Synthesis of ionic transition metal complexes and 2D perovskite characterization

Giulia Longo, Michele Sessolo and Henk J. Bolink
giulia.longo@uv.es

Instituto de Ciencia Molecular
University of Valencia, Spain.

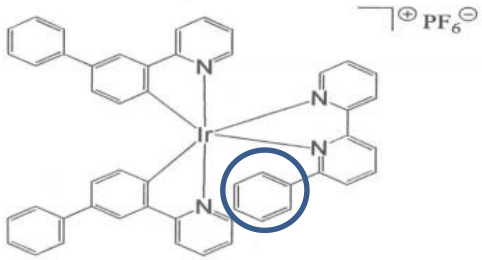
Main objectives

- Ionic transition metal complexes evaluation through preparation of light emitting devices

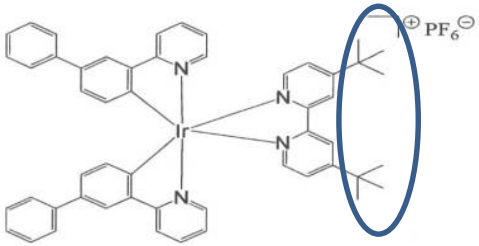
- Design of new hybrid emitting material and its optimization for devices applications

SECONDMENT at OSRAM:
Synthesis of iTMC

Synthetic modification of Ir complexes: how they affect the performances



1b



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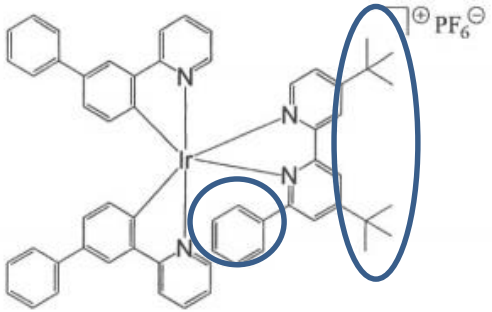
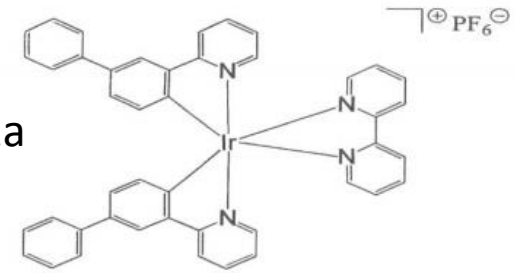
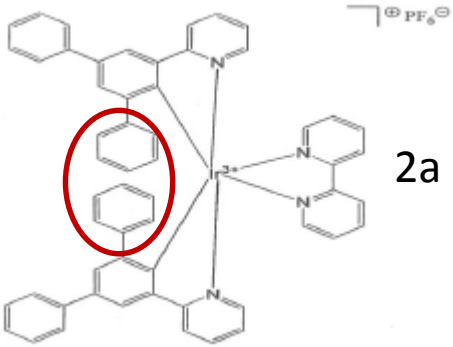


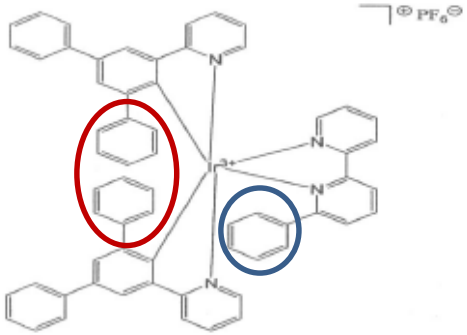
1d

1a





2a



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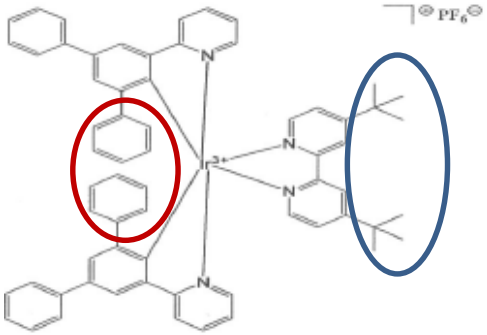

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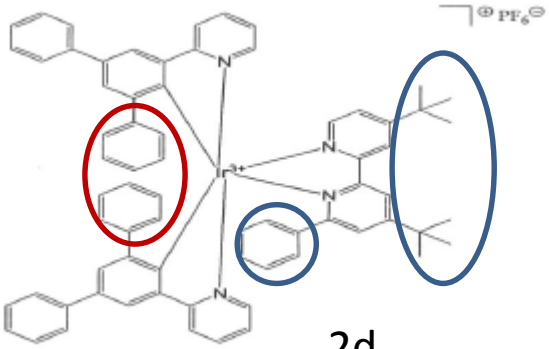
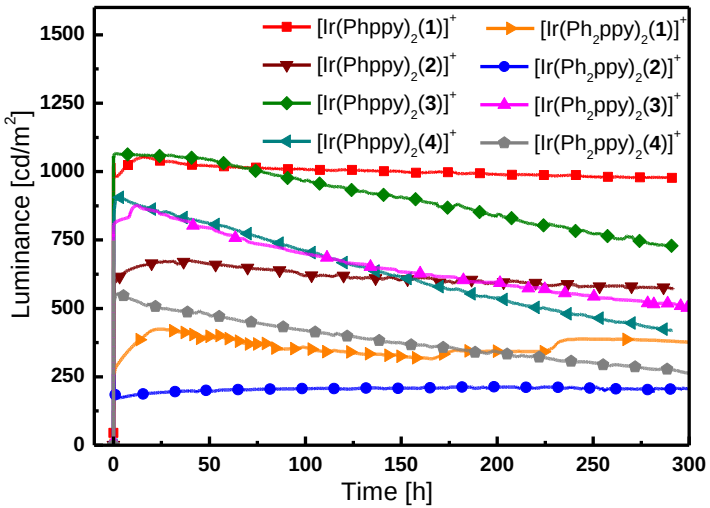
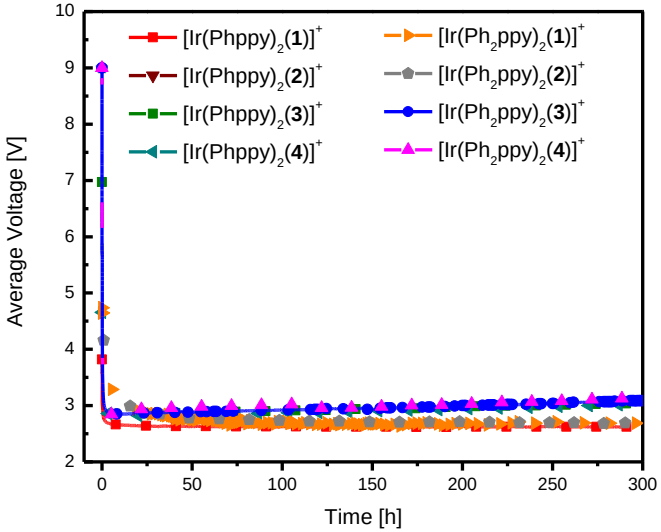


