Polymeric hole injection layers for perovskite-based Light-Emitting Diodes

Colloquium Prepared for the Degree: Master Of Science in Physics

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01.10.2018

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What is a perovskite?

A perovskite is a crystal structure, that features unique dielectric properties.

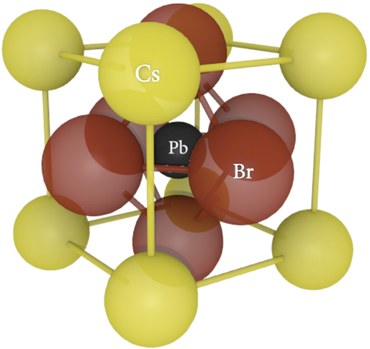


Figure 1: Illustration of the perovskite structure with the $CsPbBr_3$ perovskite as example.

- Perovskite is the retained name for $CaTiO_3$. Calling a material a perovskite refers to its crystal structure being the same as for $CaTiO_3$.
- A perovskite has a structure of ABX_3.
- Nobel price for the first high temperature super conductor.
- High electric conductivity and high absorbance.

Basic OLED stack design

An Organic Light-Emitting Diode (OLED) consists of anode, cathode and functional organic layers in between.

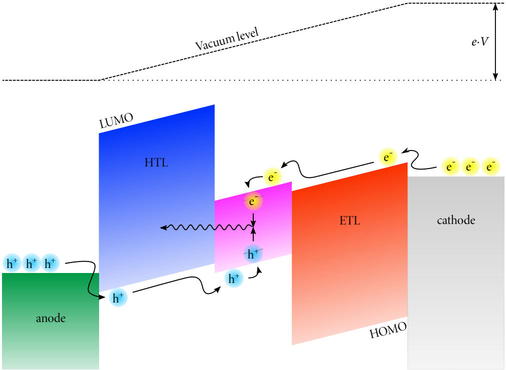


Figure 2: Simplified illustration of processes, leading to light emission, in OLEDs.

- Electrons and holes are injected by the cathode and anode respectively.
- The ETL and HTL have high mobilities for the respective charge carrier.
- Charge carriers meet to form excitons, which will decay with the emission of a photon.

Developing a suitable hole injection site

poly-TPD has several potential advantages for application in a perovskite based OLED.

Using poly-TPD as additional HIL[a] has advantages:

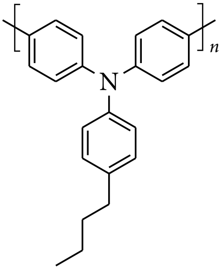


Figure 3: poly-TPD

- Optical optimization by controlling interference effects.
- Electron blocking ability, due to a high LUMO[b].
- Dried film insoluble to most solvents.
- Enhanced hole injection properties in low HOMO[c] emitting materials, enabled by a low HOMO of poly-TPD itself.
- Chemical shielding between the HIL underneath and the layer above.

[a] HIL = hole injection layer

[b] LUMO = lowest unoccupied molecular orbital

[c] HOMO = highest occupied molecular orbital

Investigation on optical properties of (MA)PbI_3

The optical properties are well-suited to verify a perovskite formation.

Experimental Details:

- Precursors PbI_2 and (MA)I[a] have been dissolved in DMF[b] with 1 M concentration.
- Two solutions have been chosen for the experiment:
  - PbI_2 in DMF (1 M).
  - PbI_2 in DMF (1 M) and (MA)I in DMF (1 M) mixed at 1:1 ratio (volumetric).
- The solutions are spin coated at 5000 rpm for 30 seconds on glass substrates and subsequently heated to 90°C for 5 minutes.
- The reflexion and transmission is measured in air.

[a] MA = Methylammonium

[b] DMF = Dimethylformamide

Investigation on optical properties of $(MA)PbI_3$

The the optical properties of PbI_2 are negligible for the mixed solvent's sample, indicating a full $(MA)PbI_3$ perovskite formation with few residual PbI_2.

