2</sup> and the experimental point of view<sup>2,3</sup>. This structure relies on the B-site substitution of Pb by Au that is likely to impact the optoelectronic properties most prominently via the BX<sub>6</sub> octahedral sub-unit in the crystal structure.

In this study, we report the fabrication of gold perovskite thin films (CsAuX<sub>3</sub>, with X = I, Br, Cl) and compare their structural and optoelectronic properties with data from the literature on corresponding single crystals. An extensive characterization of the produced thin films will be provided, including X ray Diffraction Raman and photoluminescence spectroscopy, demonstrating the photoactivity of the obtained thin films, and opening avenues towards their inclusion in optoelectronics devices..

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## Optical properties of highly calibrated CsPbBr<sub>3</sub> nanocrystals perovskites synthesized by soft chemistry.

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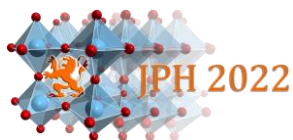
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In the context of the opto-electronics, implying various applications such as smartphones, TV, or flexible screens, alternative technologies to the classical inorganic semiconductors are demanded, due to the problems of availability of these materials. Among the alternative technologies, there are the organic semiconductors, but they don't provide the same performances as purely inorganic semiconductors. Recently, perovskite nanocrystals appear to be a suitable way to achieve new opto-electronic devices, because they present performances equivalent to classical semiconductors<sup>1,2</sup>, while being easily synthesized in solution with abundant components. CsPbBr<sub>3</sub> is one of the most potent perovskites in terms of optoelectronic properties.<sup>3,4,5</sup> To address the technological needs in terms of optoelectronic performances and conformabilities, it is essential to obtain the most homogeneous NCs in shape and size on macroscopic volumes in order to realize some thin films integrable in the devices.

LuMIn has developed a new synthesis method of CsPbBr<sub>3</sub> nanocrystals by soft chemistry. The structural characterizations by X-ray diffraction, TEM and HR-TEM, shows that this new method produces, on large scales, highly calibrated CsPbBr<sub>3</sub> nanocrystals in terms of shape and size. These structural characterizations have been supplemented by optical measurements (absorption, photoluminescence, time-resolved photoluminescence, quantum yield) on nanocrystals both in solution and in thin films. We show that the properties of the nanocrystals in solution or in film are similar, suggesting that depositing the nanocrystals in a film doesn't induce new relaxing channels for the excitons. Moreover, these nanocrystals present good ambient atmosphere resistance. These properties open the way to realize some homogeneous thin films of NCs, without modifying the optical performances of the NCs, integrable in next generation opto-electronic devices.

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## Perspective of CsPbBr<sub>3</sub> nanocrystals as active centers for liquid scintillation

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Liquid scintillation is used for ionizing radiation detection. In metrology, it is used for detection and quantification of radio-isotopes. Several standards are based on active organic molecules such as PPO (2,5-diphenyloxazole), originally dissolved in toluene, now commonly replaced by solvents such as DIN (di-isopropylnaphthalene). In some cases, wavelength shifting molecules such as POPOP (1,4-bis(5-phenyloxazol-2-yl) benzene) are used to avoid self-absorption of the scintillation light or to adapt the emission wavelength to the photodetector. CsPbBr<sub>3</sub> nanocrystals are known to be very efficient light emitters, and when embedded in polymer matrices they have demonstrated good scintillation properties [1]. In this presentation we explore the potential of nano-particles of CsPbBr<sub>3</sub> in toluene as a potential substitute of organic molecules and evaluate their scintillating performances.

The nanoparticles synthesis has been performed via a hot-injection approach reported in literature [2]: the obtained samples show high colloidal stability, which is required for the coincidence measurement.

In order to evaluate the impact of the particle size and concentration, we have prepared 6 liquid scintillators: a polydisperse sample (mean particles diameter of 12±3nm) in 3 concentrations (5.6, 0.56 and 0.056 mg/ml), and 3 samples obtained from it by fractional precipitation (mean particles diameter of 9±1nm, 11±1nm, 16±3nm) in the concentration of 0.56 mg/ml. Transmission electron microscope images of the related samples are presented figure 1. The photoluminescence (PL), the absorption properties are presented, as well as the scintillating spectral characteristics. Because the timing performances are of prior importance, PL decay time as well as scintillation decay time under x-ray with sub-ns time resolution are presented and discussed.