2d

A. M. Bünzli, C. Housecroft, G. Longo, *Chem. Sci.*, 2015, DOI:10.1039/c4sc3942d

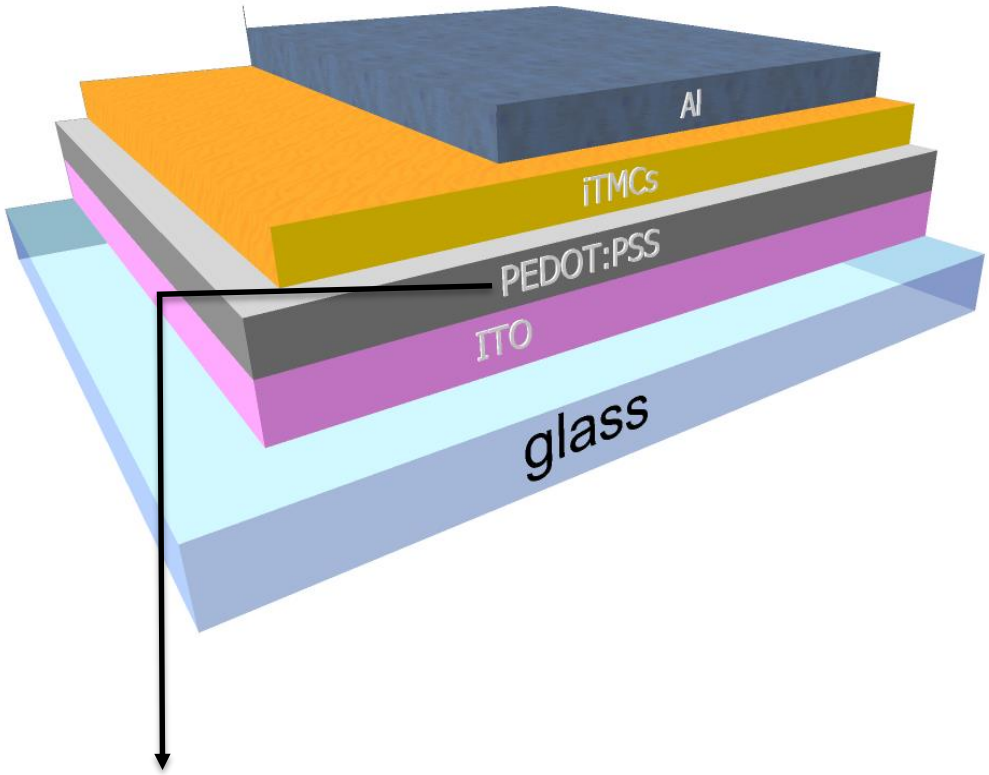


300 A/m²



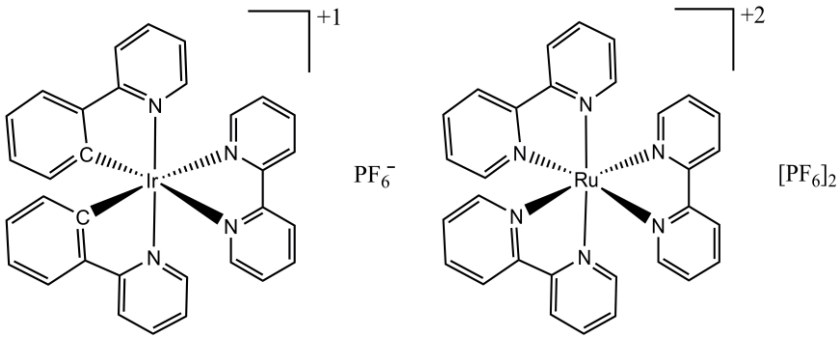
Complex	Lum max Cd/m²	Efficacy max Cd/A	T_{on} h	$T_{1/2}$ h
1a	1024	3.5	0.14	2800
1b	676	2.2	0.42	1204
1c	1090	3.5	0.03	437
1d	910	2.9	1.11	260
2a	425	1.4	1.21	260
2b	261	0.7	0.05	>2800
2c	1048	2.9	0.07	282
2d	748	1.8	0.01	147

Ionic transition metal complexes based LECs



Light Emitting Layer consists of:

Ionic transition-metal complex (iTMCs)
(and ionic liquids)



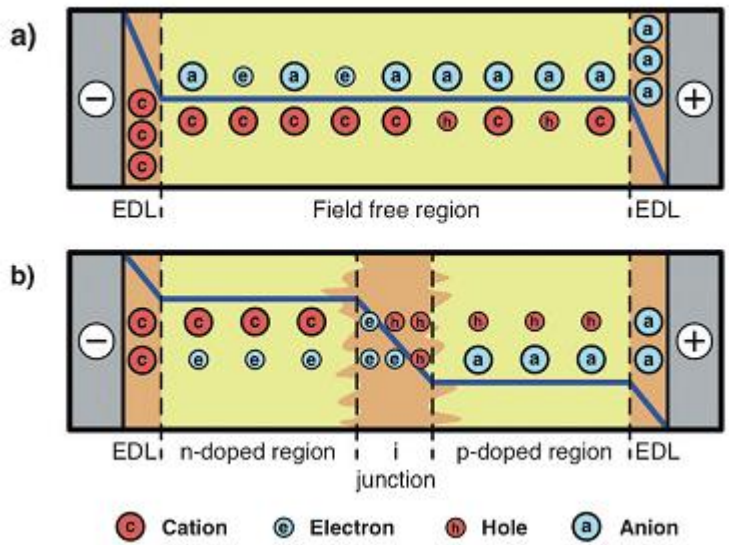
Poly(3,4-ethylenedioxythiophene):polystyrensulfonate

K. M. Maness *et al. J. Am. Chem. Soc.* **1996**, *118*, 10609.
A. Wu *et al. J. Am. Chem. Soc.* **1999**, *121*, 4883.
E. S. Handy *et al. J. Am. Chem. Soc.* **1999**, *121*, 3525.
Review: Costa, *et al. Angew. Chem. Int. Ed.* **2012**, *51*, 8178.

Mechanism of work

a) Electrodynamical model

Cations form electric double layer: drop of electric potential at the electrodes interfaces.
Cations are joined in the bulk, and there is emission only in the field free region



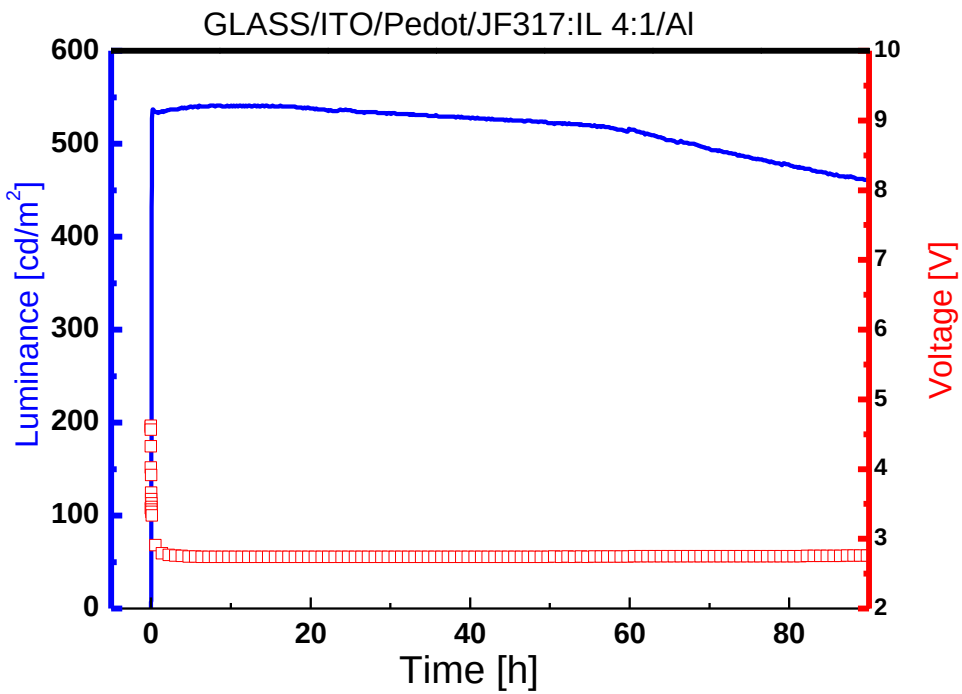
b) Electrochemical doping model

The movement of the ions leads to the formation of p- and n-doped region; the emission take place in the intrinsic region, where there is a drop in the potential, that favors the light emission.

