DROP-IT

DELIVERABLE 2.1

Inkjet printing of B-LFP materials: best suited flexible substrate

Due date of deliverable: 2020/10/31

Actual submission date: 2020/12/21

Deliverable number:	D2.1
Due date:	31.10.2020
Nature[1]:	R
Dissemination Level[1]:	PU
Work Package:	WP2
Lead Beneficiary:	UB
Contributing Beneficiaries:	SRI

[1] **Nature:** R = Report, P = Prototype, D = Demonstrator, O = Other
Dissemination level PU = Public PP = Restricted to other programme participants (including the Commission Services) RE = Restricted to a group specified by the consortium (including the Commission Services) CO = Confidential, only for members of the consortium (including the Commission Services) Restraint UE = Classified with the classification level "Restraint UE" according to Commission Deci-sion 2001/844 and amendments Confidential UE = Classified with the mention of the classification level "Confidential UE" according to Commission Decision 2001/844 and amendments Secret UE = Classified with the mention of the classification level "Secret UE" according to Commission Decision 2001/844 and amendments

This project has received funding from the European Union's Horizon 2020 research and innovation programme under **Grant Agreement No. 862656**.

DOCUMENT HISTORY

Version	Date	Reason of change
1	2020/12/01	UB
2	2020/12/02	SRI
3	2020/12/10	Final revised version and approved
4		

This project has received funding from the European Union's Horizon 2020 research and innovation programme under **Grant Agreement No. 862656**.

Table of Content

1 INTRODUCTION 4

1.1 PURPOSE OF THE REPORT 4

1.2 GENERAL CONSIDERATIONS FOR FLEXIBLE ELECTRONICS SUBSTRATES 4

1.3 FLEXIBLE SUBSTRATES FOR LED AND PV DEVICES 4

2 DESCRIPTION OF WORK & MAIN ACHIEVEMENTS 6

2.1 PROPERTIES OVERVIEW OF SELECTED FLEXIBLE PLASTIC SUBSTRATES 6

3 RESULTS 8

3.1 PLASTIC SUBSTRATES 8

3.1.1 Optical Transparency 8

3.1.2 Thermal stress 9

3.1.3 Surface smoothness and wettability 10

3.1.4 Surface treatment (surface adhesion activation) 11

3.2 TRANSPARENT ELECTRODE SUBSTRATES 13

3.2.1 Coated ITO layer under thermal stress 14

3.2.2 Coated ITO layer under bending stress 15

3.2.3 Coated ITO layer under UV stress 16

3.2.4 Solvent compatibility of coated ITO layer 16

3.3 INKJET PRINTING B-LFP ONTO SELECTED PLASTIC SUBSTRATES 17

3.3.1 Cs_2SnI_6 (from Avantama) 17

3.3.2 $FASnI_3$ (from ETHZ) 19

4 CONCLUSIONS & FUTURE DIRECTIONS 21

This project has received funding from the European Union's Horizon 2020 research and innovation programme under **Grant Agreement No. 862656**.

1 Introduction

1.1 Purpose of the report

This deliverable is about the selection of best suited flexible substrate for Drop it materials and devices. As reported on the Annex 1 of the grant agreement: The most suitable substrate will be elucidated on the basis of structural, optical and electrical properties under thermal and bending stresses. The accent is on the substrates themselves, the electrodes and transport layers and the inkjet-printed B-LFP films using optimized inks. Different flexible substrates have been explored (PET, PEN, PI), studies and the results are reported in this deliverable.

1.2 General considerations for flexible electronics substrates

Flexible electronics allows overcoming the intrinsic rigidity, fragility and limitation of standard large area substrates and materials to produce curvilinear surfaces or allow bending. On the other hand, handling flexible substrates is delicate due to the possible cracking under mechanical bending. The selection of the most suitable flexible substrate is related with: i) It's availability with transparent conducting electrodes and ii) The final requirements of the electronic application and/or the design of the device itself.

Beside the degree of bendability and its availability, there are several other properties that a flexible substrate must have to ensure the expected behaviour of the fabricated devices. In the following we explain the strategy and procedure that we have used to select the best flexible substrates for Drop it.

Suitable flexible substrates must meet properties such as dimensional stability (low shrinkage), thermal stability, low coefficient of thermal expansion (CTE), excellent solvent resistance, good barrier properties for moisture and gases, high transparency and a smooth surface. The B-LFP LEDs and solar cells are applications based on complex structures which require such a demanding property set.

From a general perspective of environmental friendliness and biodegradability, paper would be a good choice of flexible substrate. However, paper is generally a problematic substrate for printed optoelectronic applications due to its high roughness and high absorbance. Similarly, highly stretchable substrates (flexible and extensible substrates like PDMS, PU, TPU) are currently not applied to commercial flexible and wearable electronic devices because they can easily deform under external forces which can turn into electrical instabilities, interface sliding or deadhesion.

1.3 Flexible substrates for LED and PV devices

Generally, there are three types of substrate materials employed for flexible optoelectronic devices: thin glass, metal foils and plastics/polymers. It is difficult to directly compare the property sets of different film types, as information available in the public domain may not represent the films

This project has received funding from the European Union's Horizon 2020 research and innovation programme under **Grant Agreement No. 862656**.

targeted for printed electronics applications. Nevertheless, each substrate type exhibits different general properties which are briefly described below to identify main drawbacks/advantages:

Metal foil

Metal foils are preferred for their dimensional stability and long durability while sustaining very high temperatures (400 to 1000°C). They are suitable for deposition of a large amount of inorganic materials due to their chemical stability. However, the surface roughness is of about 100 nm, and thus is much worse compared with glass or plastic substrates for which is less than 1 nm. Additionally, their high cost is a drawback for their use for flexible electronics. Conducting metal foils are often used as the substrates of flexible solar cells, with aluminium (Al) being the most used, due to its flexibility and low price. Thermal expansion can be also a drawback for multilayer devices such as LEDs or solar cells.

Manufacturing of LED and PV devices with novel materials imply the need of testing both configurations, standard (PIN) and inverted (NIP). For this reason, in this project we are not going to use metal foil as starting material for the fabrication of preliminary devices.

Thin flexible glass

Glass becomes flexible when its thickness is less than 100 µm, but fragility and handling remain as the biggest drawbacks. Flexible glass is good at transparency, low roughness, chemical stability and oxidation barrier, but the availability of the flexible glass and the issue of major investment to manufacture and commercialize it for a relatively small market is challenging. As well, although thin glass is bendable, the high cost and the intrinsic brittle property limit its utility in flexible electronics.