Finally, the performances under gamma-rays using the triple to double coincidence ratio technique allows to compare the overall performance to commercial organic liquid scintillators but also to discuss the scintillating yields of the nanoparticles themselves, a parameter which is not straightforward to evaluate in the case of nanostructure matter due to the complex energy deposition scheme under ionizing radiation excitation.[3]

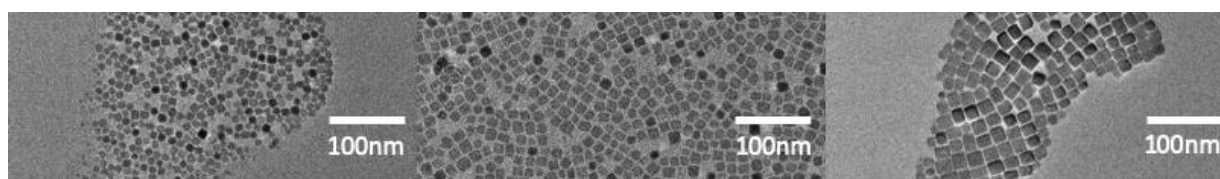
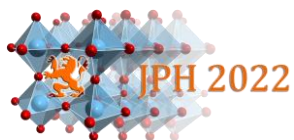


Figure 1 : TEM images of the 3 samples of nano-CsPbBr<sub>3</sub> analyzed (left,  $d=9\pm 1\text{nm}$ , middle  $d=11\pm 1\text{nm}$ , right  $d=16\pm 3\text{nm}$ )





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## Nanoimprint of Hybrid Perovskite for light management using Photonic Crystal

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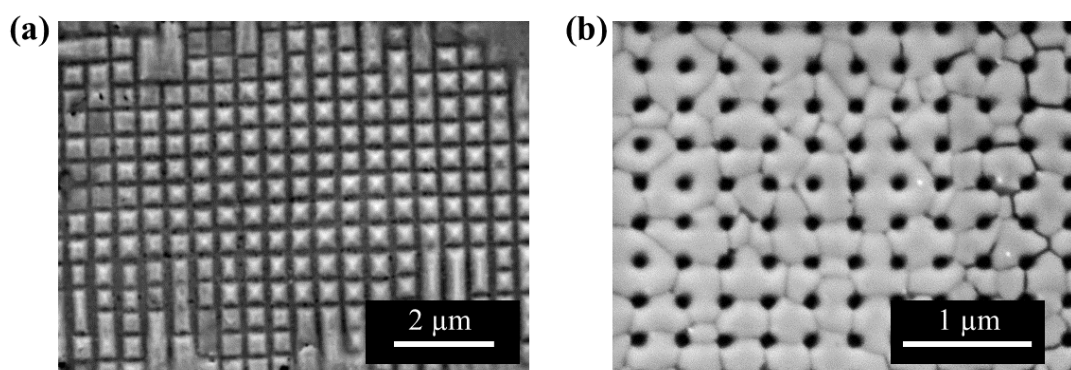
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Hybrid perovskites (PK) have attracted great interest for PV solar cells or light emitters, especially thanks to their tunable, direct bandgap and their easy deposition process.

However, light in or out coupling can be limited due the PK large refractive index. Moreover, if the thickness remains limited for the sake of photocarrier recombination, absorption at the bandedge can be reduced. We thus propose to use light management processes such as resonant light trapping and directional light extraction thanks to a high index contrast structuration of the PK. Our study focuses on the fabrication of photonic crystals (PCs) on PK by thermal-nanoimprint.

More precisely, PCs are ordered nanostructures in which two media with different refractive indices are arranged in a periodic form. According to optical simulations, we studied different kind of PCs morphology (pyramidal, holes...) to optimize extraction or collection over given wavelength ranges.

In this work, the experiments were done with two different active materials: MAPI and MAPB. Both can be used for solar cells or LEDs. We used spin coating followed by specific nanoimprint that allows both patterning and crystallization of the PK layer, leading to patterns such as those presented in figure 1. Such a patterned PK layer can be included in a suitable stack for electrical injection, paving the way for highly efficient PV cells or LED.



**Figure 1** : SEM images of imprinted MAPI (a) and MAPB (b). Resulting PC are respectively square lattices pyramidal and holes patterns.