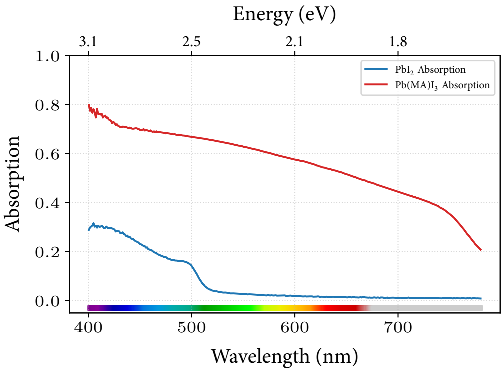


Figure 4: Absorption spectra measured by a spectrophotometer.

- The PbI_2 absorbs light of wavelengths smaller then 500 nm, which is plausible when comparing with the yellowish color of the film.
- The $(MA)PbI_3$ film is absorbing in the whole visible spectrum, which is quite expected, since the film had a black color.
- The characteristic trait of $(MA)PbI_3$ to have blackish color respectively having high absorbance can be verified.[1]

Introduction of $(MA)PbI_3$ into an OLED stack

A standard electron injection site has been chosen, for hole injection the poly-TPD-based system has been applied.

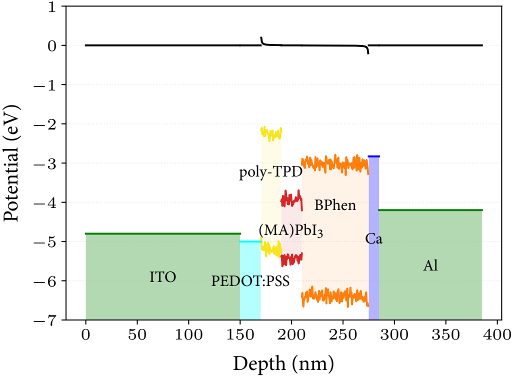


Figure 5: Schematic energy band diagram of the first $(MA)PbI_3$-based OLED sample.[2–8]

- The hole injection is performed by a PEDOT:PSS and poly-TPD layer of total thickness of 40 nm.
- The emitter is deposited by two different procedures.
  - The one-step-process: deposition by a $(MA)PbI_3$ solution.
  - The two-step-process: subsequent deposition of PbI_2 and (MA)I.
- For electron injection a 70 nm thick BPhen[a] layer was used.

[a] Bathophenanthroline

Introduction of $(MA)PbI_3$ in an OLED stack

The $(MA)PbI_3$ is deposited in two different ways, yielding comparable results.

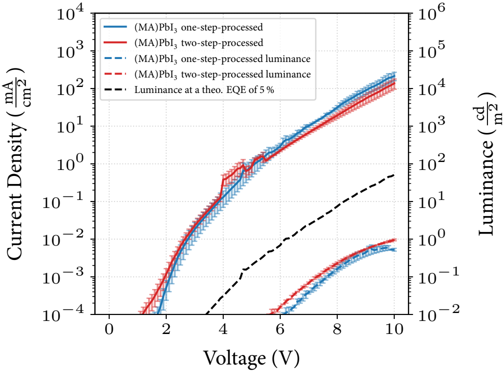


Figure 6: Current density and luminance versus driving voltage characteristics of the $(MA)PbI_3$ based OLEDs.

- The two-step-processed OLED shows higher luminance for lower currents.
- The OLED shows no (plain eyed) visible luminance. However devices detect a luminance.

Introduction of (MA)PbI_3 in an OLED stack

(MA)PbI_3's luminance is at wavelengths reaching the infrared domain.

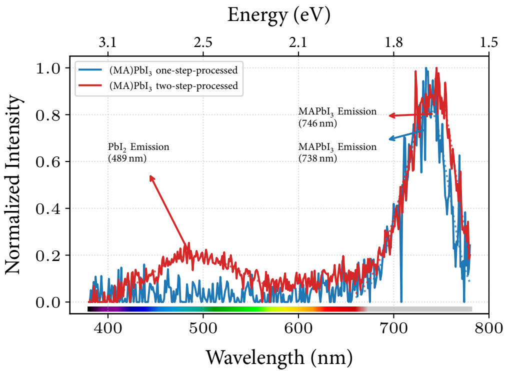


Figure 7: Electroluminescent spectrum of the (MA)PbI_3 based OLEDs.

