Precursor stoichiometry in $CH_3NH_3PbBr_3$. Structure-property relationship and LED implication

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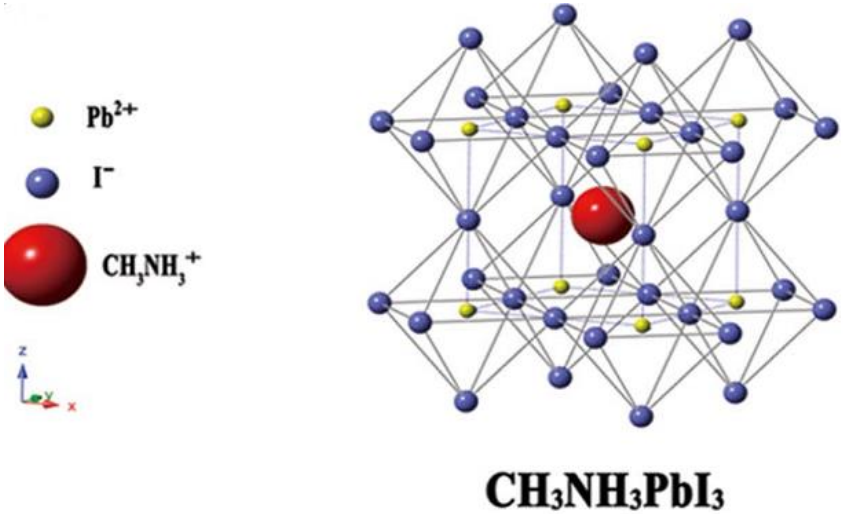
Organic-inorganic cubic perovskites



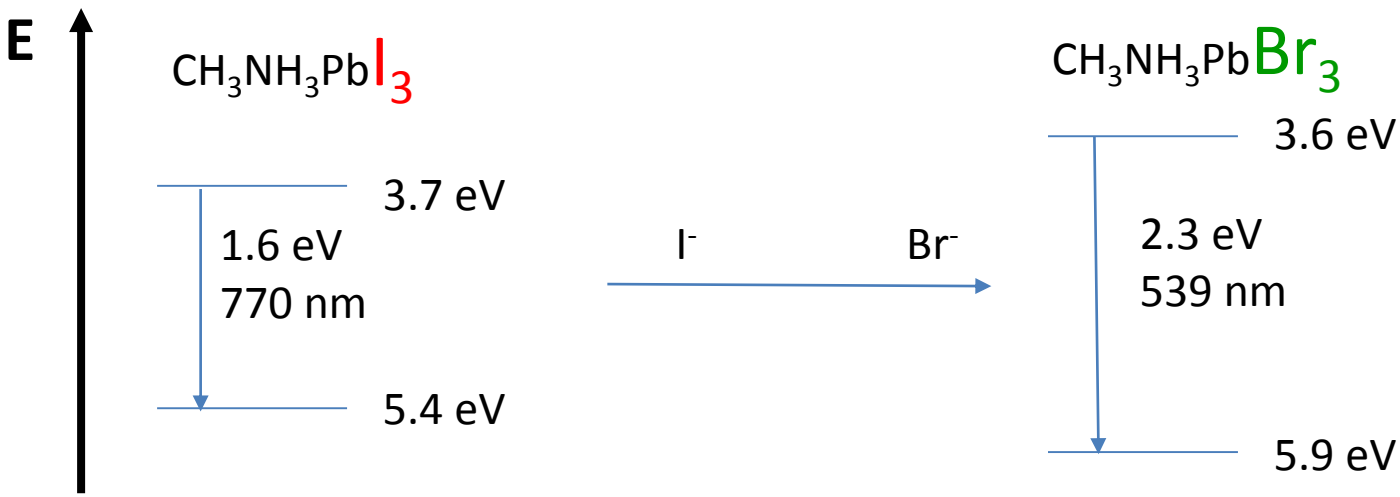
Corner sharing lead halide octahedra

(PbX_2)

+

Methylammonium halide

(CH_3NH_3X)



L- Gil-Escrig, G. Longo, A. Pertegas, C. Roldan-Carmona, A. Soriano, M. Sessolo and H. J. Bolink, *Chem. Commun*, 2015, **51**
K. Tvingstedt, O. Malinkiewicz, A. Baumann, C. Deibel, H. J. Snaith, V. Dyakonov and H. J. Bolink, *Sci. Rep.*, 2014, **4**.

