D2.1 – Development of organic/hybrid light-emitting diodes for the h-ALO sensor

Project Information

Grant Agreement Number	101016706
Project Full Title	photonic system for Adaptable muLtiple-analyte monitoring of fOod-quality
Project Acronym	h-ALO
Funding scheme	RIA
Start date of the project	1st January 2021
Duration	36 months
Project Coordinator	Stefano Toffanin (CNR-ISMN)
Project Website	https://h-alo.eu/

Deliverable Information

Deliverable n°	2.1
Deliverable title	Development of organic/hybrid light-emitting diodes for the h-ALO sensor
WP no.	2
WP Leader	1-CNR
Contributing Partners	1-CNR
Nature	Report
Authors	Emilia Benvenuti (CNR), Mario Prosa (CNR)
Contributors	Emilia Benvenuti (CNR), Mario Prosa (CNR)
Reviewers	Stefano Toffanin (CNR)
Contractual Deadline	M11 (30/11/2021)
Delivery date to EC	17/12/2021

"This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101016706".

Dissemination Level

PU	Public	**x**
PP	Restricted to other programme participants (incl. Commission Services)	
RE	Restricted to a group specified by the consortium (incl. Commission Services)	
CO	Confidential, only for the members of the consortium (incl. Commission Services)	

Document Log

Version	**Date**	**Description of Change**
V1.0	03/12/2021	First draft
V2.0	15/12/2021	First complete version
V2.1	16/12/2021	Review by the Coordinator

"This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101016706".

Table of Contents

1 Executive Summary 3
2 Introduction 3
3 OLED for LSPR 4
4 OLED for PEF 7
5 Preliminary stability test 9
6 Conclusions 10
7 References 10

1 Executive Summary

The aim of Deliverable 2.1 (D2.1) is the fabrication and characterization of two types of miniaturized light-emitting sources that enable, respectively, the localized surface plasmonic resonance (LSPR) and the plasmonic enhanced fluorescence (PEF) detection modes of the h-ALO sensor. Each detection mode is indeed triggered by a specific light-emitting source. According to the specifications defined by the "Optoplasmonic" WorkGroup, organic light-emitting diodes (OLEDs) were selected as the best light-emitting candidates, and their components and structures were reported in D1.3. This deliverable will focus on the development, the optimization, and the experimental fabrication of the designed OLEDs. Devices are encapsulated to operate under ambient atmosphere, and their optical and electrical characteristics are analyzed to fulfill the LSPR and the PEF requirements for a portable operation of the h-ALO sensor.

2 Introduction

OLEDs constitute the miniaturized light-emitting sources of the h-ALO optoplasmonic chip. OLEDs are nanometer-thick multi-layered devices where the light is generated from an organic emissive material sandwiched between two electrodes. Interlayers, that are dedicated to a specific functionality such as charge injection and exciton blocking, are included in the structure in order to obtain highly efficient and stable devices.
According to the specifications defined in D1.3, the materials, the device structure, and the spectral characteristics of each of the two OLEDs were selected to match the optical requirements of the nanoplasmonic grating (NPG), the optically selective organic photo transistor (OPT) and the fluorophores (in the case of the PEF detection). In the development of the designed OLEDs, a particular attention is devoted to the maximization of the optical power of emission of the two OLEDs since they must guarantee an output photocurrent signal that is detectable by the electronics of the h-ALO sensor. Indeed, in the scheme of detection, the light undergoes a multistep path in which it is first emitted through the semi-transparent OLED electrode, then it is modulated by the NPG to be eventually absorbed by the OPT and hence an output electrical signal is generated. On the one side, the optical power needs to be maximized to improve the output signal of the sensor, on the other side the power consumption needs to be reduced as much as possible in view of the in-field implementation of the sensor.

"This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101016706".