Consequently, regarding the printing of optoelectronic devices during this project, flexible glass is not currently considered the appropriate option due to the low degree of flexibility, high-cost materials involved (consequently not commercially available) and difficult handling.

Plastics/polymeric substrates

Commercially available polyethylene terephthalate (PET), polyethylene naphthalate (PEN), and polyimide (PI) tapes are the most widely used flexible substrates for optoelectronic devices. PET foil, with a thermotolerance of only up to 120 °C, is an inexpensive substrate but potentially not compatible with the heat (curing) treatment process required during the printing process for some inorganic materials (based on solvents of high boiling point) to be used in this project. PEN has better thermotolerance (<160 °C) and better chemical resistance than PET with a medium price (3-5 times the cost of PET). PI has the best thermotolerance, up to 450 °C, but its price is much higher, especially for the novel transparent (also known as colourless) PI tapes. However, this price is still lower than flexible glass.

The above-mentioned flexible plastic substrates pave the way for low-cost, large area, lithography free manufacturing of optoelectronic components by means of inkjet printing technology in a roll-to-roll (R2R) production line.

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under **Grant Agreement No. 862656**.

Table 1. Summary of the main characteristics of some widely used substrate materials in commercial flexible electronic devices, focusing on the flexibility, transparency, thermal and chemical stability, as well as the price.

	Transparency	**Thermotolerance (°C)**	**Chemical resistance**	**Price ($/kg) -estimated-**
PI	Low	<450	Weak acids and alkali Ethanol and acetone	10-20
Transparent PI (T-PI)	Yes	<350	Weak acids and alkali Ethanol and acetone	75–200
PET	Yes	<120	Dissolvable in acetone	1–10
PEN	Yes	<160	Weak acids and alkali Ethanol and acetone	30–200
Paper	No	<100	Poor	1–2
Metallic foils	No	<660	Weak alkali Ethanol and acetone	1–12
Flexible Glass	Yes	<250	High	50–600

2 Description of work & main achievements

2.1 Properties overview of selected flexible plastic substrates

The plastic films that are currently being considered as possible candidates for flexible electronic applications are shown in Figure 1, which lists the substrates in terms of increasing glass transition temperature (Tg), in such a way that Tg below 120°C could limit the use of the substrates to a reduced range of functional materials or material procedures. Polymers can be categorized into films that are semicrystalline (PET, PEN), whereas polycarbonate (PC), polyether sulfone (PES)) and thermoplastic (fluorene polyester and polyimide, PI) are amorphous materials.

These data suggest that the selected available plastic materials are promising substrates providing a reasonable trade-off between physical, chemical, mechanical and optical performance. The most employed plastic substrates for developing flexible electronics components are polyesters such as PEN (polyethylene naphthalene), PET (polyethylene terephthalate) and PI (polyimide) due to relatively high elastic moduli and their good resistance to chemicals. The substrates of PEN and PET are characterized by a high level of transparency, more than 80% in the visible and infrared ranges, and a low surface roughness, <15 nm and PI < 1nm (Appendix). In addition, a further property such as high conductivity (after specific coating) might be required. Finally, the film should be commercially available and with a film surface quality that can only be achieved by manufacturing at large volume scale.

Currently, the market of plastic substrates is limited to very specialized fields/areas of interest. Therefore, we selected 10 different plastic substrates requiring, above all, the availability of the raw

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under **Grant Agreement No. 862656**.

material (possibly already coated with ITO) and the best trad-off between thickness (high degree of bendability) and transparency.

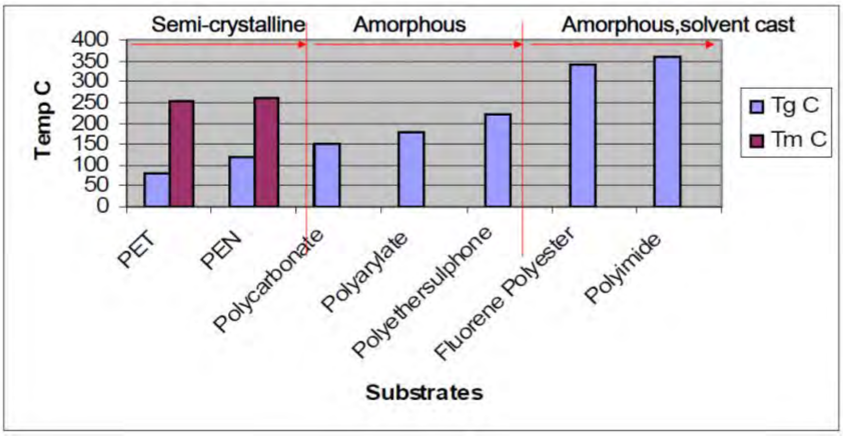


Figure 1: Glass transition temperature (Tg) and melting temperature (Tm) for different polymer materials.

Table 2 shows a summary of the different kind of plastic substrates we tested and characterized with all the data carried out from the related datasheets, which we corroborated and widened with quality factor parameters (↑ low quality, ↑↑ acceptable, ↑↑↑ good/promising) related to the applied specific laboratory tests.

Table 2: List of tested substrates versus the main requirements reported from datasheets and experimental data. Highlighted are the substrate available directly from the provider with coated ITO layer.

Material	PET	PET	PET	PEN	PPS	T-PI	T-PI	T-PI	T-PI	T-PI
Origin	Toray (Lumirror 41.31)	Biotain (Melinex ST504)	CHASM (Melinex ST504)	Biotain (Teonex Q51)	Toray (Torelina 25-3030)	Saule (ShunXuan New Material CPI02-50)	DuPont (Kapton 100CS)	DuPont (Kapton 50CS)	Tormed (Type S 12.5um)	Tormed (Type S 25um)
Internal code	149	145	145	146	150	143	147	148	151	152
Thickness (μm)	75	175	175	125	25	25	25	12.5	12.5	25
Maximum working temperature (ºC)	275 (melts)	250 (melts)	250 (melts)	250 (melts)	275 (vitrifies) - 300 (melts)	300 (vitrifies)	350	350	300 (vitrifies)	300 (vitrifies)
Thermal expansion coefficient (ppm °C^{-1})	<18	<18	<18	<18	<1	<50	<5	<5	<45	<45
Transmission (%, 400–700 nm range)	> 88	85	85	82	60 - 80	> 85	> 80	> 80	88	88
Surface Roughness R_a (nm)	5	2.2	2.2	13	30	<1	<1	<1	<1	<1
Young's modulus (GPa)	5.3	5.3	5.3	5.3	4.56	2.5	6.55	6.55	4	4
Tensile Strength (MPa)	200	225	225	257	225	69	280	280	145	178
Water absorption (%)	0.5	0.8	0.4-0.6	0.5-14		-	6.6	6.6	1.6	1.9
Solvent resistance	0.4-0.6	0.4-0.6	↑↑	0.3-0.4	0.3-0.4	0.3-0.4	0.38	0.38	1.6	1.6
Printability (coated+ITO)	↑↑	↑↑	↑↑↑	↑↑	↑	↑↑	↑↑	↑↑	↑↑	↑↑
Commercial availability	↑↑	↑↑↑	↑	↑↑↑	↑	↑↑↑	↑↑↑	↑↑↑	↑↑↑	↑↑↑
Dimensional stability	up 150ºC ↑↑	up 150ºC ↑↑	up 150ºC ↑↑	↑↑↑	↑	↑	↑↑↑	↑↑↑	↑↑↑	↑↑↑

This project has received funding from the European Union's Horizon 2020 research and innovation programme under **Grant Agreement No. 862656**.