Analyzed samples

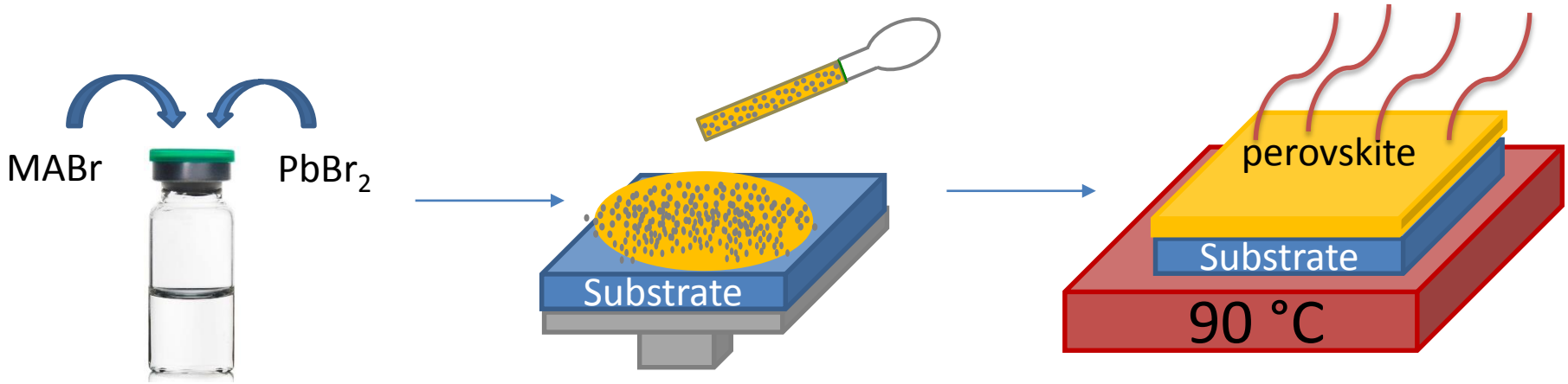
Stoichiometric

$CH_3NH_3:PbBr_2 = 1$

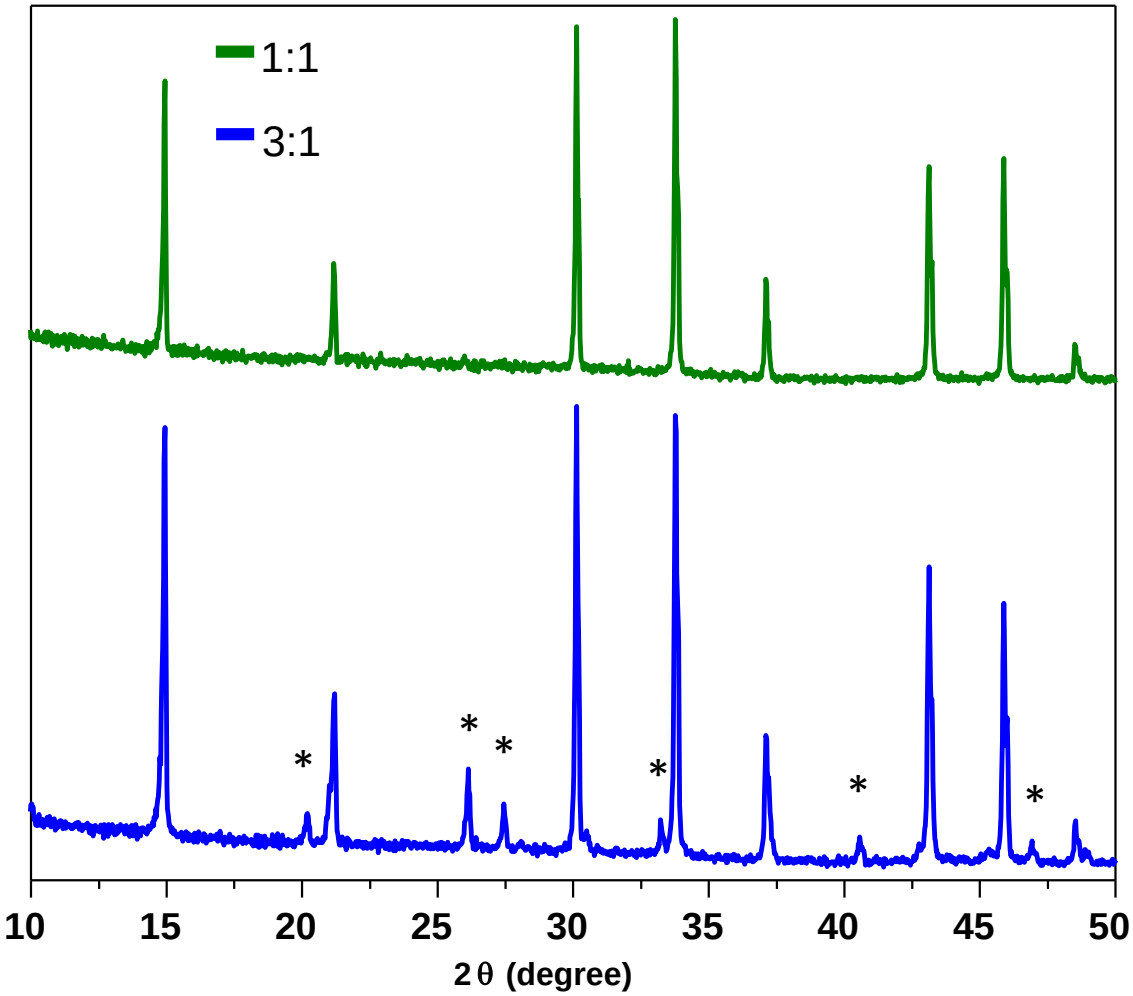
Non-stoichiometric

$CH_3NH_3:PbBr_2 = 3$

Single step deposition technique



Powder diffraction analysis

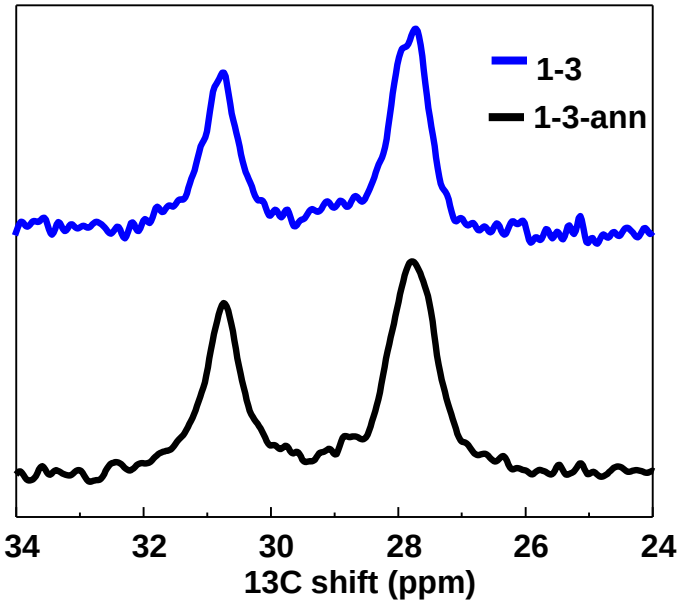


Polycristalline powders precipitated from concentrated solutions

Precipitating agent: chlorobenzene

Dryed at 75° for 48 hours, and then annealed at 90°C for 3h. Sample 3:1 was further annealed at 115°C for 24 hours