Here, all devices are fabricated by thermal deposition under high vacuum (10^{-8} mbar), by using a custom-made evaporation chamber from Kurt J. Lesker attached to a glovebox. The chamber is equipped with 8 thermal sources for the deposition of organic materials and 3 thermal sources for the deposition of inorganic materials and metals. A sample holder with slots for 25 mm x 25 mm wide substrates allows for the fabrication of 9 samples per run. Fine metal masks were designed and purchased for the deposition of 4 square OLEDs of 9mm^2 on a single substrate. The designed pattern prevents any cross-talking effects, i.e. no current leakages are presents and each device can be driven separately. It is worth to note that this pattern does not represent the one which will be adopted in the final optoplasmonic chip since at this stage of development of the optoelectronic component, we preferred to focus on the simplest OLED layout while we optimized each layer in the device multistack.
For the OLED development, experimental tests of optimization were guided by a theoretical activity. A commercial software named SETFOS, provided by Fluxim, was purchased and used to predict the optical and electrical features of the OLED devices as well as to identify the most efficient strategy to tune the device characteristics in agreement with the requirements defined in D1.3.

3 OLED for LSPR

The OLED dedicated to the LSPR detection needs to match the NPG sensitivity in the spectral region between 750 – 900 nm, in agreement with the specifications of D1.3. As a result of the a well-consolidated collaboration between CNR and PLAS on the development of LSPR sensing systems (EU H2020 project, MOLOKO – Grant Agreement n. 780839), we here developed a light-emitting source based on the phosphorescent compound PtII–tetraphenyltetrabenzoporphyrin [Pt(tpbp)] dispersed in a matrix of tris(8-hydroxyquinoline) aluminum (Alq_3). A schematic representation of the device structure is shown in Figure 1a. The resulting OLED is expected to show a strong near-infrared emission band at around 770 nm,[1] which perfectly matches the maximum sensitivity of the NPG for LSPR detection at all angles included between 0° and 15° (Figure 1b).

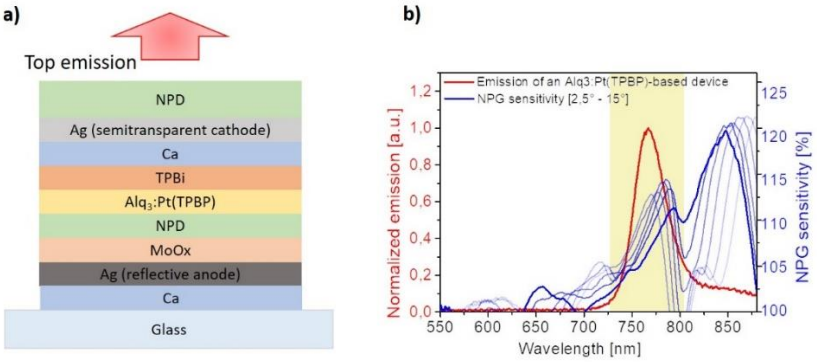

Figure 1. Schematic representation of the OLED structure (a); normalized electroluminescence from an OLED based on a Pt(TPBP) emitter, peaked at around 770 nm, perfectly matching a relative maximum of sensitivity of the NPG for LSPR detection, at all angles included between 0° and 15° (b).

The designed OLED provides a top emission of the light due to the use of a reflective bottom anode and a semi-transparent top cathode. For the experimental fabrication of the devices, a thin calcium layer was introduced between glass substrate and the anode electrode in order to prevent delamination effects and to improve the adhesion and the stability of the bottom electrode. A molybdenum oxide (MoO_x) layer was used as the hole injection layer (HIL) under an hole transport layer (HTL) composed by N,N'-Di(1- naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-

"This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101016706".