Both can occur, depending on charge injection : if we have good charge injection the electrochemical model takes place, if the injection is bad the device works under electrodynamic conditions

R. D. Costa, E. Ortí, H. J. Bolink, F. Monti, G. Accorsi and N. Armaroli, *Angewandte Chemie International Edition*, 2012, **51**, 8178-8211.

Material characterization: typical curves and figures of merit



Efficacy

Emitted light per electric flux (Cd/A)

Luminance

Flux of light emitted by the device (cd/m^2)

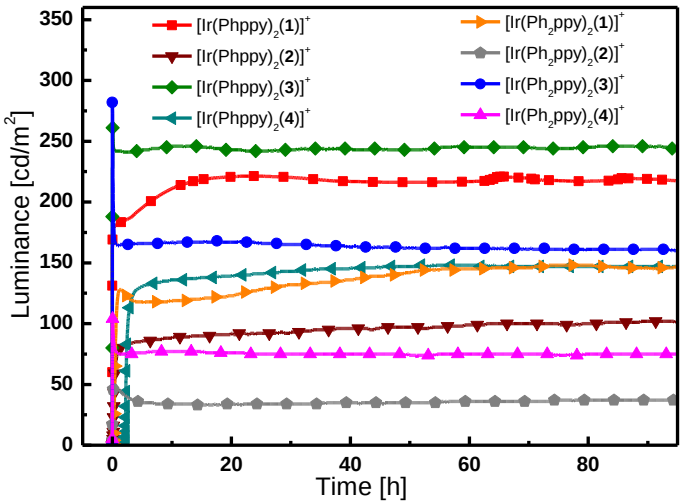
Turn on time:

Time to reach 100 cd/m^2

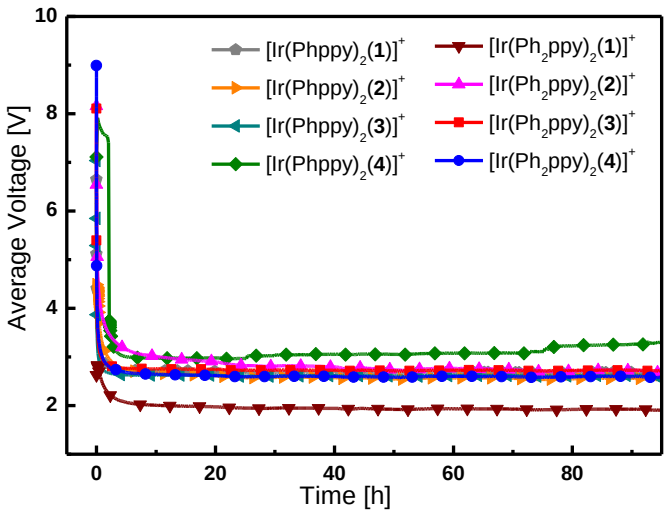
Time to reach the maximum luminance

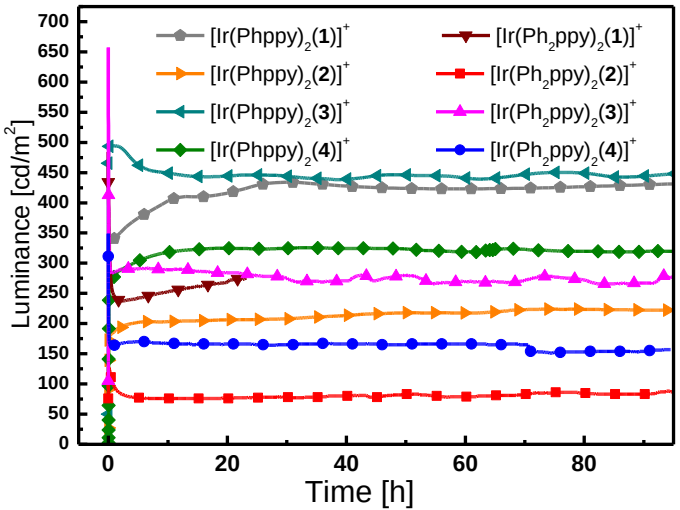
Lifetime

Time to reach half of the maximum luminance

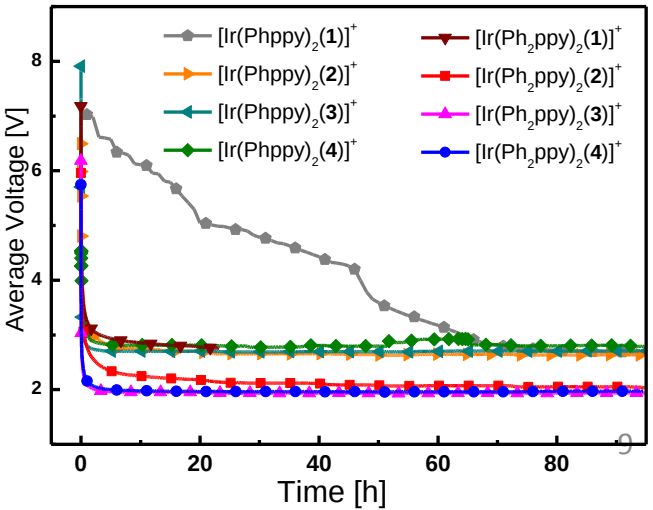


50 A/m²



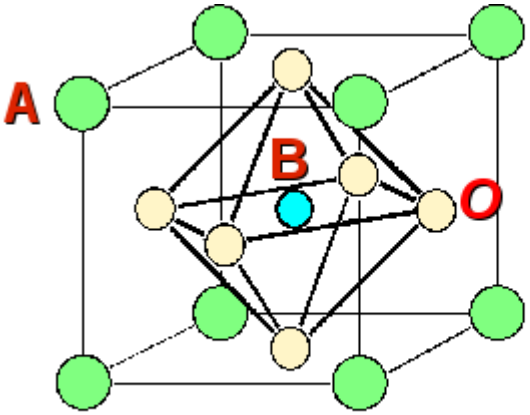


100 A/m²



Photoluminescence from hybrid perovskites

Organic-inorganic hybrid materials: perovskite



ABO_3

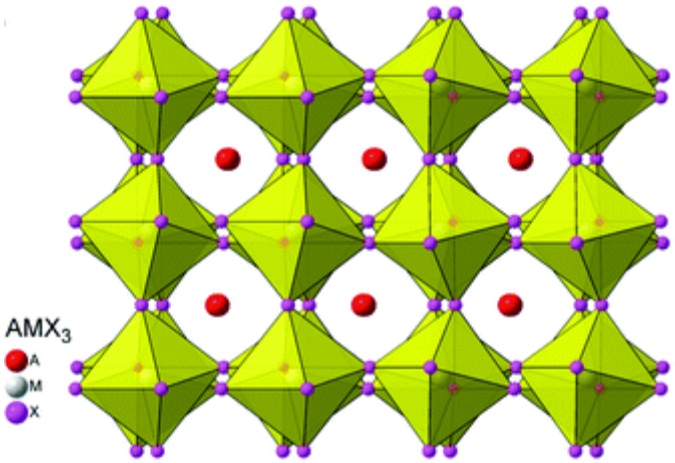
A: organic cation

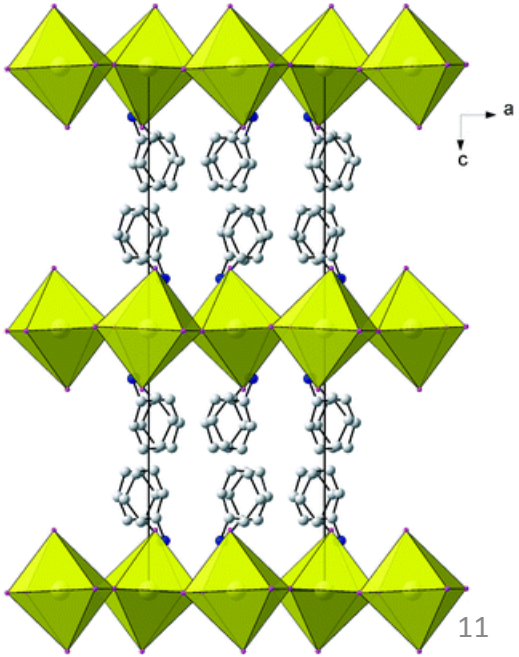
B: Inorganic cation

O: X^-

A: bigger than $CH_3NH_3^+$
layered structure

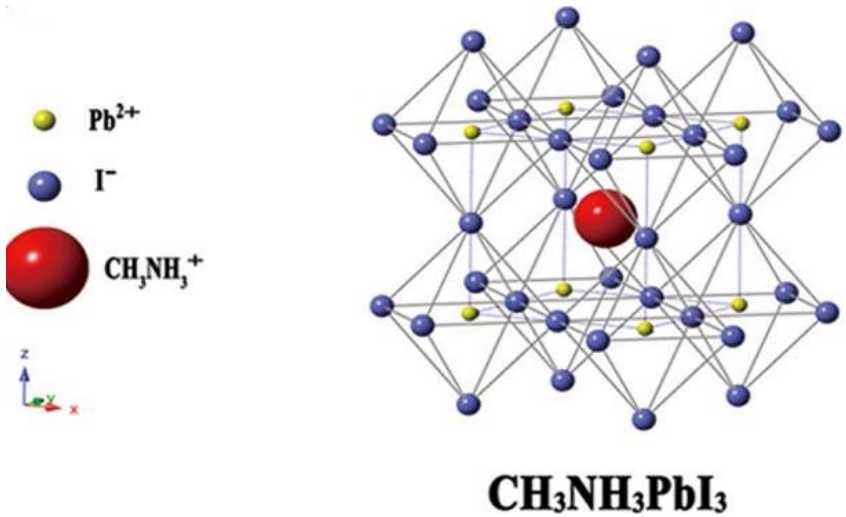
A: $CH_3NH_3^+$
Cubic structure

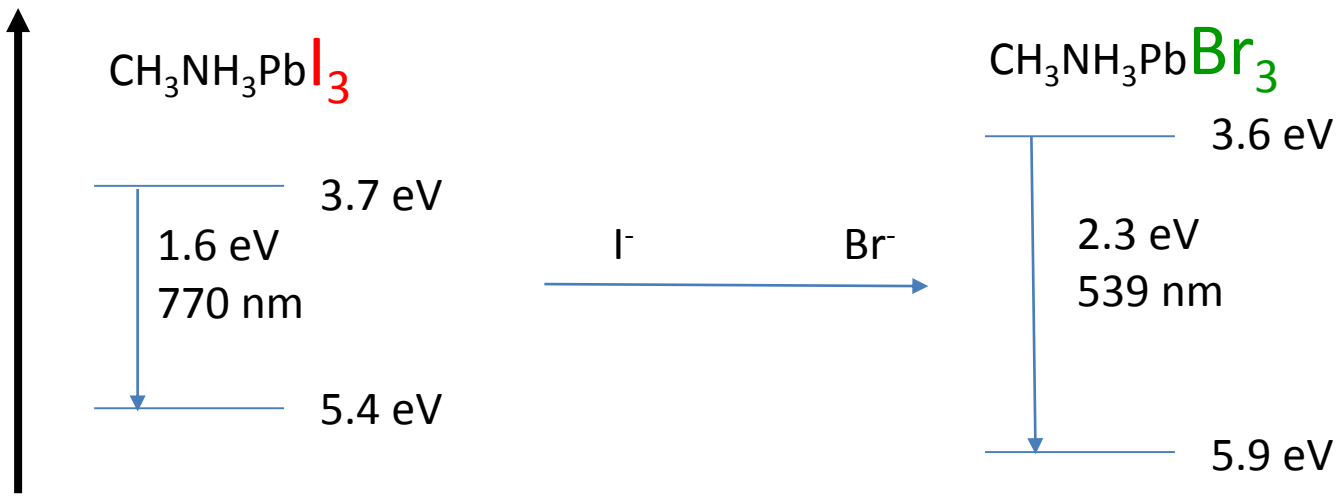




$CH_3NH_3PbI_3$-$CH_3NH_3PbBr_3$

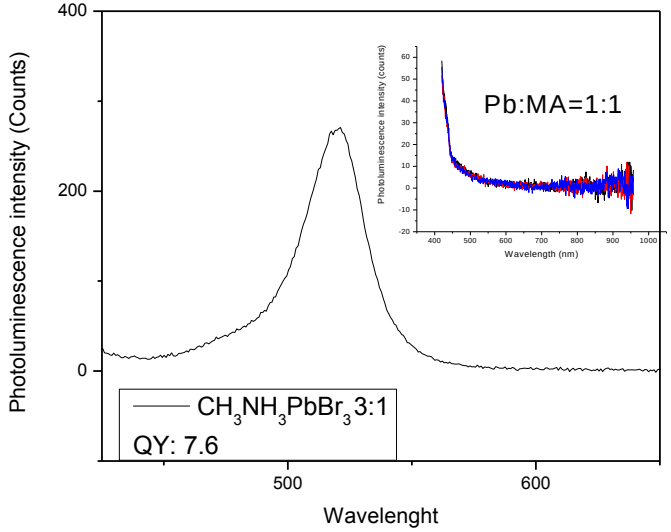
King of the solar cells: up to 19% of efficiency in three years!

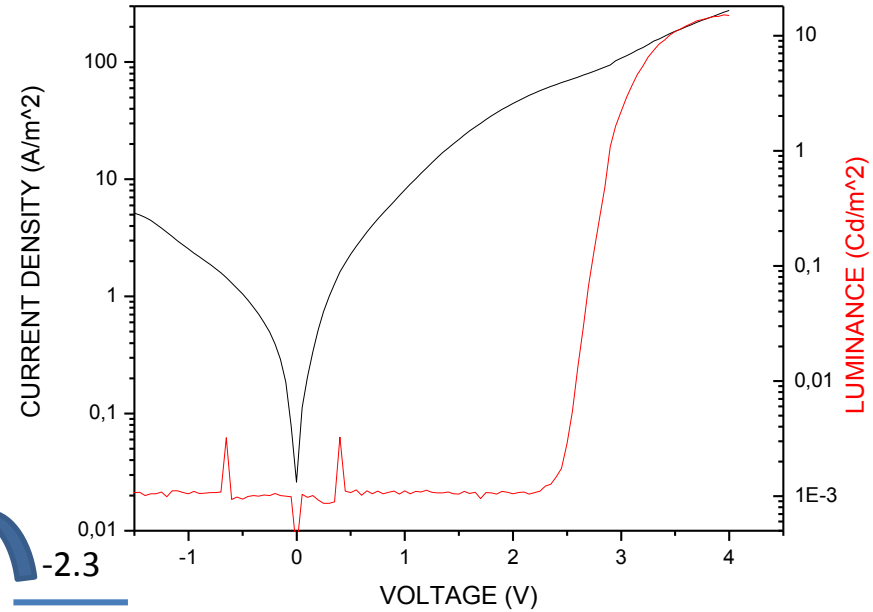


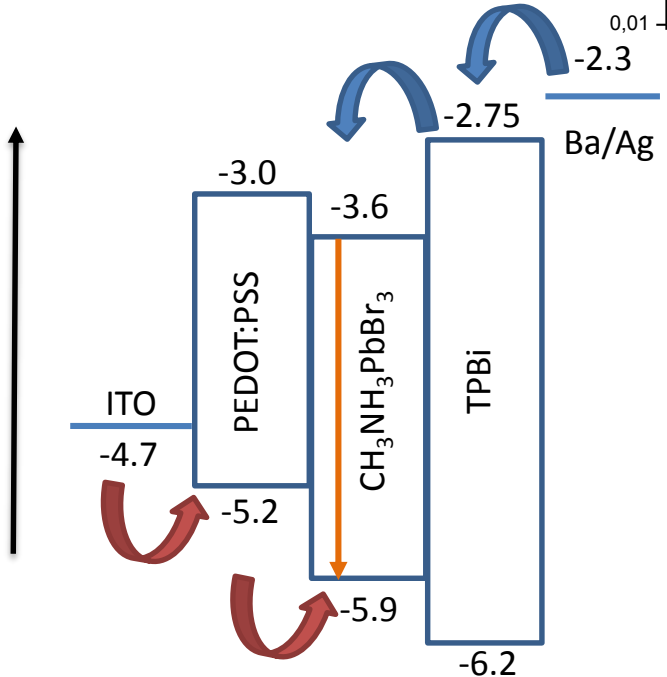


G. Longo et al, Efficient photovoltaic and electroluminescent perovskite devices, JACS, submitted
K. Tvingstedt, O. Malinkiewicz, A. Baumann, C. Deibel, H. J. Snaith, V. Dyakonov and H. J. Bolink, *Sci. Rep.*, 2014, **4**.