Solid state C^{13} NMR analysis



Bounded CH_3NH_3Br Free CH_3NH_3Br

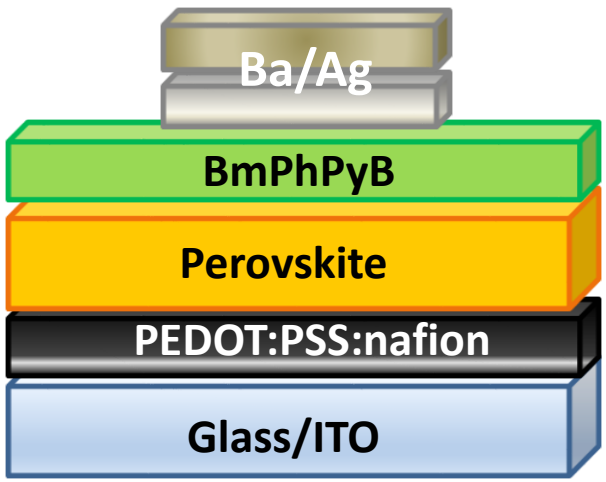
freeMA/Pb-MA= 1.38

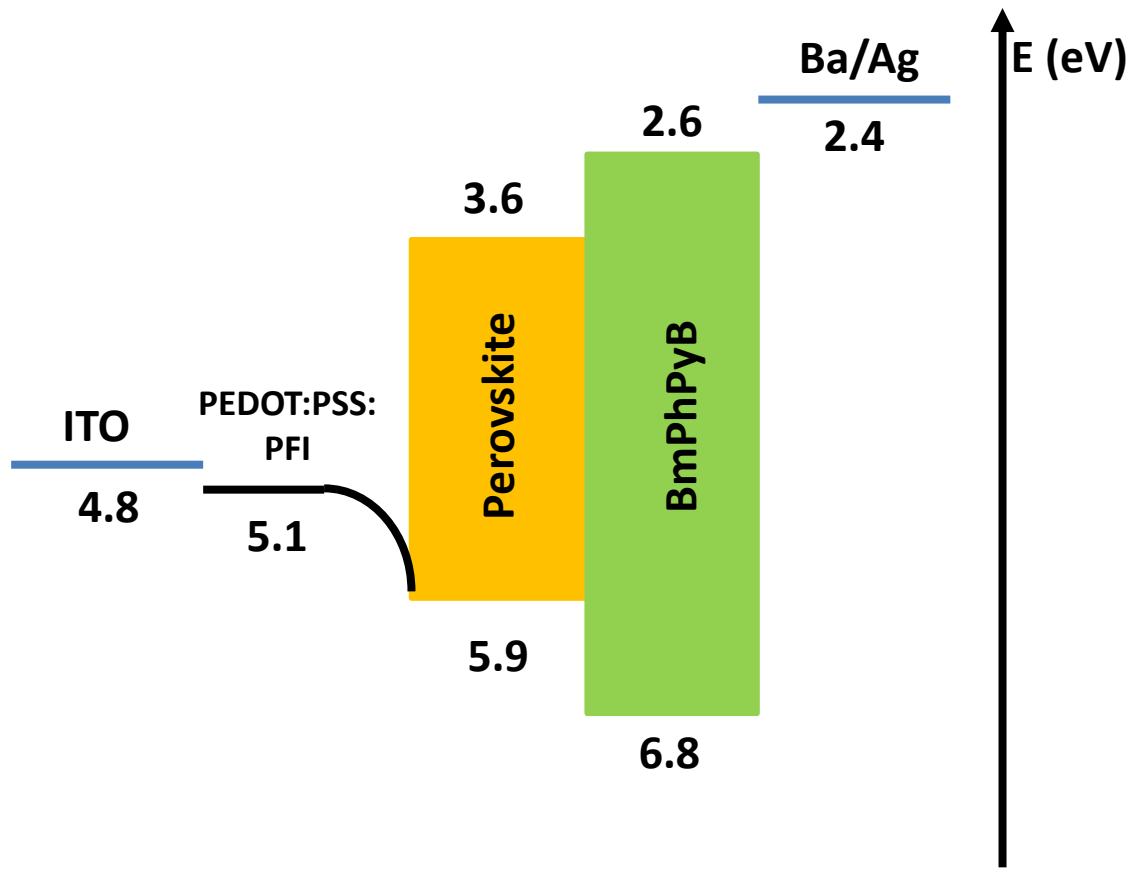
Total MA/Pb = 2.38

20% lost during thermal treatment (90°C 3 hours)

Even after thermal treatment (115°C 24h), the same ratio between bounded and unbounded methilammonium is kept