4,4′-diamine (NPD). For injection and transport of the electrons, a layer of 2,2′,2-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi) and a thin layer of calcium were deposited onto the emissive layer (EML).
To fulfil the requirements defined in D1.3, the device structure was optimized in terms of optoelectronic features by using SETFOS software. This approach allowed predicting parameters such as radiance, light outcoupling efficiency and electrical behaviour of the OLED upon tuning the thickness of a specific layer and/or the applied bias.
As a preliminary step, the simulation tool was tuned to match experimental data. Then, the performance of the OLED in terms of light outcoupling efficiency was investigated and improved by simulating the presence of a layer of NPD on top of the semi-transparent cathode.[2] The NPD layer acted as an index matching layer (IML) to further favour the process of light outcoupling.[3] Devices were therefore fabricated, encapsulated with a glass cap attached by UV cured glue, and characterized in a homemade set-up for radiance and brightness measurements. Table 1 shows the values of radiance and operating voltage recorded for different structures at a driven current of 31 mA/cm^2. The introduction of an IML of NPD allowed to almost double the radiance of the OLED, thus passing from 0.45 W/m^2*srad to 0.85 W/m^2*srad. The target radiance of 2.08 W/m^2*srad is that of the light-emitting source of the already-developed LSPR sensing system (EU H2020 project, MOLOKO – Grant Agreement n. 780839). Despite the drastic improvement of OLED performance due to the introduction of an IML, further optimization of OLED structure is needed to reach the desired optical intensity of emission to enable a suitable LSPR signal.

Table 1. Operating voltage and radiance recorded experimentally from different OLED structures as a function of the thickness of MoOx, EML and IML. Values are recorded at a driven current of 31 mA/cm^2. The last row shows the target reference.

MoOx/EML/IML	Voltage [V]	Radiance [W/m^2*srad]
10nm / 60nm / w/o	12,0	0,45
10nm / 60nm / w	11,2	0,85
40nm / 60nm / w	14,3	3,74
40nm / 30nm / w	6,8	0,88
60nm / 30nm / w	6,7	2,29
REF	6,5	2,08

In this regard, an intense fine tuning of the thickness of each layer of the OLED was carried out. Provided the same device structure, simulations showed that an increase of the MoO_x thickness from 10 to 40nm layer is correlated to an enhancement of the OLED radiance without any modifications of the electroluminescence spectrum (Figure 2). It is worth mentioning that a variation of the thickness of a layer can induce spectral modifications of the OLED emission, that are strongly undesired. Specifically, a thickness of the MoO_x layer above 40 nm leads to a red shift of the emission spectrum and the resulting increase of a shoulder at 850 nm (Figure 2b). Spectral modulations must be avoided since they could affect the effectiveness of the overlap between the light source emission and the NPG response.

"This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101016706".

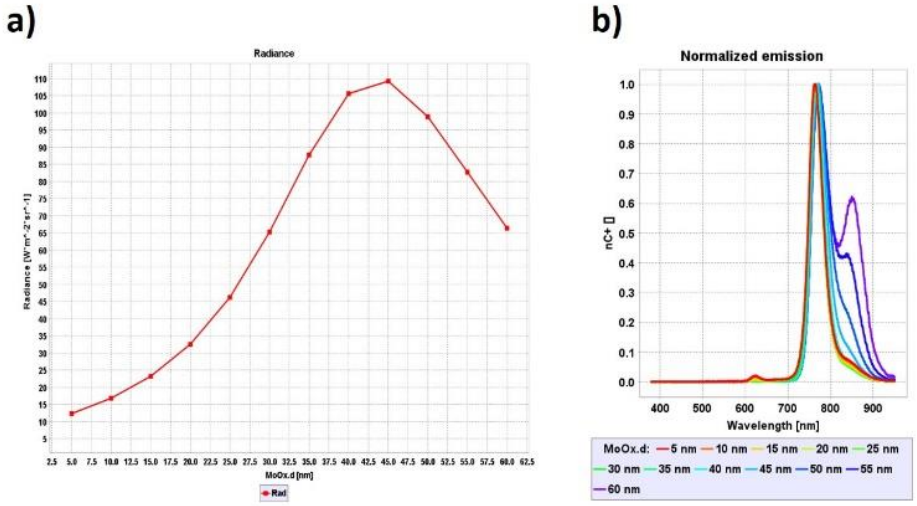

Figure 2. Simulation of radiance (a) and emission spectrum (b) of an OLED with a MoOx layer thickness ranging from 5nm to 60 nm.