In summary, considering only the datasheets from the companies, the most suitable plastic substrates are the ones highlighted in green, which represent the available materials with a high conductive ITO layer ensuring at the same time transmission in the visible range above >80%. In the following we will revise the physical, chemical, mechanical and optical performance of all the substrates in Table 2.

3 Results

3.1 PLASTIC SUBSTRATES

3.1.1 Optical Transparency

For display applications, optical clarity is important, where a total light transmission (TLT) of > 85% over a wavelength range of 400–800 nm is required. This is only required for light emission through substrates in bottom-emission displays. Except polyimide, which can be either yellow (amber) or transparent (well note as colourless), all other polymeric substrates listed in Table 1, meet the optical clarity requirements. Figure 2 visually shows the transparency and the light yellowness of the substrate we selected for this project. Although all the selected substrates reach a required transmission in the visual range >80% (Table 3), each one has a different evolution after thermal or mechanical stress due to the differences in thickness (degree of bendability) and thermotolerances.

Table 3: Optical transmission data for all the substrates.

Material	Reference	Transmittance (%)
PET	Toray (Lumirror 41.31)	> 88
PET	Biotain (Melinex ST504)	85
PET	CHASM (Melinex ST 504)	85
PEN	Biotain (Teonex Q51)	82
PPS	Toray (Torelina 25-3030)	60–80
PI	Saule (ShunXuan New Material CPI02-50)	> 85
PI	DuPont (Kapton 100CS)	> 80
PI	DuPont (Kapton 50CS)	> 80
PI	Tormed (Type S 12.5um)	> 85
PI	Tormed (Type S 25um)	> 85

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under **Grant Agreement No. 862656**.

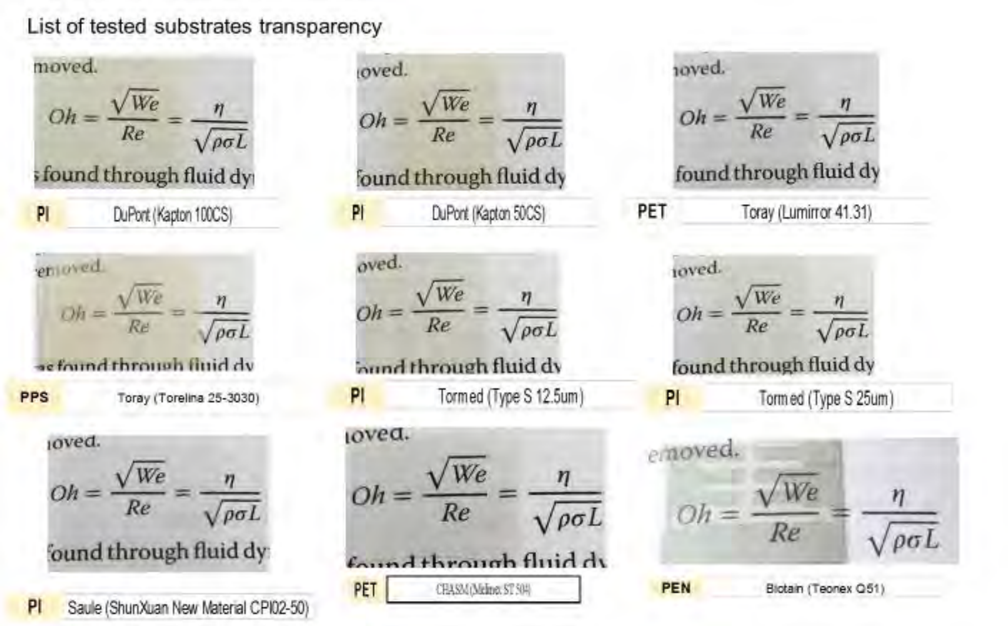


Figure 2: Visual inspection of polymer transparency over a given written paper. Polymers described in Table 2.

3.1.2 Thermal stress

Monitoring the temperature during the printing process to determine the ideal temperature range on platen substrate and post process curing is of great importance to control the film morphology of different inks and substrates. Therefore, for plastic substrates, it is important to control the maximum process temperature and not to exceed the glass transition temperature, which would involve surface deformation. Figure 3 demonstrates the effect of thermal process on several substrates which are not suitable due to the appearance of strong opacity or complete degradation of the material. For example, in our list of materials, the complete degradation of PET, PPS, PEN substrates under thermal stress of T > 175°C.

The thermal test results indicate that the selection of a certain substrate could limit/restrict the range of applicable functional inks which are based on high boiling point solvents.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under **Grant Agreement No. 862656**.