- The spectrum explains why its is hard to see with plain eye. The human eye has poor sensitivity at near infrared wavelengths.
- An emission of energies around 1.5 eV is expected, by the (MA)PbI_3's HOMO (5.4 eV[5]) and LUMO (3.9 eV[5]).
- The green emission can be ascribed to the PbI_2. Which can only be identified in the two-step-processed OLED.

Summary on $(MA)PbI_3$ films and OLEDs

- $(MA)PbI_3$ films:
  - A perovskite consisting of PbI_2 and (MA)I, $(MA)PbI_3$, can be synthesized.
  - The absorption of $(MA)PbI_3$ covers the whole spectrum, increasing towards lower wavelengths.
  - The $(MA)PbI_3$ surfaces are partly rough and holey.
  - Solution processing on hot grounds renders the film more closed.
- $(MA)PbI_3$ based OLEDs:
  - The manufactured devices work at low perfomance, sufficiently for a proof of concept.
  - The emission maximum is located at the visible spectrum threshold to the infrared spectrum.
  - For actual light-emitting diodes material systems like $(MA)PbBr_3$, are more suited to characterize.

Charaterisation of $CsPbBr_3$ layers

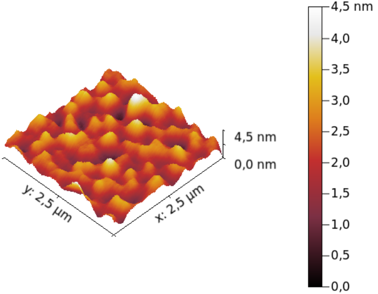
The surface texture and the layer thickness are to be determined.

Experimental Details:

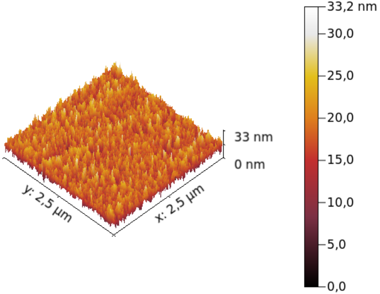
- The $CsPbBr_3$ quantum dots are present in unknown concentration solved in toluene
- The solution can be diluted and spin coating speeds can be adjusted.
- Layers of interest are the one grown on poly-TPD. So the standard PEDOT:PSS + poly-TPD layers are applied before spincoating the $CsPbBr_3$ quantum dots.
- The AFM and profilometer measurement is performed in air.

Atomic Force Microscopy of $CsPbBr_3$ layers

The surface texture is controlled by concentration and spin-coating speed.



(a) Surface morphology of a $CsPbBr_3$ quantum dots solution spin-coated at 5000 rpm on a poly-TPD coated substrate.



(b) Surface morphology of a $CsPbBr_3$ quantum dots solution spin-coated at 5000 rpm on a PMMA coated substrate.

Figure 7: AFM images of $CsPbBr_3$ quantum dot solutions spin-coated on organic layers.

Benchmark of the carrier injection in the OLED.

The charge carrier transport layers are tested with a well known phosphorent emitter.

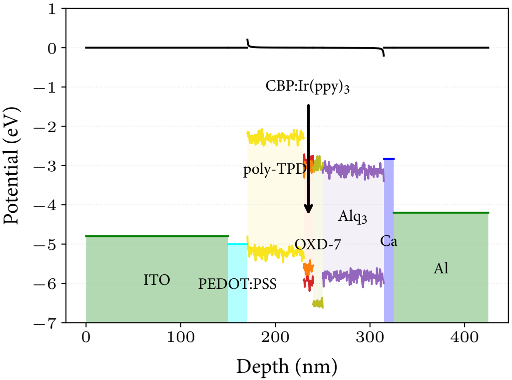


Figure 8: Schematic energy band diagram of the reference OLED sample.[9, 10]

- The CBP[a]:Ir(ppy)$_3$[b] Host-Emitter system is known to have a high efficiency.
- A doping ratio of 8% Ir(ppy)$_3$ to CBP has been determined to be the most efficient by colleagues of the chair.

[a] CBP = 4,4'-Bis(N-carbazolyl)-1,1'-biphenyl

[b] Tris[2-phenylpyridinato-C2,N]iridium(III)

Benchmark of the carrier injection in the OLED.