Experimental tests confirmed the simulated trend: by using a 40 nm-thick MoO_x layer, it was possible to increase the radiance of a factor 4 (Table 1). In particular, we realized an OLED having an emission spectrum with a maximum at 764 nm and a radiance of 3,74 W/m^2*srad, that are values higher than the target ones.

Despite the good optical performance, the OLED structure needed operating voltages of about 14 V, that is exceeding the values desired for in-field application of the h-ALO sensor. According to simulations, the thickness of the EML was therefore reduced to allow lowering the operational voltage. This trend was confirmed experimentally (Table 1): by halving the EML thickness, the OLED working voltage was around 6,8 V. However, a reduction of the intensity of emission was eventually observed. A further optimization of the MoO_x layer thickness to 60 nm allowed gaining the radiance back without affecting the spectral features of emission. The optimized OLED structure showed an operating voltage of 6,7 V, an optical power of about 30 µW, and a radiance of 2.29 W/m^2*srad at 31 mA/cm^2 (Figure 3). The resulting figures of merit are in very good agreement with the requirements for LSPR detection.

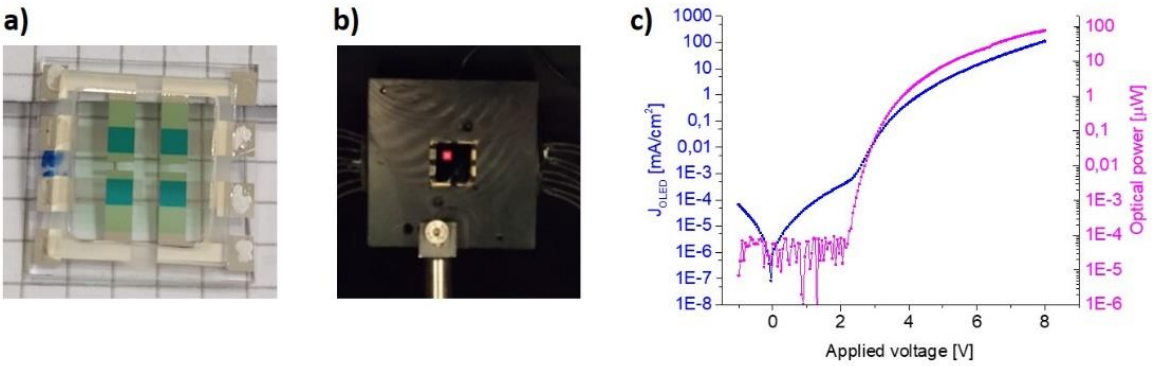

Figure 3. Picture of the optimized OLEDs in the OFF state (a) and in the ON state (b). Current density (blue line) and optical power of emission (pink line) of the OLED for LSPR detection as a function of the applied voltage.

"This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101016706".

4 OLED for PEF

In PEF detection, fluorophores are bound to the NPG surface to interact with the confined electrical and optical field of surface plasmons. An enhancement of the emission is therefore induced. The OLED needs to be designed so as to trigger the fluorophore absorption in an efficient way, once the light is transmitted through the NPG. A high optical power of the OLED emission is desired. Since a portion of the OLED light will be backscattered by the NPG towards the OPT, a resulting background signal would cause a low signal-to-noise ratio of the OPT. In this regard, the introduction of an optical filter between the NPG and the detector will avoid this reflected component of the light to reach the OPT. A narrow emission profile of the OLED, in conjunction with a large stoke shift with respect to the fluorophore absorption, is therefore desired to facilitate the development of the optical filter.