Bulk $CH_3NH_3PbBr_3$



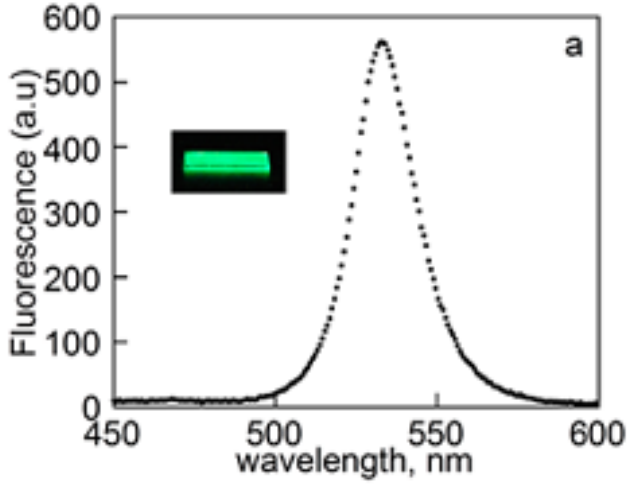




Size effect in $CH_3NH_3PbBr_3$

How to improve PLQY?

Perovskite NPs showed very high quantum effieciency

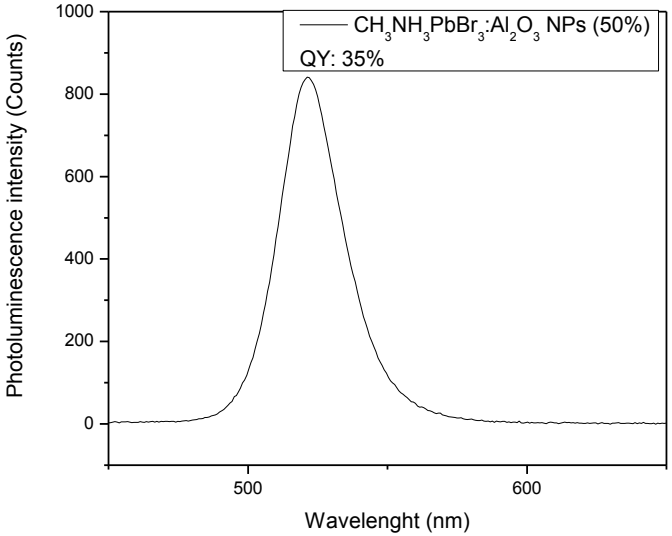


PLQY ≈ 35%

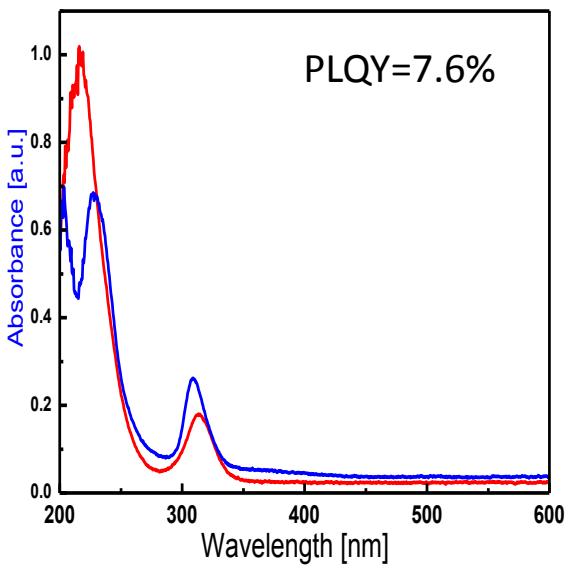
L. C. Schmidt et al, *Nontemplate Synthesis of $CH_3NH_3PbBr_3$ Perovskite Nanoparticles, JACS,* **2014**, *136,* 850

Add materials that could confine the crystal growth of the perovskite, as nanoparticles, small molecules or polymers