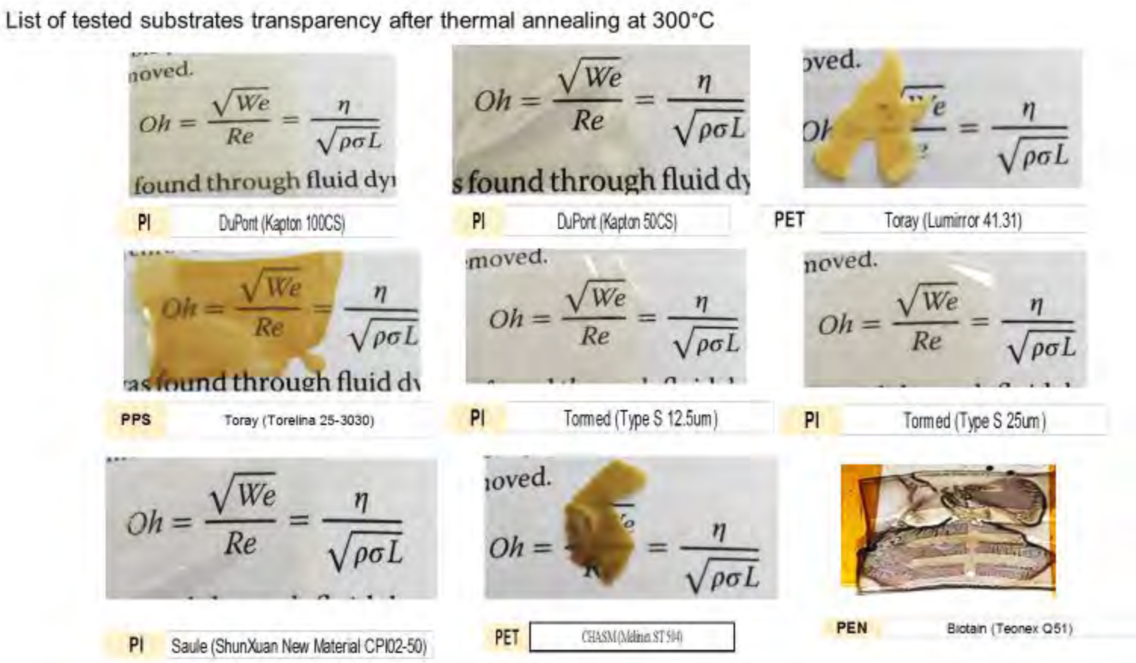
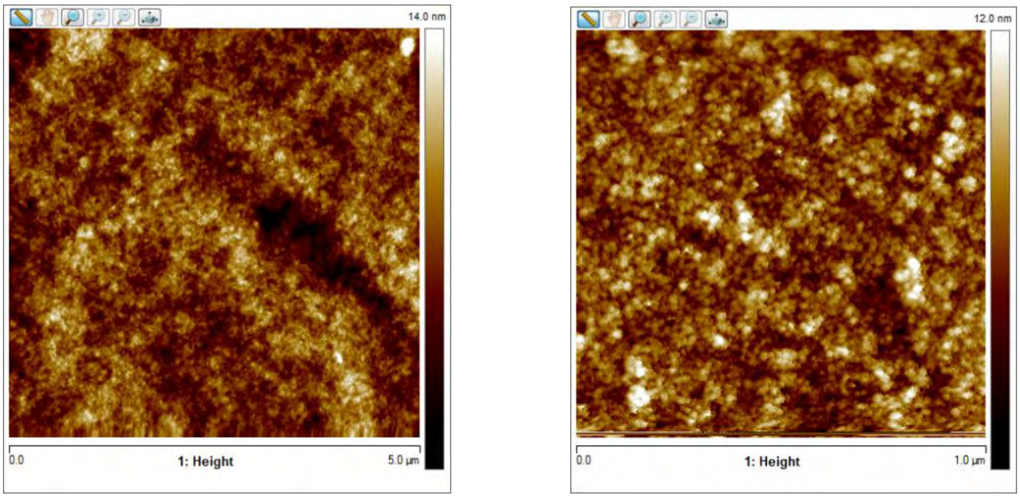


Figure 3: Visual inspection of thermal stress test (175ºC) on polymer materials after.

3.1.3 Surface smoothness and wettability

Smoothness and wettability are other relevant characteristics. To reliably print electronic devices, these factors must all be carefully considered. The smoothness is generally given by (or required to) the provider and checked by atomic force microscopy (AFM) by measurements/inspections of the surface of the substrate, as showed in Figure 4. A top-view AFM image of the plastic PET and PEN, as examples, after being stressed thermally. The layer exhibits an RMS roughness value lower than 12 nm, which suggests a value around the expected from the datasheet of the provider and compatible with the required thicknesses of the functional materials to be inkjet printed on top.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under **Grant Agreement No. 862656**.



PEN PET

Figure 4: Atomic force micrograph of PEN and PET substrates.

3.1.4 Surface treatment (surface adhesion activation)

The perfect plastic substrate should have high solvent resistance and low CTE among the semicrystalline oriented polymers (PET, PEN, PPS) and the thermal stability of amorphous polymers (PI). The major drawback of plastic substrates lies on their low surface energy. Substrate properties affects crystallization and thin-film microstructure. Consequently, flexible plastic foils/tapes normally require a previous surface treatment before printing to tune the wettability and adhesion of inkjet-printed droplets. Pre-process coating, UV ozone cleaning, plasma treatment (O_2, N_2, Ar) or corona discharge are possible procedures in order to provide a favourable homogeneous nucleation of the inkjet-printed B-LFPs.

Contact angle of droplets on the selected substrates, according the Young's equation, is the technique which allows to determine the wettability and the adhesion of ink solvents (vehicles) on the different substrates giving the match between the surface energy of the solid surface substrate (coated or pre-processed) and the solvent surface tension of the functional material.

There is not a right value for the contact angle of a functional ink material with a specific surface substrate. Depending on the final objective and application there are three possible scenarios that can be obtained by engineering the substrate with a pre-process as above mentioned.

When we are looking for a very thin layer, order of 30-100 nm (like perovskite layer for LED devices or transport layers ETL and HTL), we can promote complete wettability (hydrophilic substrate) of the plastic tape coated with ITO employing plasma treatment (O_2) as pre-process, no matter the functional droplet ejected as showed in Figure 5, on the left Cs_2SnI_6 and on the right side PEDOT:PSS.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under **Grant Agreement No. 862656**.

Figure 5: Complete wettability by contact angle of ~ 0°. Left, Cs_2SnI_6 ink on PET. Right, HTL PEDOT:PSS ink on PEN.

In order to reach thickness higher than 200 nm with single pass or reduced printing process we must ensure a contact line pinning at the hedge of the ejected droplet. By exposing the substrate to the UV ozone cleaner (UV lamp with adjustable timer,) we can tune the contact angle, then controlling the evolution of the thickness and adhesion. Figure 6 demonstrates how the same ink Cs_2SnI_6 is ejected on different substrate (PET on the left, PEN on the right) and we can obtain the same value of contact angle by only changing the amount of time exposure to the UV lamp.

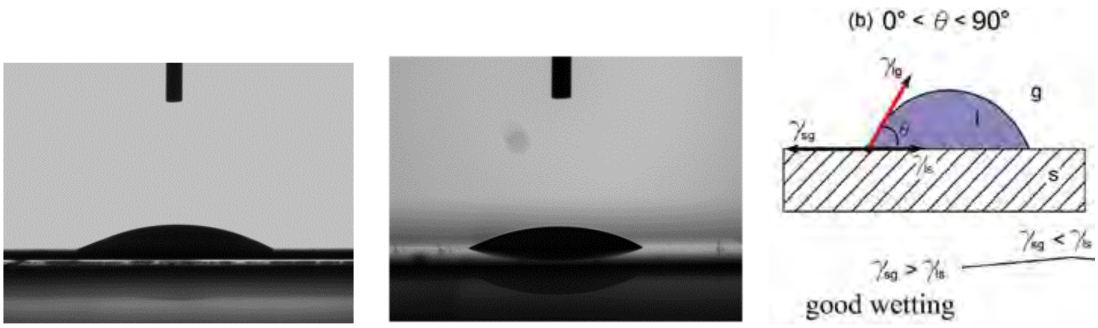


Figure 6: Good wettability by contact angle of ~ 25°. Left, Cs_2SnI_6 ink on PET. Right, Cs_2SnI_6 ink on PEN.