The CBP:Ir(ppy)$_3$ device is performing well; so the charge transport layers do not have inheritely an issue.

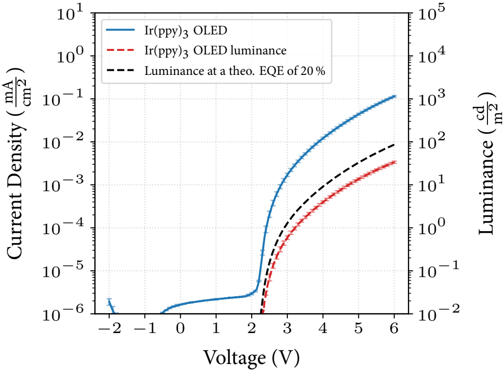


Figure 9: Current density and luminance versus driving voltage characteristics of the Ir(ppy)$_3$-based OLED.

- The luminance is about half as high as the one for an ideal (isotropic) phosphorent emitter.[a]
- Around the onset the sample is nearly ideal.
- No fast degradation for driving voltages up to 10 V can be observed.

[a] A theoretical device with a constant EQE of 20 %, the same voltage-current dependence, and the same emission spectrum.

Introduction of $CsPbBr_3$ in an OLED stack

For electron injection an Alq_3-OXD7 based system, and for hole injection the poly-TPD-based system has been applied.

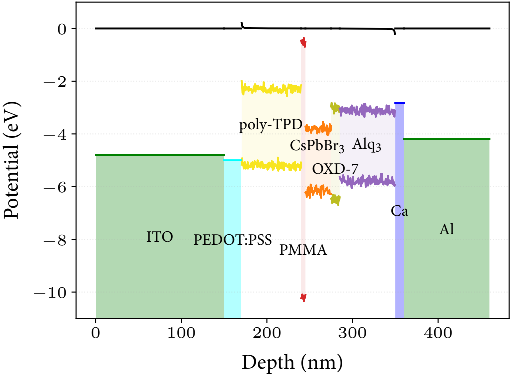


Figure 10: Schematic energy band diagram of the first $CsPbBr_3$-based OLED sample.[11, 12]

- The hole injection is performed by a PEDOT:PSS and poly-TPD layer of total thickness of 90 nm.
- The Alq_3-OXD7 shows superior performance as electron transport system, because the OXD-7 probably has a strong hole blocking ability.
- An optional PMMA spacer is added to the system for better film growth.

Introduction of $CsPbBr_3$ in an OLED stack

The $CsPbBr_3$ device's color is as expected a green-cyan tone.

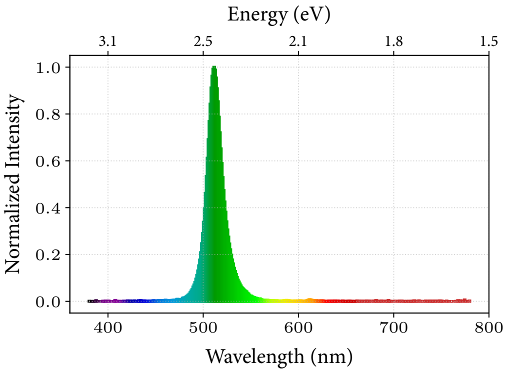


Figure 11: Electroluminescent spectrum of the $CsPbBr_3$ based OLEDs.

- The peak at 513 nm has a FWHM[a] of approximately 20 nm, which is quite good for application in display devices.
- Groups of references 12–14 get very similar electroluminescent spectra.

[a] FWHM = full width half maximum

Introduction of $CsPbBr_3$ in an OLED stack

The $CsPbBr_3$ device is not performing very well, when considering the high quantum yield of $CsPbBr_3$ quantum dots in general.[15]

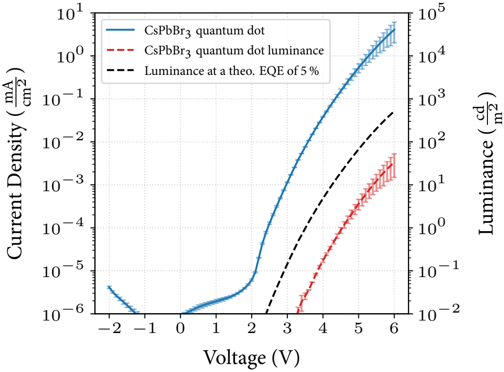


Figure 12: Current density and luminance versus driving voltage characteristics of the $CsPbBr_3$-based OLEDs.