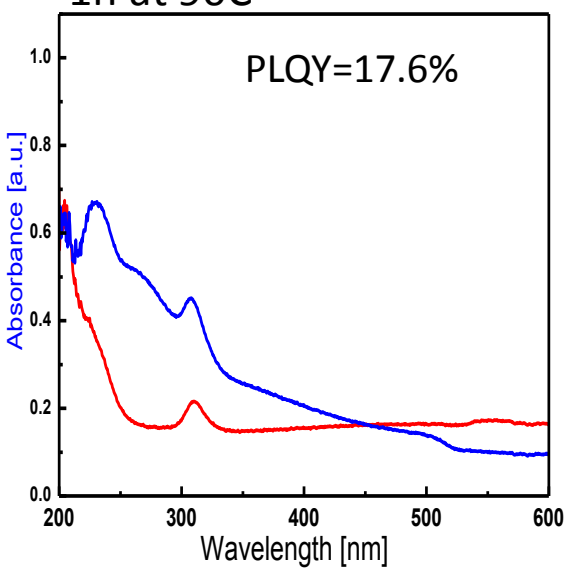
$CH_3NH_3PbBr_3$ with Al_2O_3 NPs



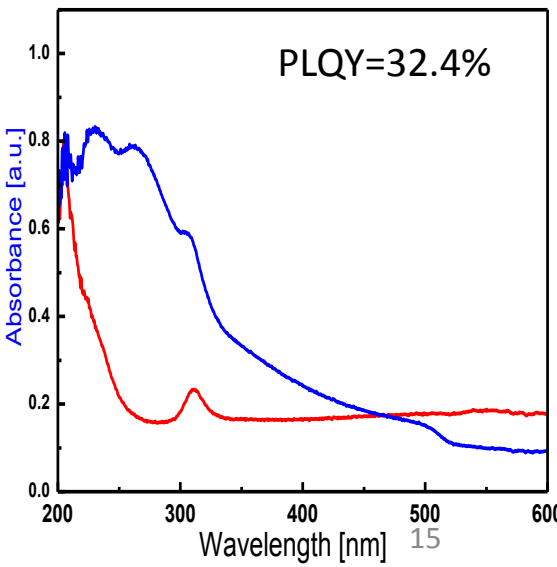
30 min at 90C



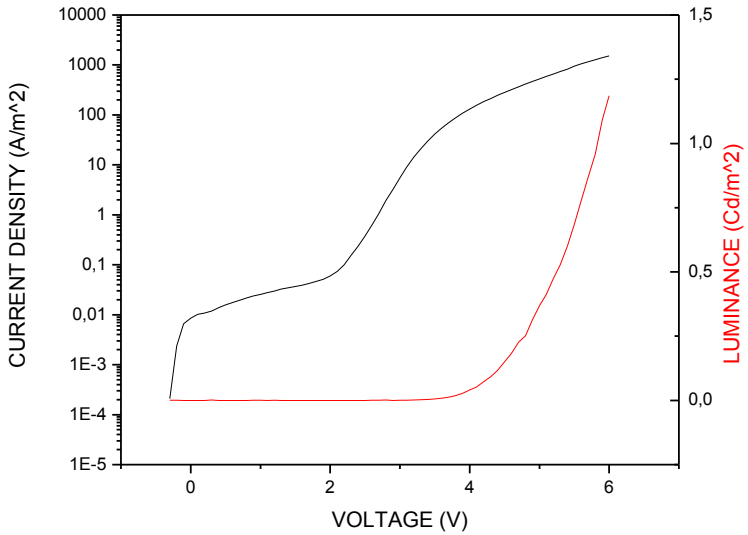
1h at 90C

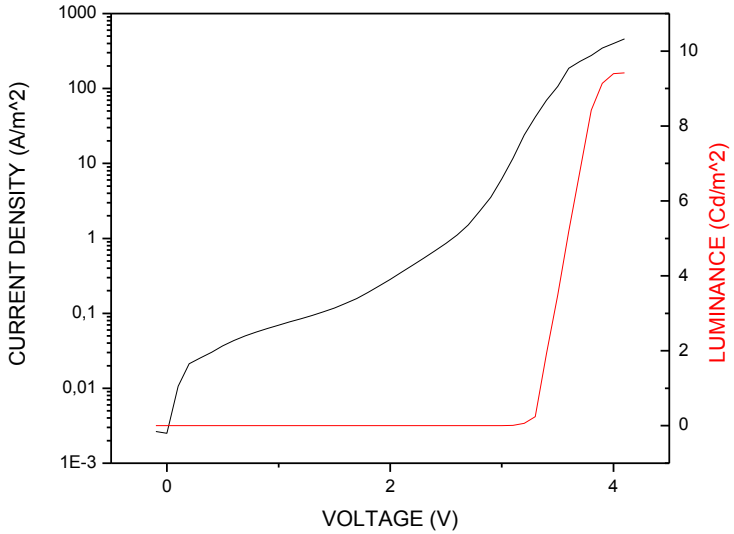


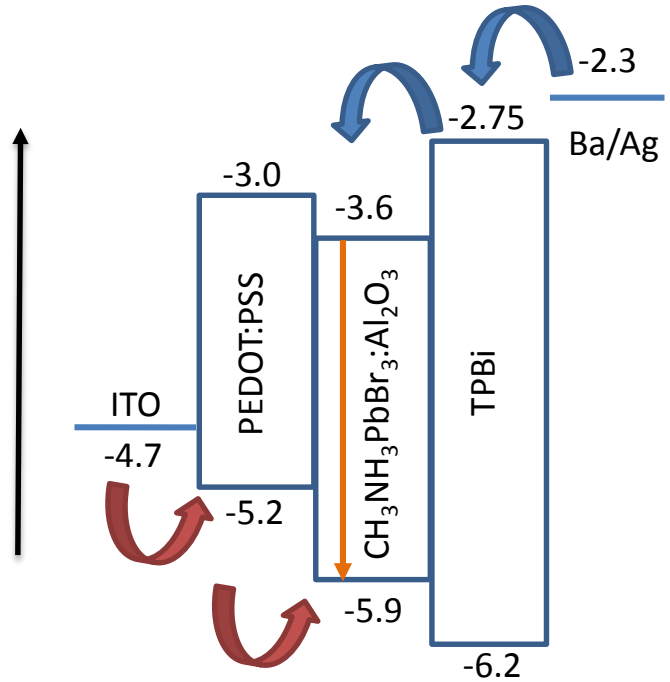
2h 90C



$CH_3NH_3PbBr_3$ with Al_2O_3 NPs







Low luminescence intensity
High leakage current
Different results with the same device structure

$CH_3NH_3PbBr_3$ with Al_2O_3 NPs

% wt Alumina	PLQY / % Series 1	PLQY / % Series 2	PLQY / % Series 3
6	0.0	--	--
11	0.0	--	--
15	4.2	--	--
20	4.5	--	0.2
27	4.9	--	0.4
38	10.8	--	0.7
42	--	16.8	4.4
48	25.5	20.5	19.1
55	--	15.4	28.7
60	14.4	--	34.9
68	10.6	--	24.0
75	9.2	11.1	--

NPs: dispersion not stable in time

Filtering: change the concentration

No filtering: possible shorts

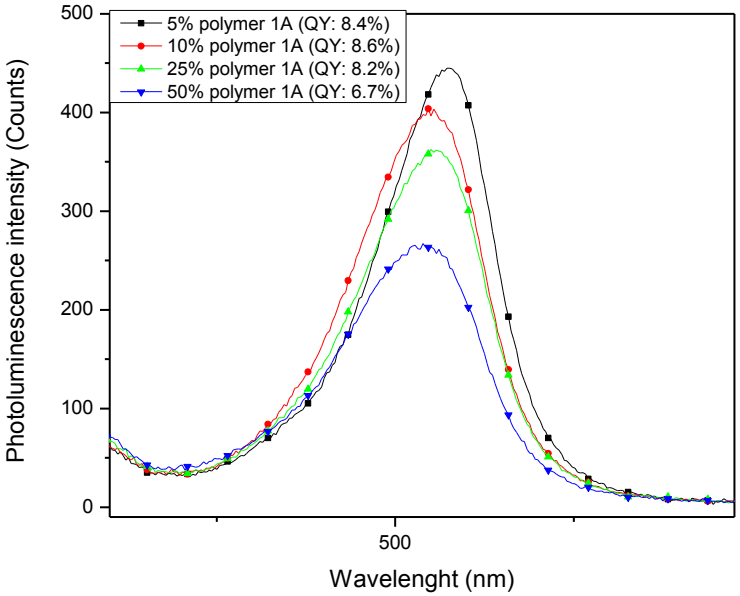
Very low reproduibility

$CH_3NH_3PbBr_3$ with polymers

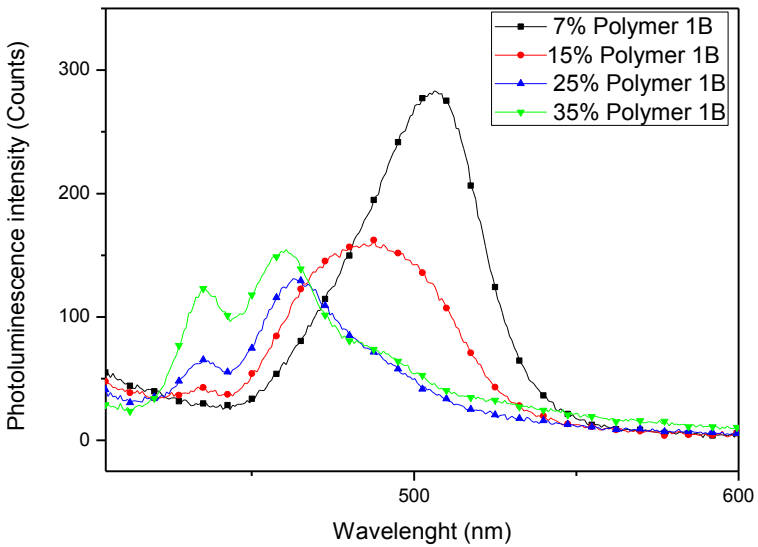
- Possibility to patent, so they will be called polymer 1, 2, 3