Although the third and last case, when contact angle is ≥ 90°, by definition is considered bad wettability (hydrophobic substrate), we take advantage of this activation of the substrate or surface in order to print a single pass thick PV layers. Long exposure to UV lamp (UV ozone cleaner) can promote this surface activation as shown in Figure 7, where Ag_3BiI_6 ink is ejected on the PET and PEN substrates.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under **Grant Agreement No. 862656**.

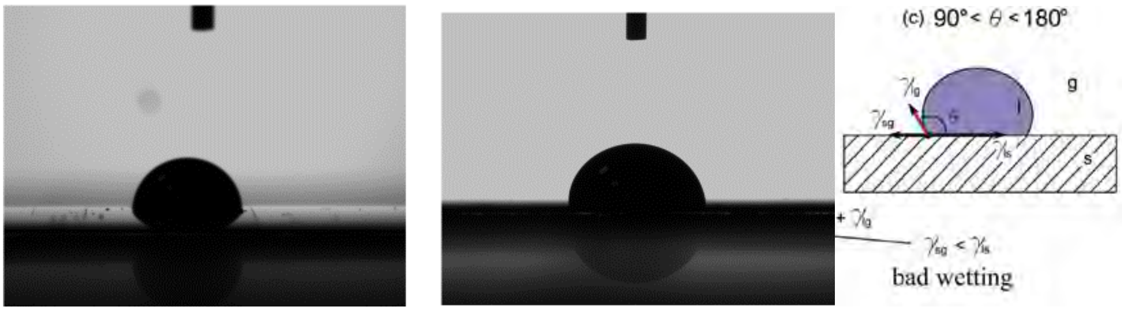


Figure 7: No wettability with contact angle of ~ 90°. Left, Ag_3BiI_6 ink on PET. Right, Ag ink on PEN.

3.2 Transparent electrode substrates

In order to use flexible plastic foils as transparent electrode substrates, they are typically coated with transparent conducting oxides (TCO) such as indium tin oxide (ITO) or fluorine tin oxide (FTO). Due to their promising good transparency and electrical conductivity, plastic/ITO substrates were characterized by several techniques. Figure 8 demonstrates the high transparency resuming the list of the selected 10 plastic substrates coated with 100 nm of sputtered ITO in our facilities or provided by the companies (example are Biotain or Chasm). We observed as the optical properties and degree of bendability changed after the coating process, which no requires any thermal treatment. Table 4 summarizes the comparison between available cheap commercial plastic/ITO structures and promising substrates coated with ITO in our facilities.

Table 4: Comparison between commercial ITO-coated substrates and custom ones. (EBE, electron beam evaporation)

Material combination	Commercially available	Thickness	Transmittance	Electrical conductivity
PET/ITO	Yes	135 nm Controllable	> 80% Controllable	10–15 Ω/□ Controllable
PEN/ITO	Yes	185 nm Controllable	> 80% Controllable	6–8 Ω/□ Controllable
EBE ITO onto PET/PES/PI	No (at UB facility)	75–100 nm Uncontrollable	> 80% Uncontrollable	150–200 Ω/□ Uncontrollable
Sputtering ITO onto PET/PES/PI	No (at UB facility)	75–100 nm Controllable	> 80% Controllable	50–60 Ω/□ Controllable

This project has received funding from the European Union's Horizon 2020 research and innovation programme under **Grant Agreement No. 862656**.

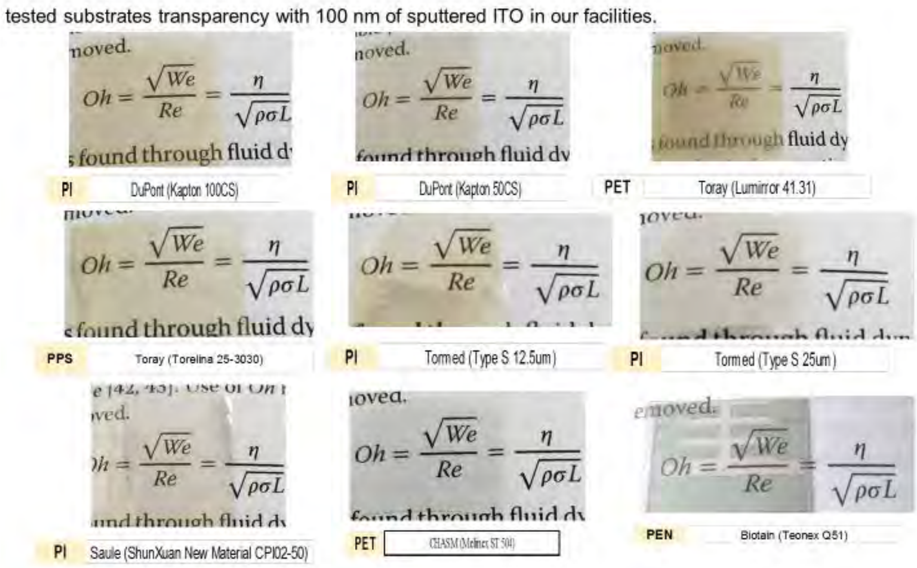


Figure 8: Selected substrate with ITO layer coated by provider or within our facilities.

3.2.1 Coated ITO layer under thermal stress

ITO is a brittle material, so it can be damaged during thermal stress (Figure 9), or bending stress, leading to an increase in substrate resistance and propagation of cracks to the active layers. Nevertheless, it is sufficient to avoid curving devices below the safe bending radius of ITO (that depends on the ITO thickness) to prevent any degradation. For instance, it has been shown that the safe bending radius for PET/ITO, with sheet resistance of 15 Ω/□, is equal to 14 mm.[1] Secondly, ITO layers that are annealed at low temperatures show reduced chemical resistance with respect to crystalline ITO or FTO, and may induce degradation in the perovskite film if they are not carefully covered by pinhole-free compact layers.