- The luminance is an order of magnitude smaller than for an ideal fluorescent emitter.[a]
- The currents are two orders of magnitude higher than the ones for the $Ir(ppy)_3$ based device.
- The device starts degrading within seconds when driven at voltages higher than 6 volts.

[a] A theoretical device with a constant EQE of 5 %, the same voltage-current dependence, and the same emission spectrum.

Influence of PMMA in the $CsPbBr_3$-OLED

The PMMA improves the EQE of the devices by a factor of 1.5.

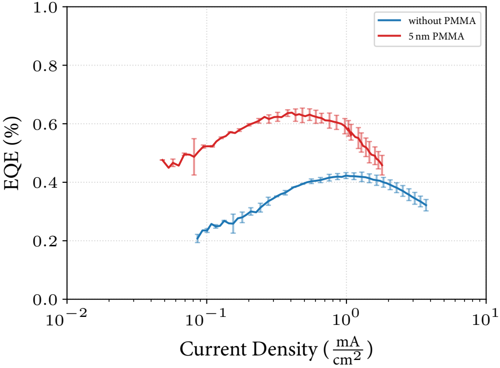


Figure 13: EQE versus driving voltage characteristics of the $CsPbBr_3$-based OLEDs.

- The PMMA layers leads to an increased EQE.
- However, the EQEs of both devices are an order of magntitude lower than the theoretical limit.

Performance of tolene-free $CsPbBr_3$-OLEDs

Hexane based samples achieve higher efficiencies.

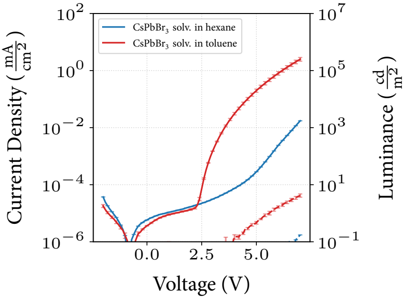


Figure 14: Current density and luminance versus driving voltage characteristics of the hexane-$CsPbBr_3$-based OLEDs.

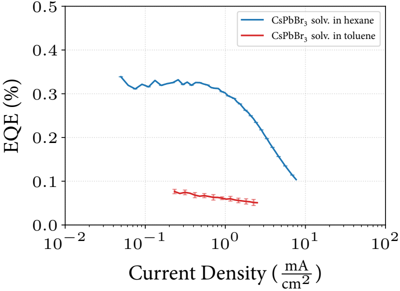


Figure 15: EQE versus driving voltage characteristics of the hexane-$CsPbBr_3$-based OLEDs.

- The hexane based QDs show worse injection, while showing higher EQE.

1. Introduction
2. Development of a suitable hole injection site
3. Design of OLED's based on the $(MA)PbI_3$ perovskite
   - Synthesis and characterization of $(MA)PbI_3$ layers
   - Characterization of OLEDs based on $(MA)PbI_3$ perovskite
4. Design of OLED's based on the $CsPbBr_3$ perovskite quantum dots
   - Characterization of $CsPbBr_3$ quantum dot layers
   - Characterization of OLEDs based on $CsPbBr_3$ quantum dots
5. **Summary and Outlook**
6. Additional Slides for Disscussion

Summary

Perovskite based OLEDs could be created. However the efficiency is very low.

- $(MA)PbI_3$ based OLEDs:
  - Nearly infrared light is emitted.
  - Highly depending on environmental conditions during manufacturing.
  - Very poor performance.
- $CsPbBr_3$ based OLEDs:
  - Green-cyan color, small peak width.
  - Impaired hole injection, which is a major shortcoming in present devices.
  - Performance depending on used solvent.

Outlook

(MA)PbI$_3$ based OLEDs will be dropped. CsPbBr$_3$ based OLEDs, need further investigation.