**Optoelectronic properties of CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> thick polycrystalline layers under X-rays and electron beam**

Y. Faucheux<sup>1,3</sup>, F. Donatini<sup>2</sup> & E. Gros d'Aillon<sup>1</sup>

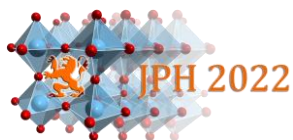
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Metal Halide Perovskite (MPH) are semiconductor materials of interest in many optoelectronic fields, among them X-ray detection. This is due to their strong X-ray absorption (particularly with lead based MPH), their easy synthesis and their good charge carrier transport properties. Whereas most research these recent years focused on single crystal properties or thin polycrystalline layers for solar cells applications, few studies have been published on the effect of grain boundaries in thick and large polycrystalline layers necessary in medical X-ray imaging. Consequently, the influence and behavior of grain boundaries in thick perovskite layers is still discussed. Using MAPbBr<sub>3</sub> polycrystalline samples synthesized in solution in collaboration with Néel Institute in Grenoble, we present recent works on these thick layers to characterize their optoelectronic properties. Macroscopic optoelectronic measurements (X-rays photocurrent, laser time of flight) are presented in regards of comparable monocrystalline samples to highlight the progress needed for operational perovskite X-rays imagers. To understand the link between macroscopic properties and grain boundaries, Electron Beam Induced Current measurements were performed on polished samples to characterize the carrier generation with high spatial resolution.



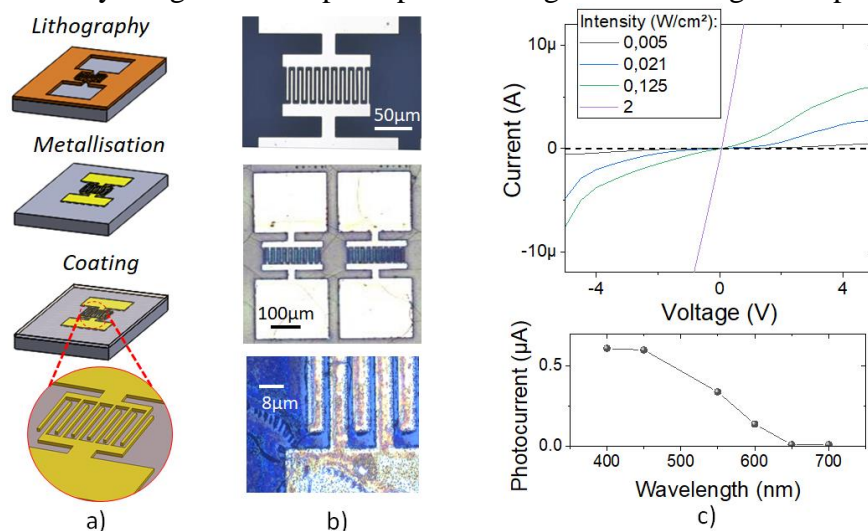
## Study of photodetectors based on hybrid MAPbBr<sub>3</sub> perovskite thin film

Pavlo Mai<sup>1</sup>, Julien Houel<sup>1</sup>, Nathan Drevet<sup>1</sup>, Benoit Malher<sup>1</sup>, Christophe Dujardin<sup>1</sup> and Alban Gassenq<sup>1</sup>

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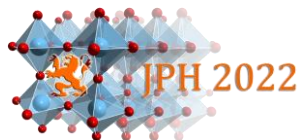
Hybrid organic-inorganic lead halide perovskites present excellent optoelectronic properties for visible wavelength-range applications like solar cells [1] light-emitting diodes [2] and photodetectors [3,4]. For photodetection, interdigitated detectors based on such materials offers high detection for fast and economic fabrication with different materials like MaPbI<sub>3</sub>[5], MaPbCl<sub>3</sub> [6] or MaPbBr<sub>3-x</sub>I<sub>x</sub> [7]. However, optical responsivities are still limited and detailed studies are needed to optimize and explore in more details such promising photodetectors. In this work we have developed planar photodetector based on MaPbBr<sub>3</sub> perovskite layers. 100 nm thin film have been first characterized by absorption and photoluminescence measurement showing high absorption at 520 nm and strong emission at 535 nm wavelength, as expected. Planar photodetectors were then fabricated with such layers directly deposited on top of interdigital electrode on SiO<sub>2</sub> substrates. The different design parameters we have investigated show that the detected photocurrent is strongly dependent of the design parameters (electrode distance, detector surface...), the input light properties (wavelength, intensity....) and the applied electric field. Using such optimizations photocurrent up to 0.1 mA was demonstrated and different ways for responsivity improvement will be discussed. This work allows envisioning higher performances with such photodetectors for many practical applications like photodetectors directly integrated on top of optical waveguides for integrated optics.