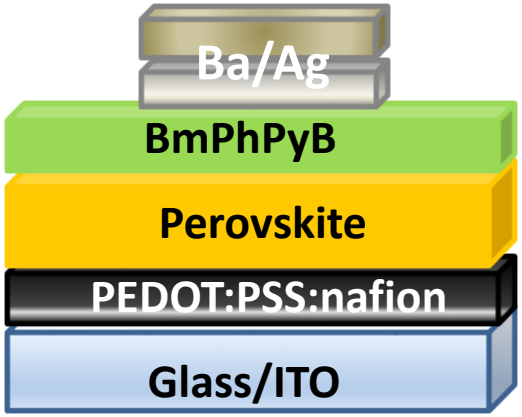
Device structure



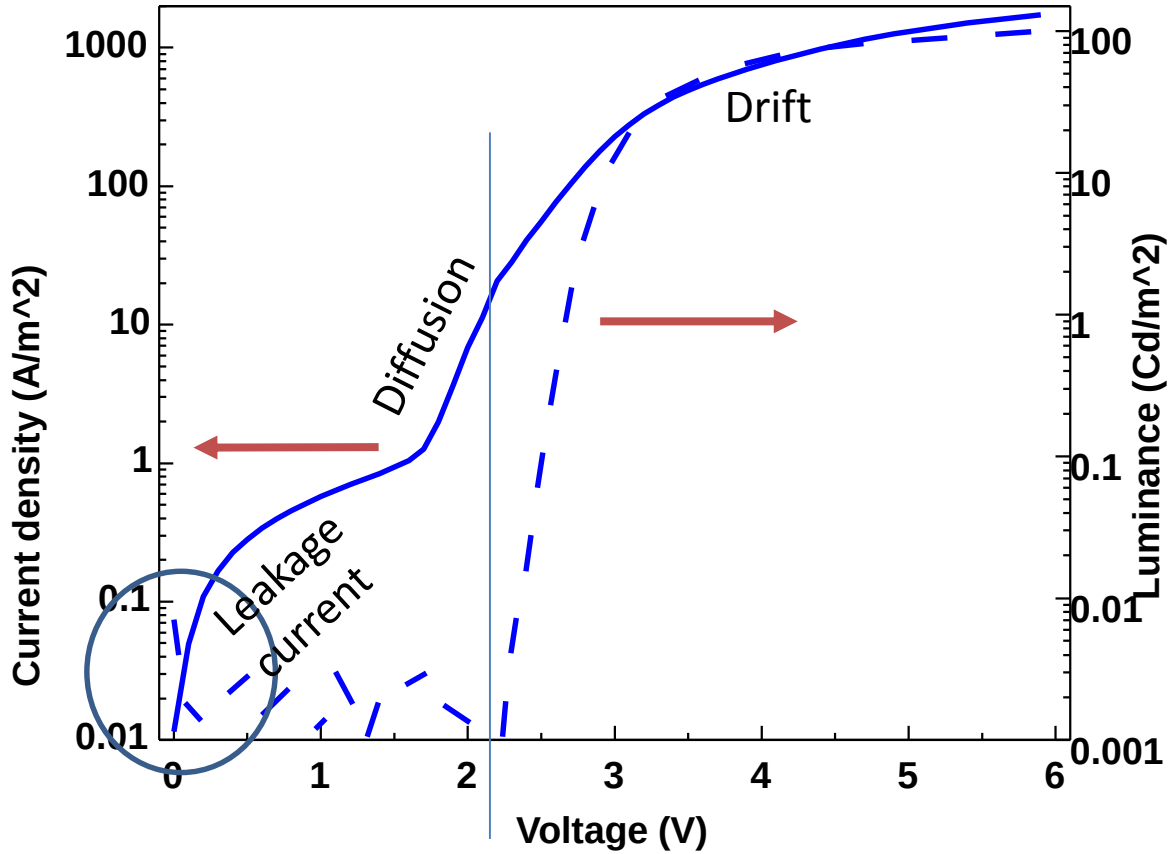


H. Cho *et al.*,*Science*, 2016,350,1222-1225

3-1 OLED device

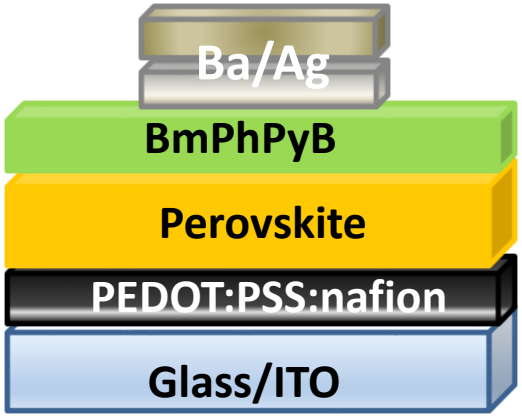


$CH_3NH_3Br/PbBr_2$=3