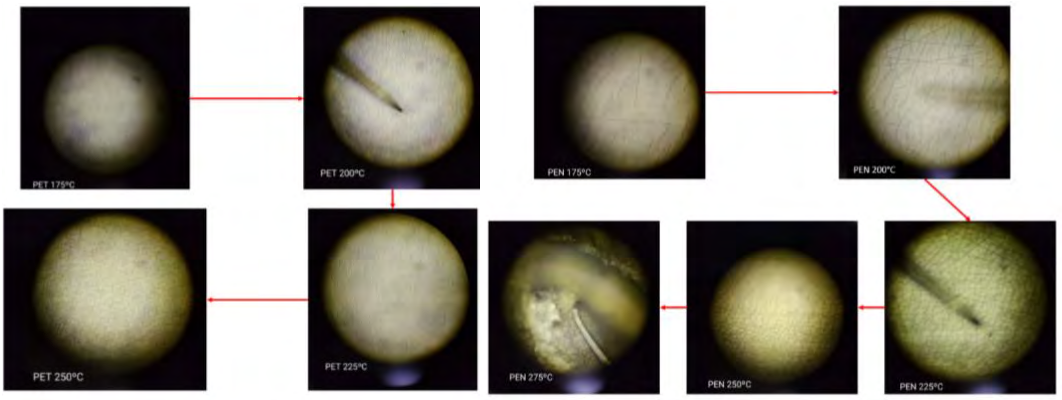


Figure 9: Degradation of commercial coated ITO on PET and PEN under substrate thermal stress.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under **Grant Agreement No. 862656**.

First, we investigated the effect of a temperature treatment (from room temperature up to 300 °C, when allowed by the substrate) on the sheet resistance of flexible foils (for example PET/ITO, PEN/ITO, PI/ITO) as showed in Figure 10. As expected, PI/ITO can withstand higher temperatures and it exhibits higher conductivity than coated PET and PEN foils. Consequently, we could estimate the temperature limit beyond which substrate deformation takes place after thermal stress treatments, to highlight the degradation of flexible structure.

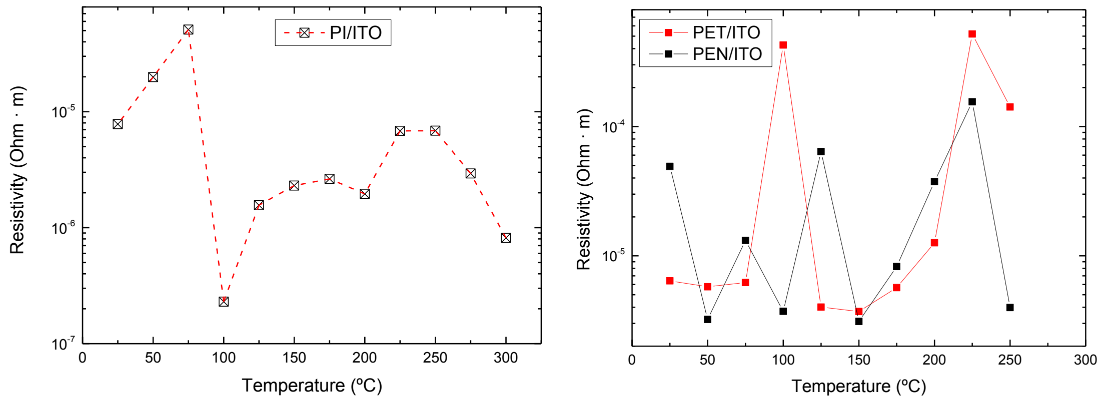


Figure 10: Resistivity versus temperature. Left, PI/ITO. Right, PET/ITO and PEN/ITO.

3.2.2 Coated ITO layer under bending stress

We evaluated the mechanical stability of substrates covered with ITO by monitoring the change of the sheet resistance of the selected conductive type of substrates (PET/ITO, PEN/ITO, PI/ITO) under stress for different radii of curvature. Because ITO is rigid and brittle, it cracked when it was bent and stretched, leading to a dramatic decrease in its conductivity. Cracking occurred under tensile stress for bending radii ≤ 12.5 mm, but depending on the flexing conditions. Tensile stress was more damaging than compressive stress (see Figure 11).

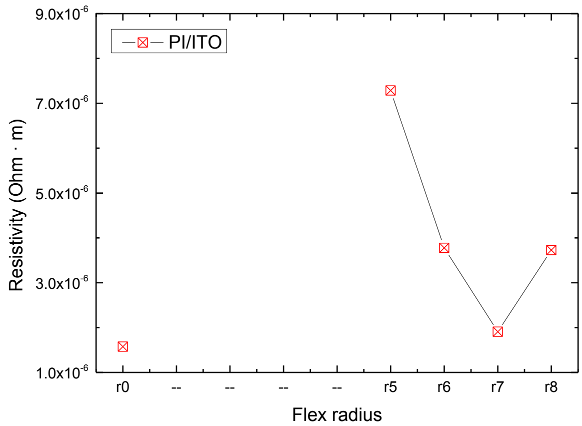


Figure 11. Measurements of resistivity versus bending radius for PI/ITO substrates (r8=75 mm, r7=50mm, r6=25mm, r5=12.5mm, r0 flat).

This project has received funding from the European Union's Horizon 2020 research and innovation programme under **Grant Agreement No. 862656**.

3.2.3 Coated ITO layer under UV stress

Optical degradation was monitored after UV treatment leading to a certain loss of transparency and some yellowing, particularly on PEN and PPS substrates.

Table 5: Optical transparency degradation/loss after UV treatment measured at 550nm.

Material	Reference	Original substrate Transmittance (%)	Loss of Transparency
PET	Toray (Lumirror 41.31)	> 88	<1% after 150‘ exposure Estimated 1-2% after 100 Hours
PET	Biotain (Melinex ST504)	85	<1% after 150‘ exposure Estimated 1-2% after 100 Hours
PET	CHASM (Melinex ST 504)	85	<1% after 150‘ exposure Estimated 1-2% after 100 Hours
PEN	Biotain (Teonex Q51)	82	5% after 150‘ Estimated 10% after 100 Hours
PPS	Toray (Torelina 25-3030)	60–80	10-15% after 150‘
PI	Saule (ShunXuan New Material CPI02-50)	> 85	<1% after 150‘ exposure Estimated <1% after 100 Hours
PI	DuPont (Kapton 100CS)	> 80	<1% after 150‘ exposure Estimated <1% after 100 Hours
PI	DuPont (Kapton 50CS)	> 80	<1% after 150‘ exposure Estimated <1% after 100 Hours
PI	Tormed (Type S 12.5um)	> 85	<1% after 150‘ exposure Estimated <2% after 100 Hours
PI	Tormed (Type S 25um)	> 85	<1% after 150‘ exposure Estimated <2% after 100 Hours