**Figure 1** : photodetectors based on hybrid MAPbBr<sub>3</sub> perovskite thin films with a) the processing steps, b) wide-field optical microscopy images of the fabricated samples and c) opto-electrical characterizations.

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## **Engineering approaches to enhance the efficiency and stability of perovskite solar cells**

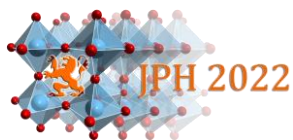
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**Abstract:** Organic-inorganic hybrid perovskite solar cells (PSCs) have attracted much attention due to their high power conversion efficiency (>25%) and low-cost fabrication. Yet, improvements are still needed for more stable and higher performing solar cells. In this presentation, three engineering approaches are proposed to enhance the photovoltaic efficiency and stability of PSCs: (1) On the first method, a series of highly oriented vertical TiO<sub>2</sub> nanocolumn electron-transporting photonic structures were intentionally fabricated on half of the compact TiO<sub>2</sub>-coated fluorine-doped tin oxide substrate by glancing angle deposition with magnetron sputtering. These vertically aligned nanocolumn arrays were then applied as the electron transport layer into triple-cation lead halide perovskite solar cells based on Cs<sub>0.05</sub>(FA<sub>0.83</sub>MA<sub>0.17</sub>)<sub>0.95</sub>Pb(I<sub>0.83</sub>Br<sub>0.17</sub>)<sub>3</sub>. (2) On the second method, we investigated the effect of removing the excess PbI<sub>2</sub> at the interface between the triple-cation Cs<sub>0.05</sub>(FA<sub>0.83</sub>MA<sub>0.17</sub>)<sub>0.95</sub>Pb(I<sub>0.83</sub>Br<sub>0.17</sub>)<sub>3</sub> perovskite and the Spiro-OMETAD hole-transport layer. For this purpose, four different organic salts, including methylammonium iodide (MAI), formamidinium iodide (FAI), methylammonium bromide (MABr) and methylammonium chloride (MACl) were applied and compared. (3) The last aspect that will be presented involves the application of the downshifting optical property of colloidal carbon quantum dots to enhance the stability of perovskite solar cells against UV degradation.

On the above-mentioned engineering methods, different characterization methods, including far-field and near-field optical experiments, structural and spectroscopic investigations, impedance spectroscopy, together with solar cell efficiency and in particular device stability measurements are presented together in order to understand the underlying origins of the efficiency and stability enhancement observed in triple-cation perovskite solar cells.



## Functionalization of mp-TiO<sub>2</sub> metallic oxide by Amidine based Self-Assembled Monolayers for MAPbI<sub>3</sub> perovskite solar cells

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In order to control the growth and stability of halogenated perovskite (HP) used in photovoltaic solar cells, we aim to graft adequate functionalized Self-Assembled Monolayers (SAMs) on the intermediate MO<sub>x</sub> layers.

Electron transport layers (ETL) are inserted between the conducting electrodes (FTO, metals) and the active layer. SAMs aim to adjust the electronic levels of the MO<sub>x</sub> layers with those of the HP, to optimize global properties of the active film.

We address here the grafting of molecules terminated by Amidine and Amino groups.

Several molecules were used in this work: Molecules A, B and C terminated with Amino groups [HO<sub>2</sub>C-PP-CH<sub>2</sub>-NH<sub>3</sub>Cl (A)] [HO<sub>2</sub>C-CH<sub>2</sub>-PP-CH<sub>2</sub>-NH<sub>3</sub>Cl (B)], [HO<sub>2</sub>C-PP-NH<sub>3</sub>I (C)] which were synthesized from SAM S [HO<sub>2</sub>C-PP-NH<sub>2</sub>] [1], and those whose terminal group is an Amidine, [HO<sub>2</sub>C-P-NH<sub>2</sub>NH (D)] and [HO<sub>2</sub>C-PP-NH<sub>2</sub>NH (E)], (P= Phenyl) on MO<sub>x</sub> layers such as mesoporous TiO<sub>2</sub> (mp-TiO<sub>2</sub>) which has the role of (ETL).