Following the requirements reported in D1.3, AlexaFluor 750 is the fluorophore of interest and two different emitters are identified for the development of the OLED structure dedicated to PEF detection:

- Platinum(II)2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrin, Pt(OEP) (largest spectral shift)
- Tris(1-phenylisoquinoline)iridium(III), $Ir(piq)_3$ (highest PEF factor)[a]

Pt(OEP) is selected for its a narrow emission spectrum that minimize the spectral overlap (i.e. favours the spectral separation) with the fluorophore emission band. On the contrary, the relatively higher quantum yield of emission of $Ir(piq)_3$ favours a higher PEF signal at the expense of a reduction of spectral separation with the fluorophore emission peak. $Ir(piq)_3$ is indeed characterized by a relatively large emission band.

By using the same device structure of the OLED dedicated to LSPR detection (Figure 1a), the selected dyes were introduced in the EML, and an optimization of each interlayer was carried out in terms of thickness to obtain the desired OLED optoelectronic features. In particular, the optical power, the brightness and the emission spectrum were first simulated as a function of the device structure and then the experimental fabrication of the OLEDs was carried out accordingly. The optimized OLEDs and their optoelectronic performance are reported in Figure 4.

[a] The PEF factor is an indicator of the theoretical PEF efficiency of the optoplasmonic chip obtained on the basis of spectral features and optical figures of merit of different OLED-fluorophore couples.

"This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101016706".