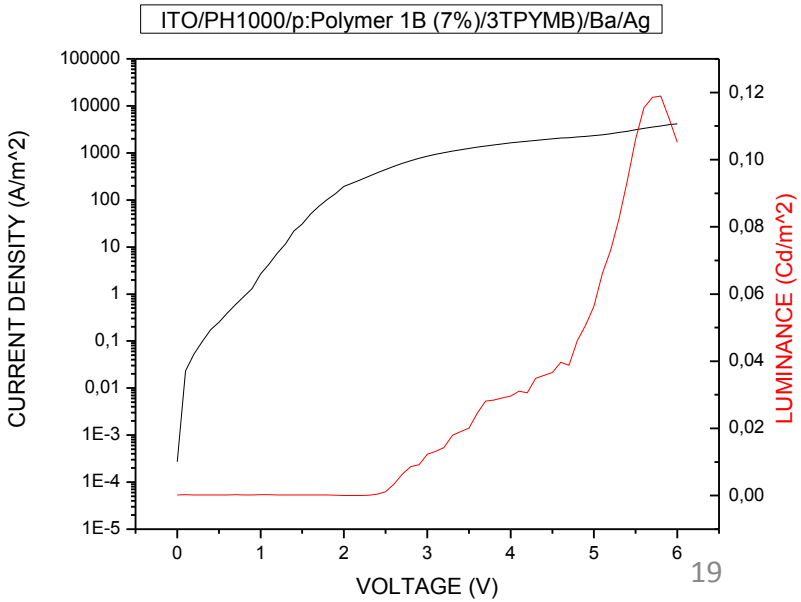
- Three main behavior for the tested polymer were found

$CH_3NH_3PbBr_3$ with polymer 1

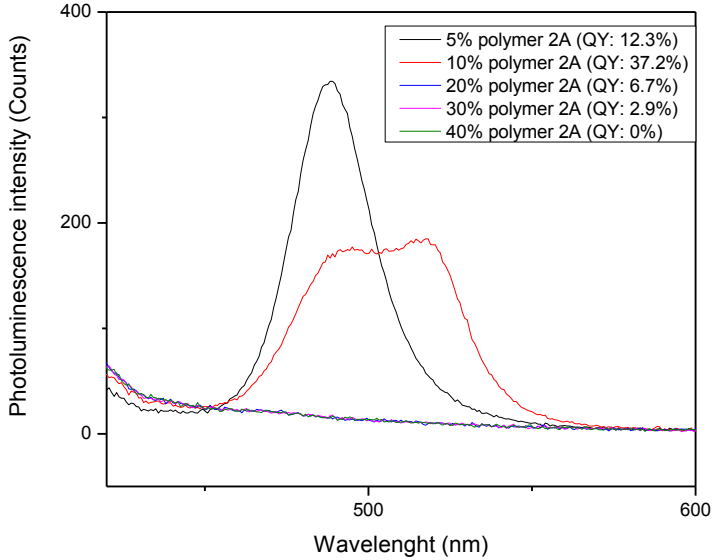


- Low photoluminescence
- Almost independent from polymer concentration
- Detrimental effect of thermal annealing
- Low electroluminescence

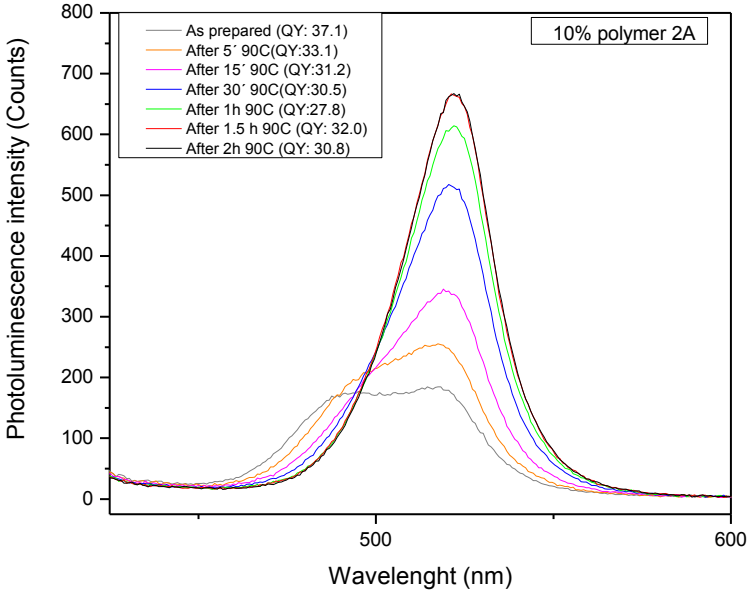


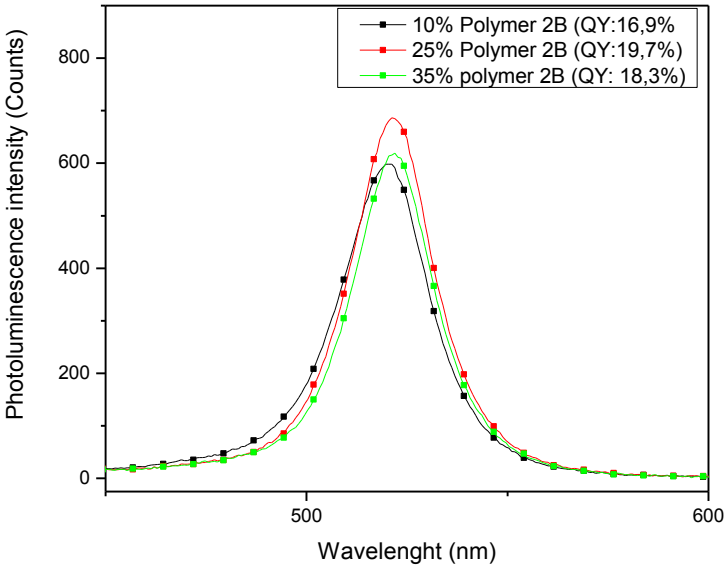


$CH_3NH_3PbBr_3$ with polymer 2

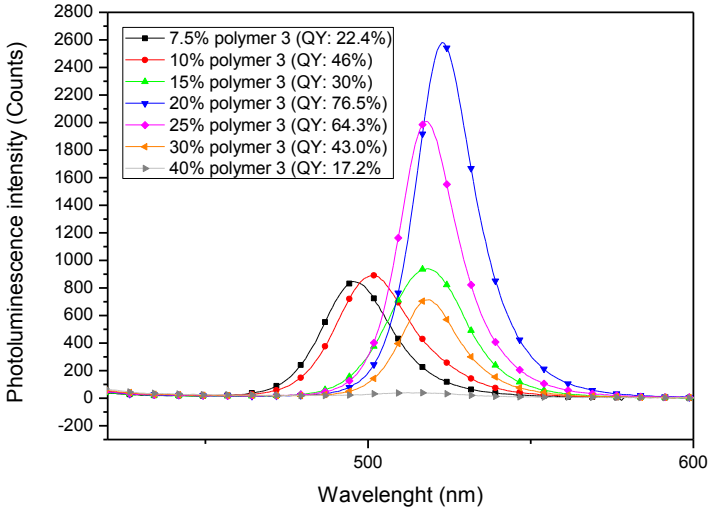


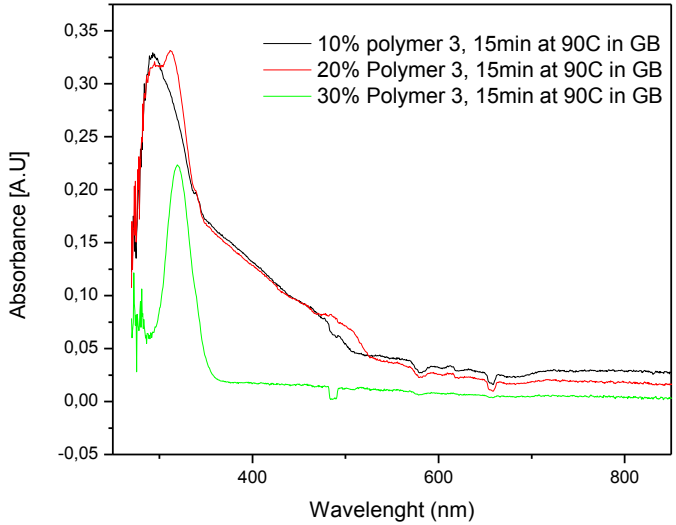
- Good photoluminescence
- Strongly dependent from polymer concentration
- Big effect of thermal annealing