SAMs grafting have been analyzed by IR spectroscopy (ATR). Then we studied and compared the influence of such SAMs on the structure of MAPbI<sub>3</sub> perovskite film by UV-Vis spectroscopy, XR diffraction and Scanning Electron Microscopy SEM.

In this study, we highlight the influence of SAMs on photovoltaic performances and stability of perovskite solar cells. This effect is due to the terminal poles (NH<sub>2</sub>, NH<sub>3</sub> and NH<sub>2</sub>NH) which may constitute a common plane with the perovskite layer simultaneously allowing better growth and orientation of the crystallization planes of the MAPbI<sub>3</sub> and improving the photovoltaic parameters of the solar cells.

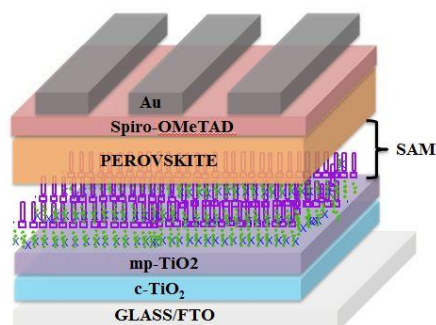


Fig.1: Perovskite-based cells deposited on a mp-TiO<sub>2</sub> layer functionalized by self-assembled monolayers SAMs.

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## Investigating polymorphism in MAPbI<sub>3</sub> from first principles calculations

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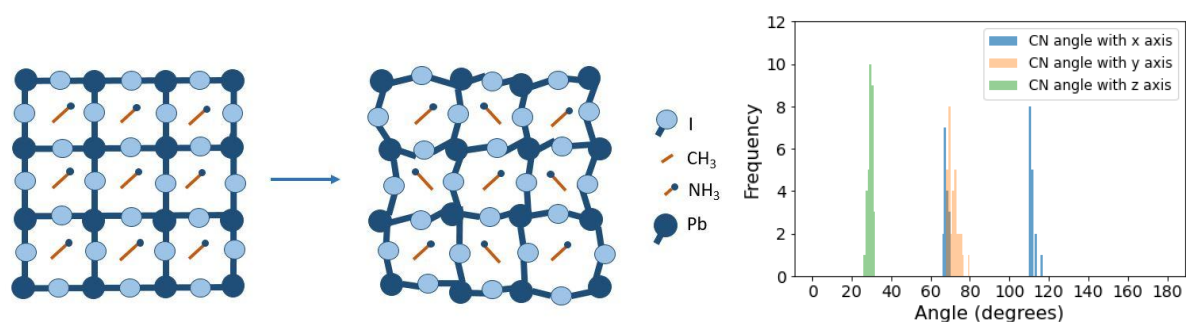
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Methylammonium lead iodide (MAPI) is the reference of hybrid halide perovskites whose promise for photovoltaics and other applications has sparked an impressive research activity in the last decade. In the high-temperature cubic phase of MAPI it was soon recognized that the organic cations rotate freely [1]. However, it was very recently shown, through Density Functional Theory (DFT) calculations, that a form of disorder in cubic MAPI is expected even at zero temperature, i.e., without any entropic contribution to the free energy of the system. Such inherent disorder, dubbed “polymorphism”, reflects the fact that the system can lower its energy by a distorted variant of the usual cubic perovskite structure resulting in a large unit cell containing hundreds of atoms [2].

Here we present DFT results of a few calculated polymorphous structures and analyze them with the goal of understanding the reasons underlying such tendency to disordering. We checked the presence of polymorphism in all three phases of MAPI, orthorhombic, tetragonal, and cubic. We found polymorphous structures only in the cubic case, with energy lower by approximately 70 meV per formula unit, with respect to the monomorphous counterpart, in agreement with previous reports [2]. We analyze the polymorphous structure in terms of angular distribution of the inorganic cage distortions and of molecular orientations, for which we highlight a bimodal distribution. Ongoing work focuses on the influence of polymorphism on the properties of vacancies in MAPI.



**Figure 1:** Left: sketch of the transformation of the monomorphous structure of MAPI into a more stable polymorphous structure. Right: distribution of the orientations of the methylammonium cation.

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