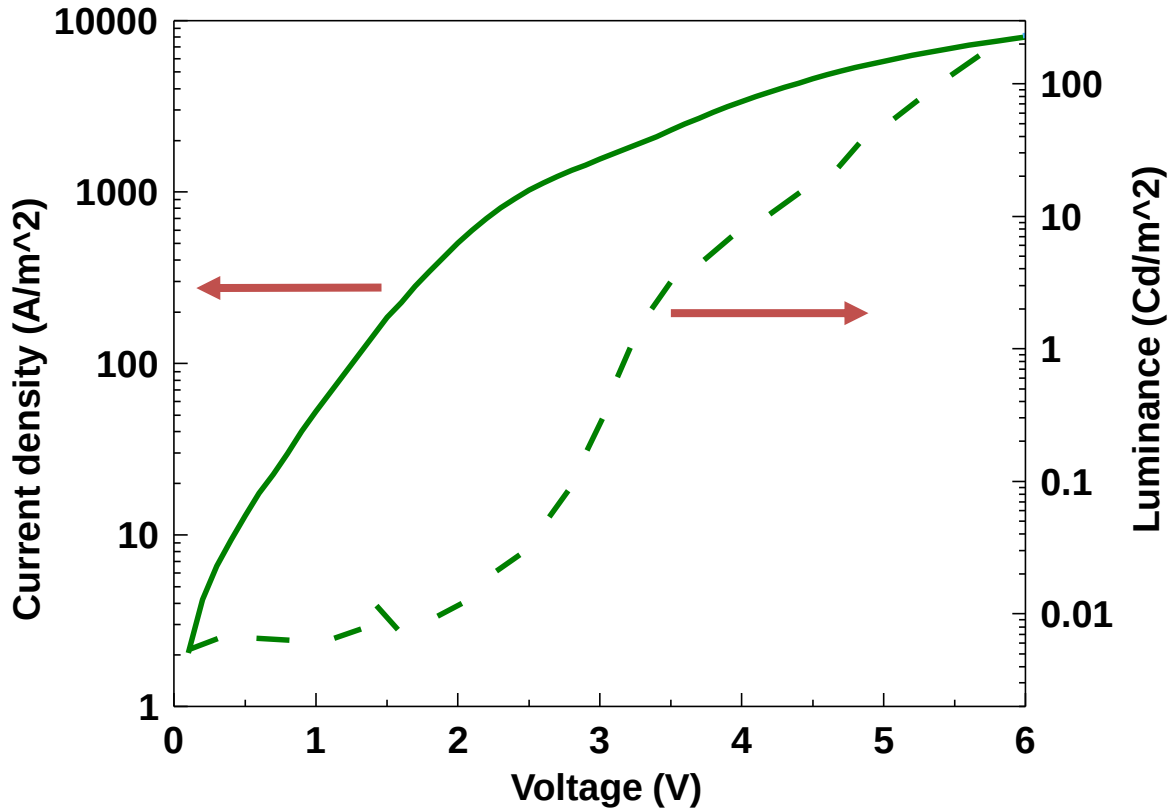


Built-in voltage

1-1 OLED device



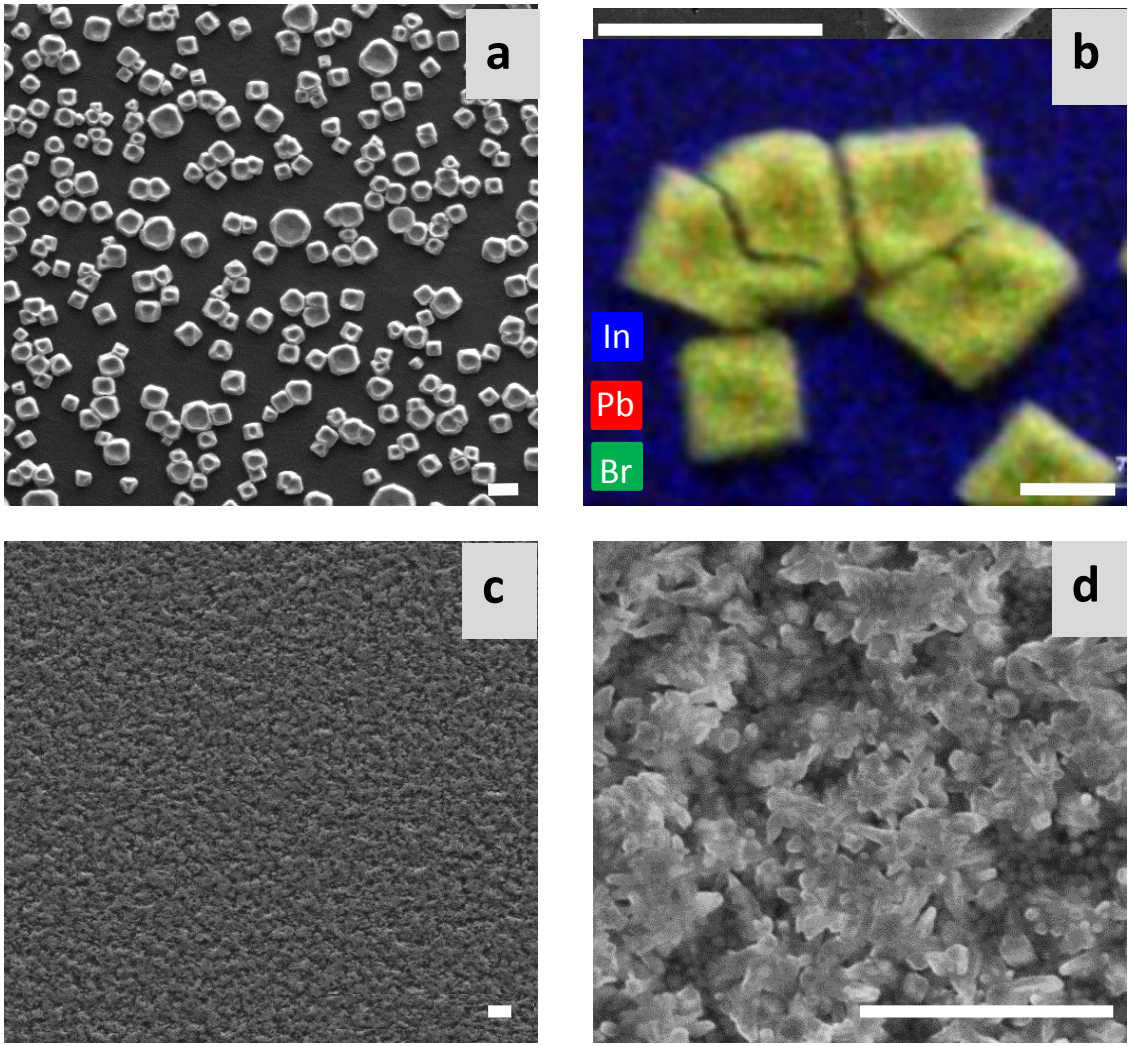
$CH_3NH_3Br/PbBr_2=1$



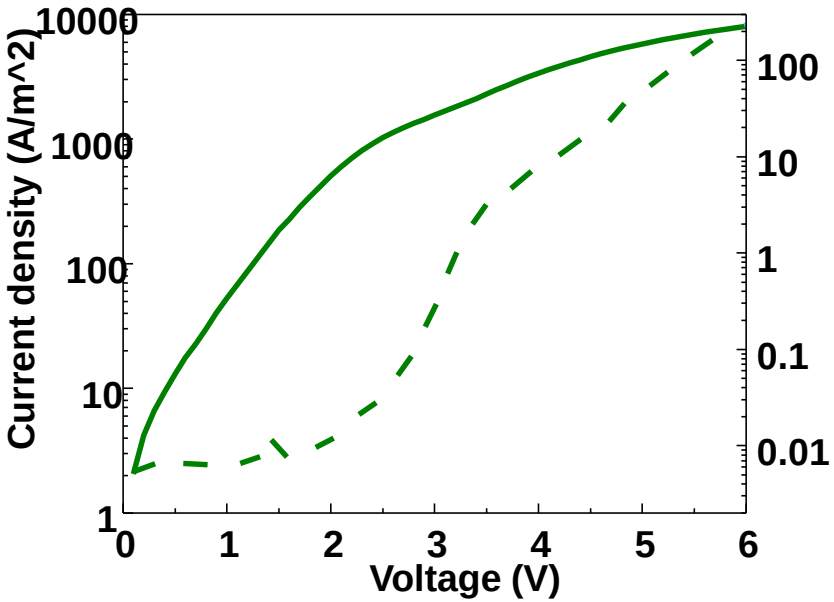
Morphological study