3.2.4 Solvent compatibility of coated ITO layer

Finally, we have observed that all the plastic substrates, PI/ITO, PET/ITO and PEN/ITO, show remarkable stability to treatments under the most common polar and non-polar solvents commonly used in the inkjet

This project has received funding from the European Union's Horizon 2020 research and innovation programme under **Grant Agreement No. 862656**.

printing technology for the fabrication of flexible electronic devices. List of compatible solvents with the substrate and the printer's technology employed into the project:

a) Aliphatic alcohols (high boiling point better than low in all cases)
b) Aromatic hydrocarbons such as anisole, trimethylbenzene
c) Aliphatic hydrocarbons such as hexane, dodecane,
d) Cellulose
e) Glycols
f) Lactate esters
g) Aliphatic and aromatic ketones including tetrahydrofuran (evaporates quickly)
h) Polyethylene glycols, polypropylene glycols

3.3 Inkjet printing B-LFP onto selected plastic substrates

In order to complete the printability tests, we inkjet-printed the selected B-LFP layers which arrived during June/July 2020 over the best flexible substrates coated with ITO to study the optical and electrical stability of the system under thermal and mechanical stresses even after the most demanding bending tests. Following, it is presented the list of tested B-LFP printed layers onto some of the selected best flexible substrates with a main surface characterization.

3.3.1 Cs_2SnI_6 (from Avantama)

We obtained a stable and printable ink based on the inorganic double perovskite Cs_2SnI_6. The inkjet-printed layers onto PET/ITO, PEN/ITO, PI/TO substrates appear homogeneous, flat and without wrinkles or cracks after standard bending stress as presented on Figure 12 (AFM topography on PET/ITO surface) and Figure 13 (SEM inspections on PET/ITO surface).

This project has received funding from the European Union's Horizon 2020 research and innovation programme under **Grant Agreement No. 862656**.

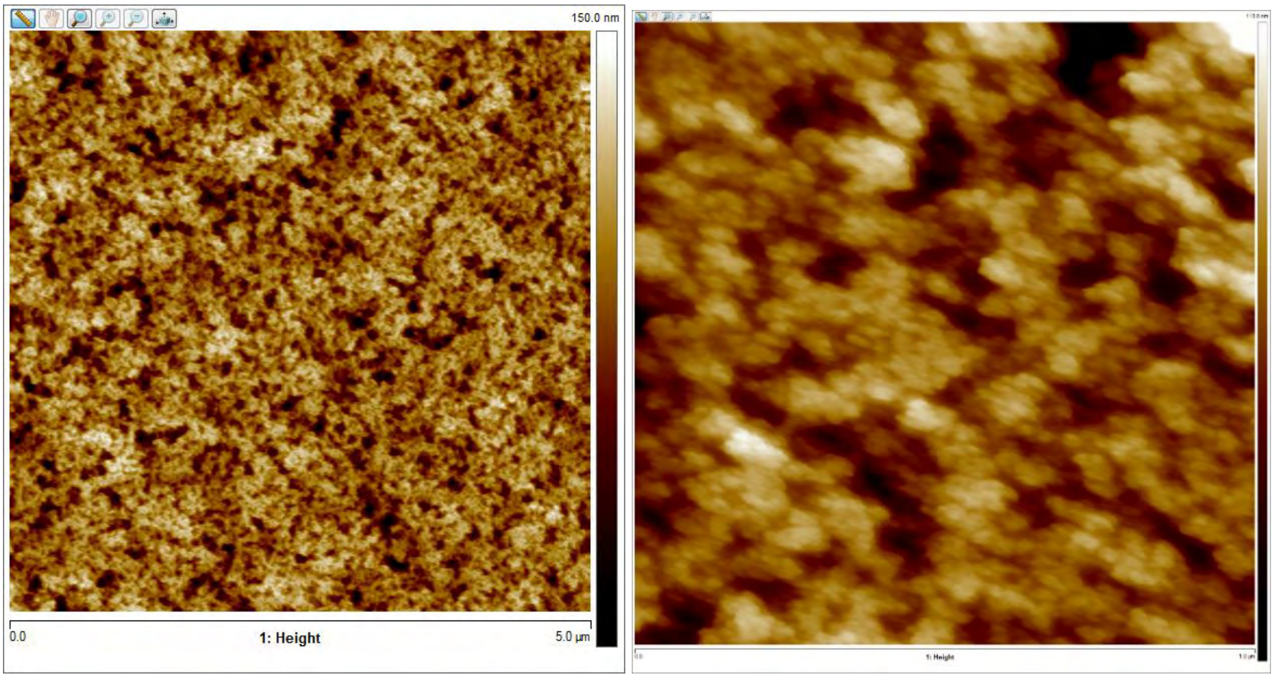


Figure 12: AFM top view topography of Cs2SnI6 on PET/ITO substrate.

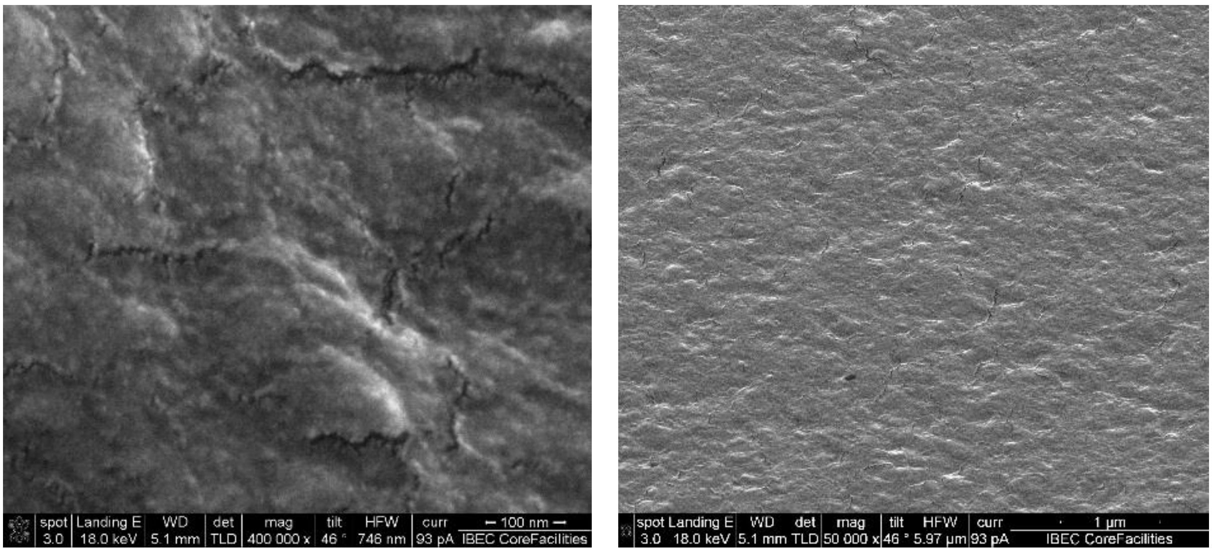


Figure 13: SEM images at different magnification of Cs_2SnI_6 on PET/ITO substrate.