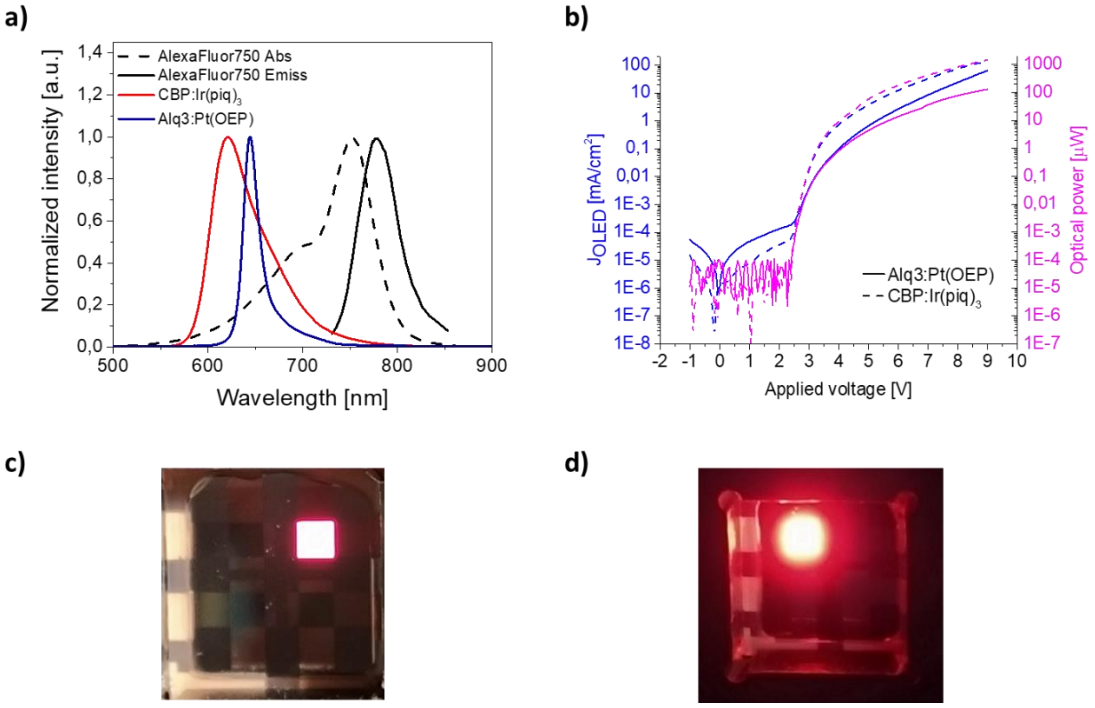

Figure 4. a) Normalized absorption (dotted black line) and emission (black line) spectra of the AlexaFluor750 dye in comparison with the normalized emission spectrum of Pt(OEP)-based OLEDs (blue line) and Ir(piq)$_3$-based OLEDs (red line), respectively. b) Current density (blue lines) and optical power of emission (pink lines) of Pt(OEP)-based OLEDs (solid line) and Ir(piq)$_3$-based OLEDs (dotted line), respectively, as a function of the applied voltage; c) d) corresponding pictures of the two types of OLED on a 25 mm x 25 mm wide glass substrate.

Specifically, Pt(OEP) was dispersed in the Alq_3 matrix and two different doping percentages were tested, i.e. 4% and 10%, respectively. A doping percentage of 10% led to a slightly higher optical power and it was therefore selected for the development of the device structure. The use of an EML of 30 nm, like in the case of the OLED for the LSPR detection, guaranteed an operating voltage of 7.9 V that is suitable for in-field applications (Table 2). However, this device stack led to a modulation of the spectral emission in comparison with the emissive spectrum of the EML itself. An additional spectral shoulder at around 712 nm was indeed observed. To prevent these undesired cavity effects, simulations showed that a reduction of the MoO_x thickness could be a good strategy to avoid cavity effects while maximizing the OLED radiance. The fabrication of a stack having a MoO_x layer with 40 nm thickness led to OLEDs with an almost 4-time increased radiance of 3.8 W/m^2*srad, an emission peak at 644 nm, and a full width at half maximum (FWHM) of 20nm (Figure 4a and Table 2), in great agreement with target values.

Table 2. Optoelectronic performance recorded for OLED structures realized for PEF detection. All the values are referred to a driven current of 31 mA/cm^2.

EML	MoO_x/IML	Voltage [V]	Opt. pow. [µW]	R [W/m^2*srad]	L [cd/m^2]
Alq_3:Pt(OEP)	60nm/60nm	7,9	46	1,0	50
Alq_3:Pt(OEP)	40nm/60nm	7,9	90	3,8	322
CBP:Ir(piq)$_3$	40nm/60nm	7,4	380	13,2	2061
CBP:Ir(piq)$_3$	40nm/120nm	7,5	394	15,4	2889

"This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101016706".

Since cavity effects are strongly depending on the correlation between the spectral region of emission and the overall thickness of the OLED stack, the device structure based on Pt(OEP) was used as the starting point to develop OLEDs based on the other emitter, that is $Ir(piq)_3$, because of their similar spectral region of emission. In the case of $Ir(piq)_3$, the best hosting matrix is instead 4,4'-Bis(N-carbazolyl)-1,1'-biphenyl (CBP), that enables an efficient emission at around 621 nm. Different doping percentages were first tested, and a doping of 10% was chosen as the best values since it led to a lower operating voltage of the device. Simulations showed that an increase of the IML from 60 nm to 120 nm allows for a more efficient light outcoupling process. Accordingly, OLEDs were fabricated, and an increase of the brightness was obtained, thus passing from 2061 cd/m^2 to 2889 cd/m^2 (Table 2). It is worth mentioning that the brightness is calculated for OLEDs dedicated to PEF detection because their region of emission is in the visible region. Instead, in order to favour a comparative analysis, radiance is calculated for all OLEDs since it is a more exhaustive parameter that is independent on the region of emission.