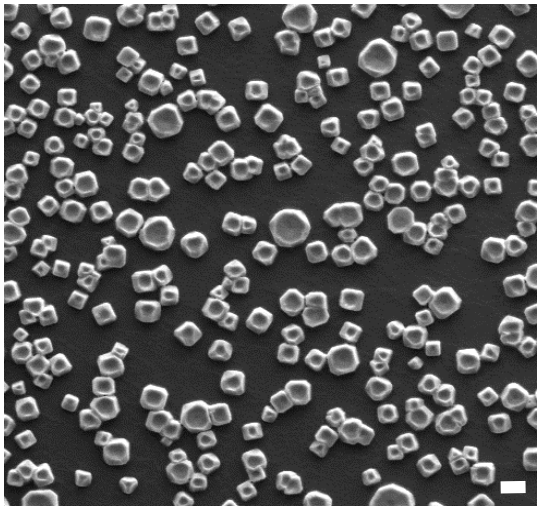
MA/Pb =1

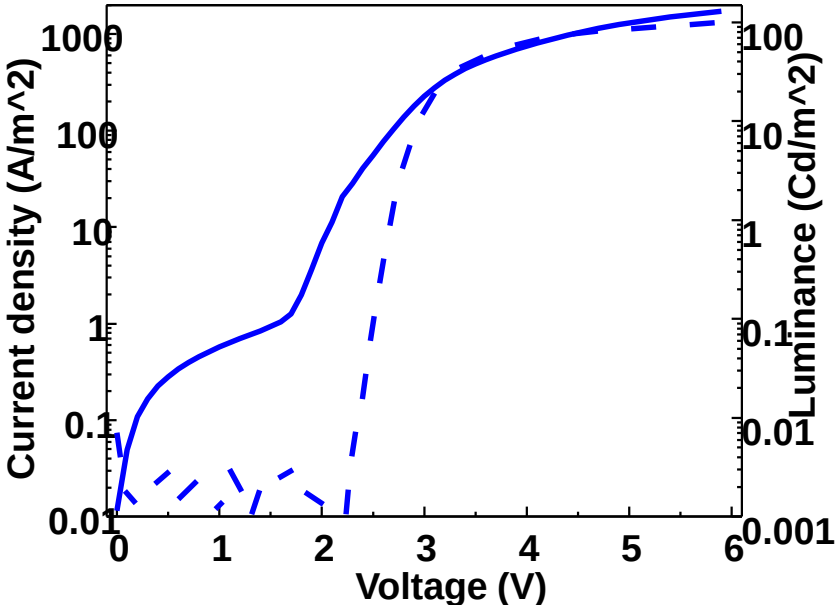
MA/Pb =3

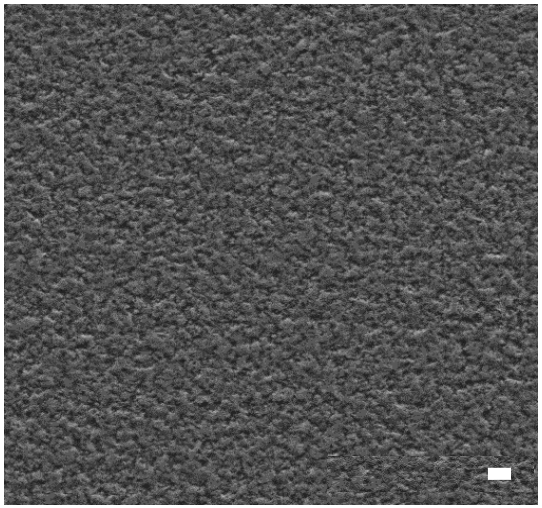


Relationship of performances and structure

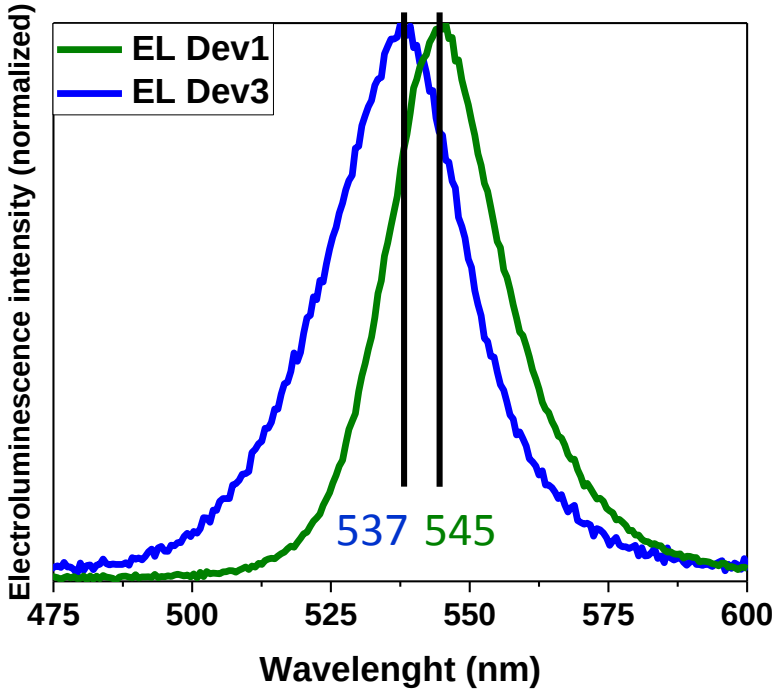