Optical and electrical characterization are still under study and to be improved due to the degradation of the printed layers when characterized in ambient condition (clean room facilities). The possible degradation

This project has received funding from the European Union's Horizon 2020 research and innovation programme under **Grant Agreement No. 862656**.

of the precursors could be the cause of the absence of expected photoluminescent (PL) signal (Figure 14) or electrical conductivity.

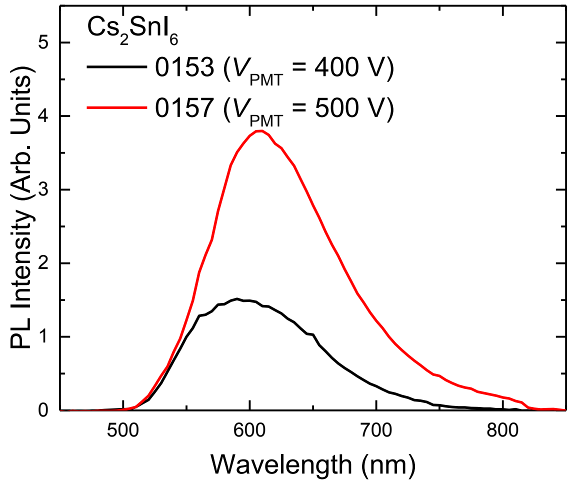


Figure 14: PL measurement of different inks of Cs2SnI6 on Si/SiO2 substrate.

We expect a band gap for Cs_2SnI_6 of about 1.45 eV (PL 850 nm and beyond) although for small nanocrystals PL is shifted to about 700-800 nm, but we did not detect, which is explained by the very low photoluminescence quantum yield of these nanocrystals even at low temperatures (see Deliverable D1.3). We do not get either good absorption even though it is reported in excess of 10^5 cm^{-1}. With the partner AVANTAMA we are working on new batches of the raw materials for new inks formulations. We tested four possible inks formulation in order to avoid layer degradation, listed below, but the main drawback, which is promoting the printed layer degradation, is the impossibility of installing the inkjet printer into an inert atmosphere glovebox chamber.

a. Cs_2SnI_6 in Dodecane + Polyisobutylene additive (9:1)
b. Cs_2SnI_6 in Dodecane + Toluene (6:4)
c. Cs_2SnI_6 in Dodecane + Hexane (3:1)
d. Cs_2SnI_6 in Dodecane

Issue of formulated inks up to date: thermal post process require temperature around 155°C -200ºC to remove the ink solvents vehicles, reducing the range of substrate applications.

3.3.2 $FASnI_3$ (from ETHZ)

Hybrid organic−inorganic halide perovskite $FASnI_6$ has been inkjet-printed in two different ink formulation onto PET/ITO, PEN/ITO, PI/TO substrates. The inkjet-printed layers show expected brown-red

This project has received funding from the European Union's Horizon 2020 research and innovation programme under **Grant Agreement No. 862656**.

appearance and homogeneous morphology (Figure 15). The achieved ink (Figure 15, left) was formulated for the Dimatix cartridges inside the glovebox. The disadvantages of this formulations are the low stability when inkjet-printed, due to the Dimatix printer operation outside of the Glovebox (in ambient environment).

As can be observed in Figure 16 right, the inks into the isolated cartridges show a clear change of properties due to the degradation of the solution. The inks were changing after few minutes from dark red to transparent yellowish.

Figure 15: Preparation of ink and printhead into the glovebox of $FASnI_3$ based on hexane+dodecane.

Optical and electrical characterization are still under study, and degradation improvement of the printed layers outside of glove box. The perovskite is strongly sensitive to moisture, which causes the oxidation of the Sn^{+2} to Sn^{+4} (Figure 16), then the absence of expected PL signal or electrical conductivity. With the partner ETHZ we are working on new batches of the raw materials for new inks formulations.

We tested two possible inks formulation in order to avoid layer degradation, listed below, but the main drawback, which is promoting the inks and printed layer degradation, seems related to the process of fast oxidation during printing because of combined oxygen and humidity exposure in ambient environment.

a. $FASnI_3$ in Dodecane + Polyisobutylene additive (9:1)
b. $FASnI_3$ in Dodecane + Hexane (3:1)

This project has received funding from the European Union's Horizon 2020 research and innovation programme under **Grant Agreement No. 862656**.

Figure 16: Degradation of the ink outside the glovebox. Inkjet printed $FASnI_3$ on PI/ITO flexible substrate attached on a glass slide.

4 Conclusions & Future directions

We demonstrated the selected 10 commercially available plastic substrates through a range of tests simulating typical conditions of device fabrication. With this aim, we have carried out a broad, comprehensive systematic investigation encompassing optical properties, mechanical flexibility (under different types of compressive stress –bending– with and without an inkjet-printed layer on top), stability to temperature treatment (electrical conductivity and deformation) and to UV irradiation, of selected substrates, both in their bare form but also when coated with ITO.

We have ranked the flexible substrates covered with ITO and printed with B-LFPs for optoelectronic applications in solar cells and LEDs. We have taken into consideration the following properties in order of importance:

1) Resistance to relatively high temperature processing maintaining transparency
2) Commercial availability of substrate covered with ITO with reasonable price
3) Transmission in the visible over 80%
4) Good performance on test of resistivity versus bending radius
5) Good printability of substrate/ITO with B-LFP inks, even if their films appear to be degraded in ambient conditions.
6) Good performance in optical and bendability test of printed B-LFP layers

Considering this, the ranked list of chosen substrates is the following:

- T-PI substrate from Tormed (Type S 25um): high temperature processing, easy/quick access to the product with coated ITO, high transmission and good printability.
- T-PI substrate from DuPont (Type S 25um): similar to the previous one
- PEN substrate from Biotain (Teonex Q51): easy/quick access to the product with coated ITO, good performance and transmission except for high temperature
- PET substrate from Biotain (Melinex ST504): similar to the previous one, lower cost, not usable for high temperature process

This project has received funding from the European Union's Horizon 2020 research and innovation programme under **Grant Agreement No. 862656**.