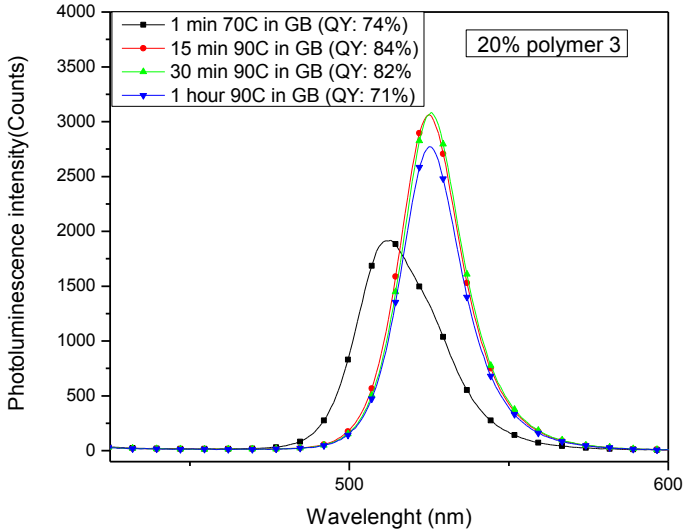




$CH_3NH_3PbBr_3$ with polymer 3

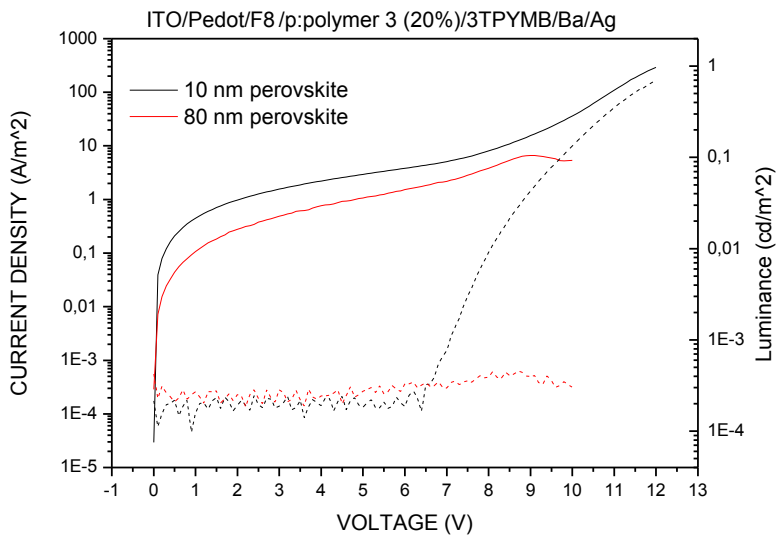


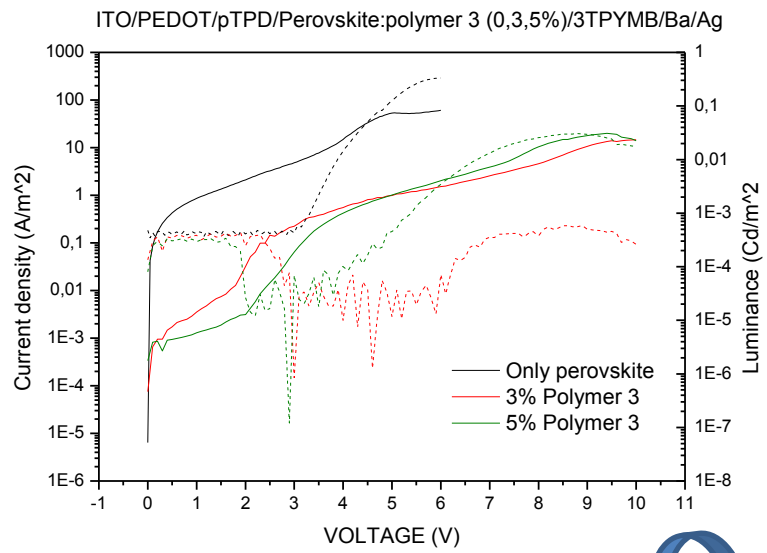


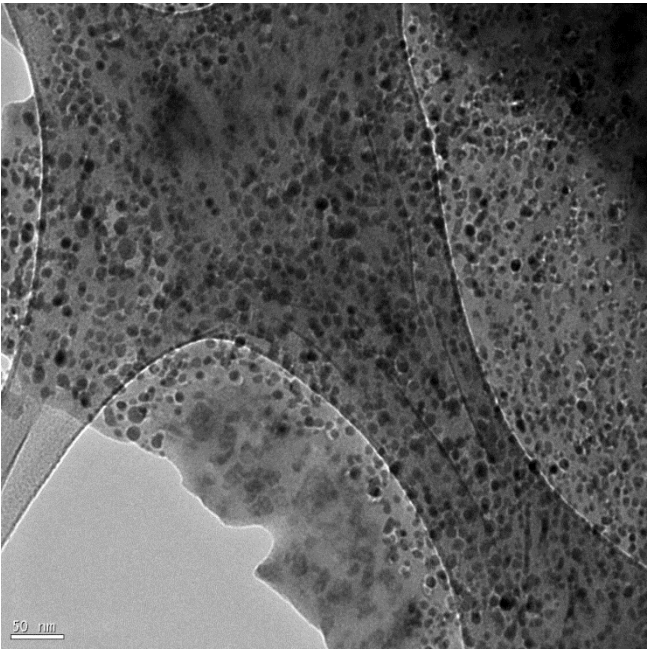


- Very high photoluminescence
- Three behavior with different concentrations
- Good effect of thermal annealing

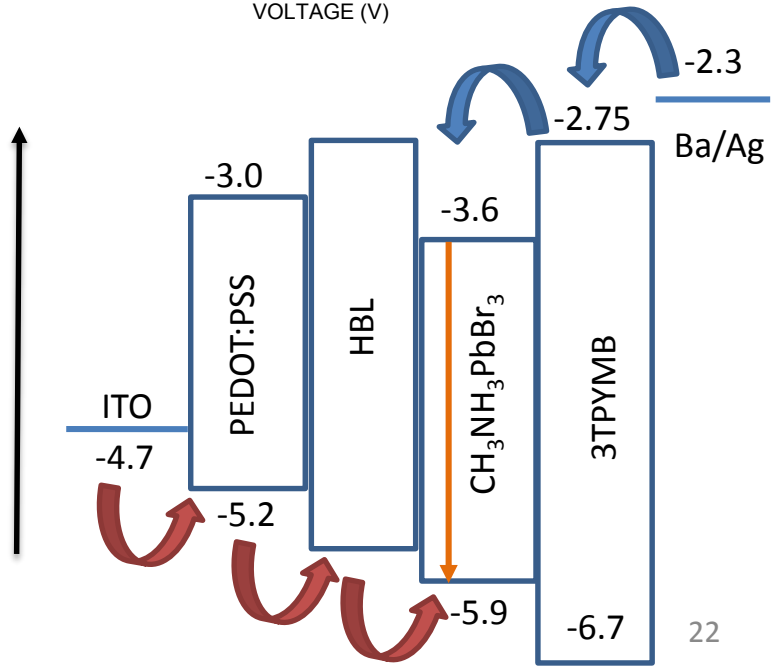
OLED with perovskite:polymer 3 active layer







Average size: 10nm
Min. size: 5 nm
Max size: 24 nm



Conclusions

Conclusions

- High influence of size confinement and surface passivation on perovskite photoluminescence

- Higher photoluminescence for polymer 3, possibly due to better nanoparticles passivation than other polymers. To be tested soon by high sensibility EQE measurments.

- Bad oled performances, probably due to the separation between perovskite nanoparticles and insulating character of the polymer

Acknowledgments

- EU Marie Curie LUMINET project
- University of Valencia, ICMol
- My supervisors, Henk Bolink and Michele Sessolo

Thank you for your attention!