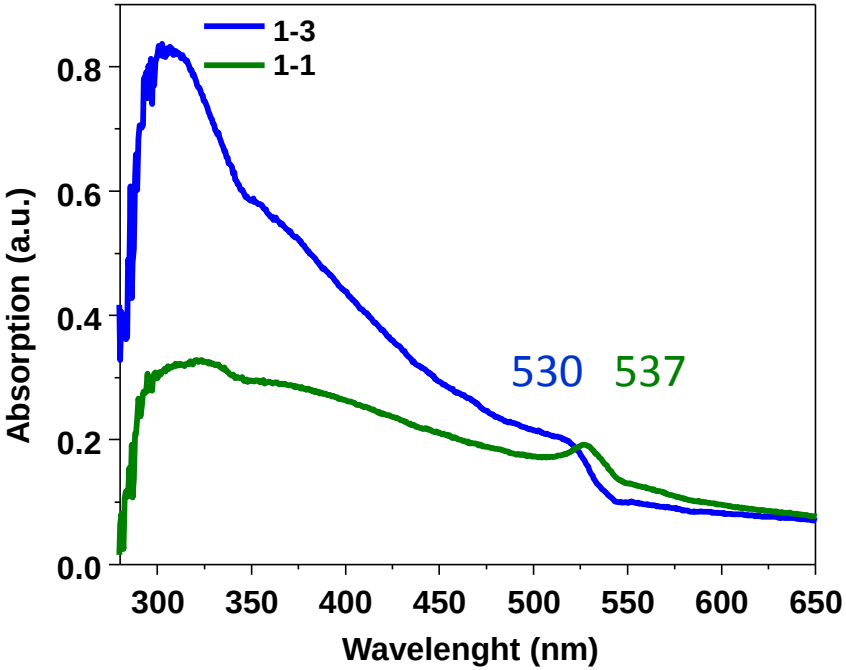




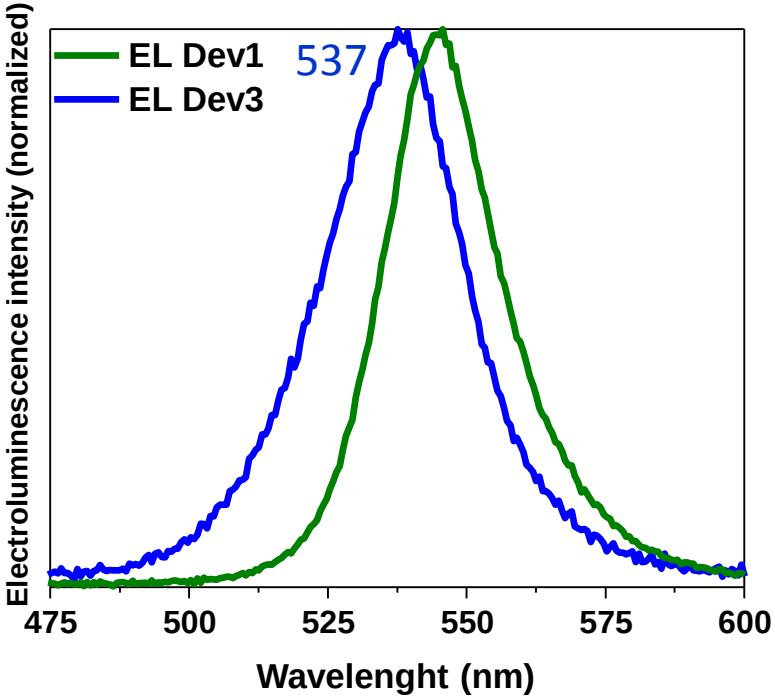


Optical behavior

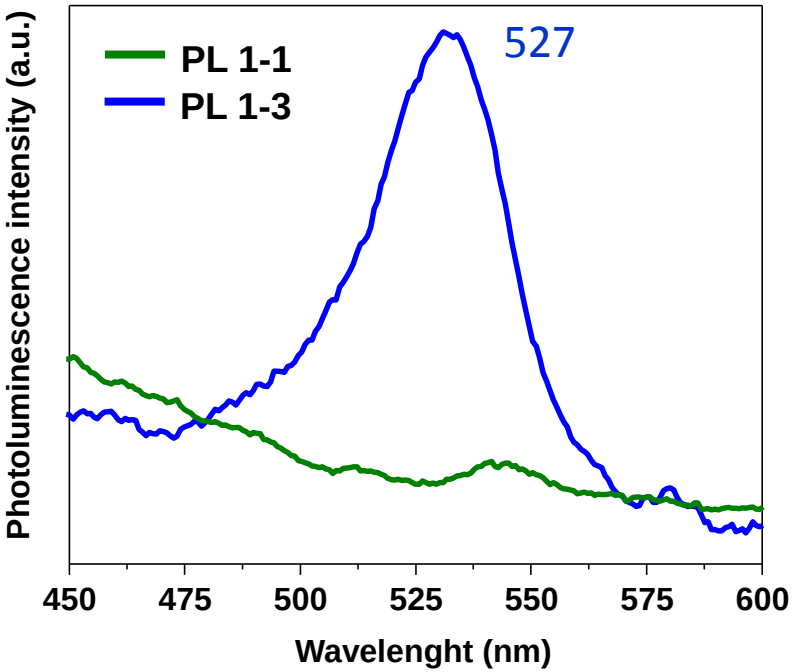




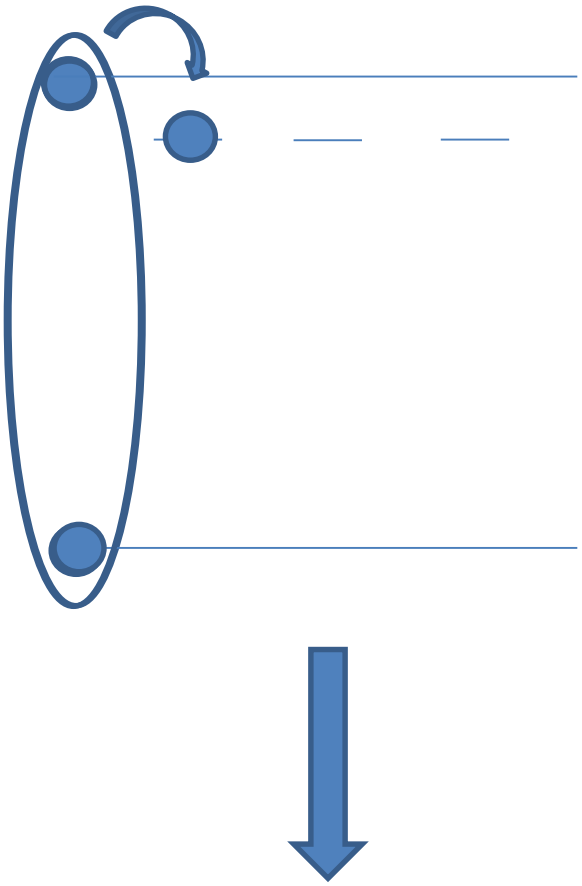
Electroluminescence and photoluminescence