- (MA)PbI$_3$ based OLEDs:
  - Switching to (MA)PbBr$_3$ to get actual optical devices.
  - For further investigation as IR-diode the intial results were too poor and the required equipment is not present.
- CsPbBr$_3$ based OLEDs:
  - Some optical measurement of the CsPbBr$_3$ layer may help to find other limiting factors.
  - Easing the hole-injection with new or new combination of the HILs
  - New batches of CsPbBr$_3$ with different solvents and ligand density should help finding a suitable hole injection system.
  - An inverted device, where ITO-ZnO is used for electron injection and hole injection can be done by well-known evaporated organics.

Thousand thanks to:

- Professor Wolfgang Brütting.
- Manuel Engelmayer, Florian Graßl and Thomas Lampe, for mentoring.
- Matthew Jurow (University of Berkeley) for supplying the $CsPbBr_3$ quantum dot solutions.
- All other colleagues of the Chair of Experimental Physics IV.
- and You for Your attention.

Hole Only Devices

The hole conductivity is greatly increased by $CsPbBr_3$ deposition.

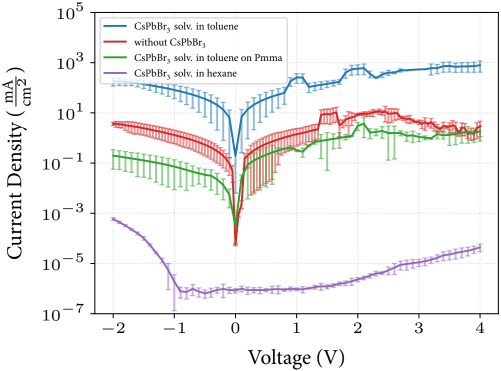


Figure 16: Current density versus driving voltage characteristics of hole only devices.

- The $CsPbBr_3$ solved in toluene device a resistance of only 120 Ω.
- PMMA intervenes, so that the resistance is higher than it is for the $CsPbBr_3$ free.
- Hexane based $CsPbBr_3$ devices show extremely low hole conductivity.

Solution Processed $Ir(ppy)_3$

The toluene susceptibility is still present, but it enhances the efficiency.

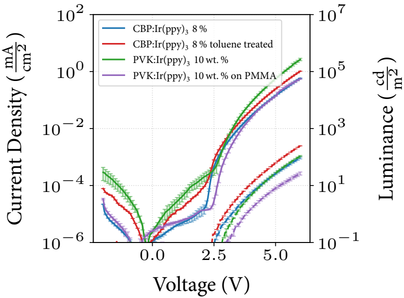


Figure 17: Current density versus driving voltage characteristics of solution processed $Ir(ppy)_3$ based devices.

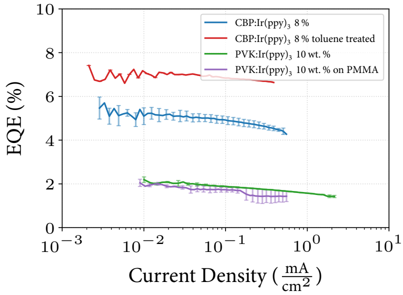


Figure 18: Current density versus driving voltage characteristics solution processed $Ir(ppy)_3$ based devices.

- PMMA does not increase the EQE, but toluene on does.

Switching ETL

TBPi increases the current and the luminance.

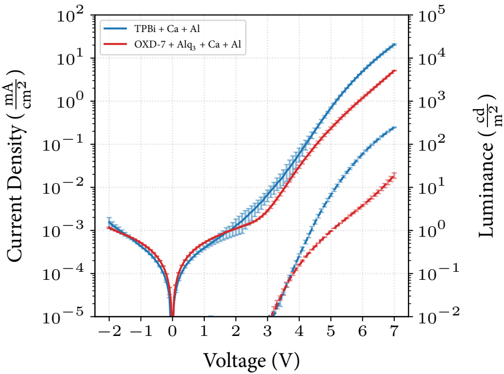


Figure 19: Current density versus driving voltage characteristics of TPBi based devices.

- TPBi leads to higher currents.
- But it also leads to overproportionally more luminance.
- This matter of facts contradicts the with a bad hole injection.

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