5 Preliminary stability test

In view of developing a protocol of operation of the h-ALO sensor, a suitable operational stability of the light-emitting sources needs to be guaranteed. Although an in-depth analysis will be given in D2.4 (due date at M18), preliminary tests were carried out on the here developed OLEDs. Specifically, the OLED was driven at a constant current density of 31 mA/cm^2 for ten minutes while both the operating voltage and the optical power of emission were recorded. Two identical cycles of measurement were repeated on the same OLED in order to estimate the percentage of recovery of the figures of merit after a period of cooling down of the device.
Figure 5 shows the results obtained from Alq_3:Pt(TPBP)–based OLEDs. A slight reduction of the optical power of about 1,3% and 1,1% was recorded after the first and the second cycle of test, respectively. Interestingly, the intensity of the light emission was partially recovered once the OLED is kept in the OFF state for a few minutes before starting the second test. Results are quite promising. Nevertheless, further in-depth tests will be carried out on the OLEDs for PEF detection.

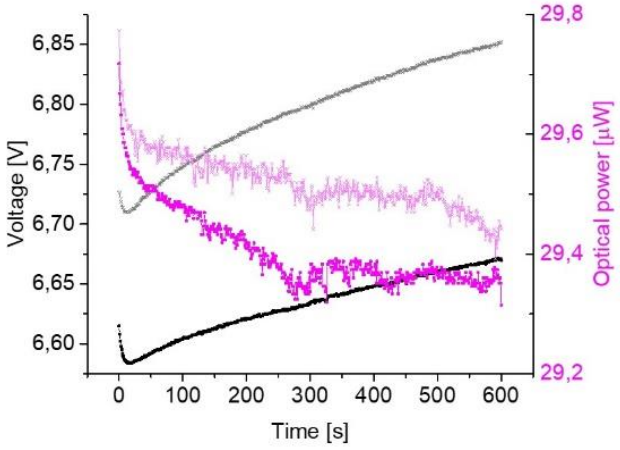

Figure 5. Operating voltage (black lines) and optical power (pink lines) recorded during the stability test on OLEDs for LSPR detection: 2 cycles of ten minutes were performed on the OLED at 31mA/cm^2. The second cycle is reported in lighter colours.

"This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101016706".

6 Conclusions

Three OLEDs were developed and fabricated as the light sources to be integrated in the h-ALO sensor.
The first one, dedicated to the LSPR detection, is based on a Alq_3:Pt(TPBP) host-guest system and shows an electroluminescence emission at 764 nm which matches the plasmonic resonance peak of the NPG. The optimization of the device structure led to a suitable operating voltage of 6,7 V, and a radiance as high as 2.29 W/m^2*srad at driven current density of 31 mA/cm^2. These values are expected to guarantee an effective operation of the light source within the sensor.

For the PEF detection, two different OLEDs were developed and fabricated. The first option is based on Pt(OEP) as emissive dye and it showed a suitable operating voltage of 7,9 V, a radiance as high as of 3,8 W/m^2*srad, that corresponds to a brightness of 322 cd/m^2. Due to its narrow emission at 644 nm, this first option may enable an easy development of the optical filter to be insert between the NPG and the detector. The second OLED is based on the more efficient $Ir(piq)_3$ emitter. Unlike the first option, a broader emission spectrum was recorded. On the contrary, a radiance of 15,4 W/m^2*srad and a brightness of 2889 cd/m^2 were recorded at an operating voltage as low as of 7,5 V. Although the maximum radiance of two OLEDs is significantly different because of the different quantum yields of the two emitters, an additional fine tuning of device structure can be performed on Pt(OEP)-based OLEDs to further boost the intensity of emission.

7 References

[1] M. Prosa, E. Benvenuti, D. Kallweit, P. Pellacani, M. Toerker, M. Bolognesi, L. Lopez-Sanchez, V. Ragona, F. Marabelli, S. Toffanin, *Adv. Funct. Mater.* **2021**, *31*, 2104927.

[2] A. Salehi, X. Fu, D. H. Shin, F. So, *Adv. Funct. Mater.* **2019**, *29*.

[3] J. J. Lee, P. Li, H. T. Kung, Z. H. Lu, *J. Appl. Phys.* **2019**, *125*.

"This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101016706".