Excitation wavelength: 365nm

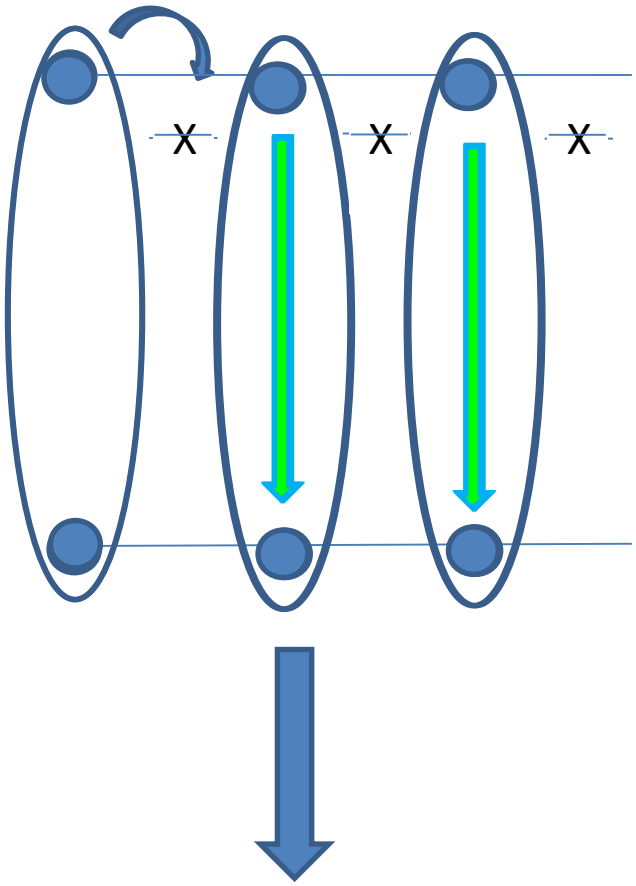


Trap states filling



1-1 sample

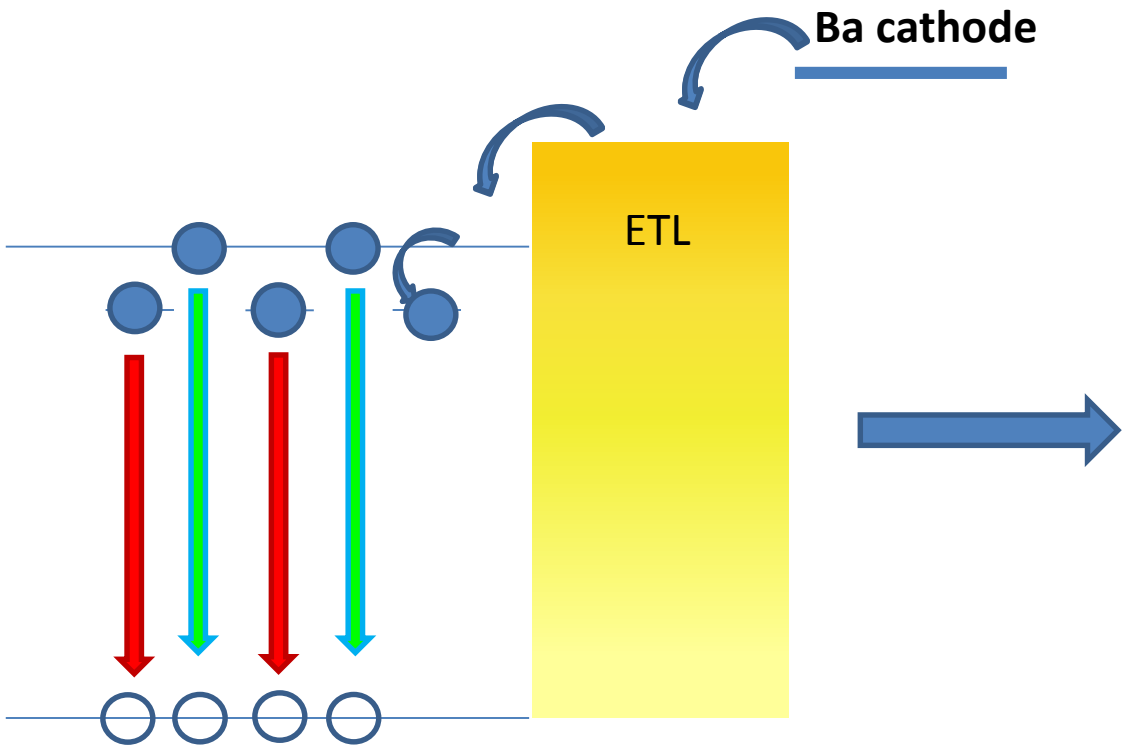
No photoluminescence



1-3 sample

Photoluminescence at 527nm

Trap assisted recombination



1-3 photoluminescence: 527 nm

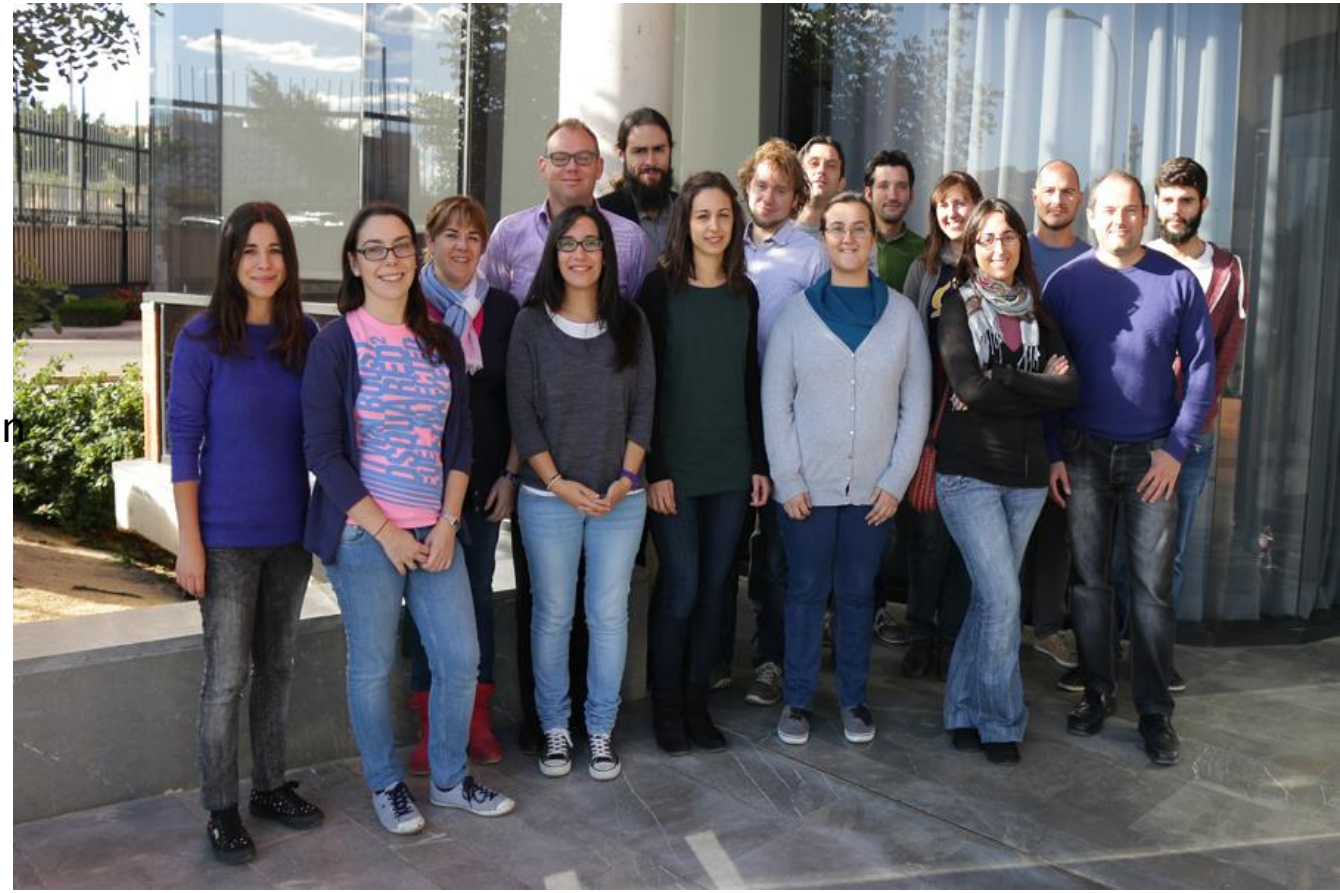
1-3 electroluminescence: 537 nm

Conclusions

- Precursor stoichiometry of $CH_3NH_3PbBr_3$ have a fundamental role in the optoelectronic properties and in film formation
- An excess of methylammonium affects the perovskite bandgap
- An excess of methylammonium bromide favors the surface coverage and the creation of a compact and uniform perovskite layer, suitable for optoelectronic application
- The excess of MABr passivates the trapping states present on the crystals allowing photoluminescence even at low excitation intensities
- The electroluminescence in the device likely derives from trap assisted recombination processes.

Acknowledgments

Dr. Henk J. Bolink
Dr. Michele Sessolo
Dr. Maria Monrabal-Capilla
Lidon Gil-Escrig
Laura Martinez-Sarti
Mª Cristina Momblona Rincon
David Forgacs
Enrico Bandiello
Antonio Pertegas-Ojeda
Jorge Pablo Avila-Gomez
Jorge Ferrando-Garcia
Araceli Miquel-Sempere



Thank you for your attention!

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