D2.2 – OPD technology and parameters

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1 Executive Summary

This deliverable reports on design, fabrication and optimization of organic photodetectors (OPDs) in terms of device architectures, figures-of-merit (FOMs) and spectral characteristics. The activities reported herein are part of work package 2 (WP2), and specifically related to the work performed by FEP in order to fine-tune the characteristics of their core-technology component (i.e. OPD) in view of the integration into the organic photonic module of the MOLOKO sensor. In particular, the OPD represents the light detector of the module, while an organic light-emitting transistor (OLET) constitutes the light emitting source. These two elements, once designed and optimized in WP2, are monolithically integrated and then coupled with the nanoplasmonic grating (see D1.2), for realizing the optoplasmonic module that is the core of the MOLOKO detection scheme to reveal biochemical inputs.

The major development work described within this deliverable is the realization of a top-side absorbing OPD with high external quantum efficiency (EQE) at the wavelength of 766 nm. This constraint on the wavelength of detection is related to the emission spectrum of the OLET component (see infra) and the reflectivity efficiency of the nanoplasmonic grating. The overall development target is resulting from the work described in deliverables D1.1, D1.2, D1.3 and D2.1.

This deliverable 2.2 summarizes the work carried out within Task 2.2 of WP2 which involves the development and optimization of OPD stack architectures on test-device level. Fraunhofer FEP is the principal investigator of T2.2 in jointly collaboration with CNR and PLASMORE.

T2.2 includes:

- selection of stack options
- implementation and characterization of required new materials
- optical simulation
- OPD fabrication, optimization, and optoelectronic characterization

2 Background of the OPD technology

Within the optoplasmonic module of the MOLOKO sensor, light emitted by the OLET and reflected from the plasmonic grating is finally detected by the OPD. The basic OPD device structure is comprised of a bottom contact, a hole transport layer (HTL), an absorbing layer (AL), an electron transport layer (ETL) and a top contact. The photocurrent generation is based on the following processes: i) photon absorptance in the AL leading to the formation of excitons, ii) exciton diffusion, iii) charge transfer and dissociation of the electron-hole pairs, iv) charge transport and v) charge collection at the electrodes. The AL can be based on a planar junction or a so-called bulk-hetero junction (BHJ). In case of a planar junction, donor and acceptor materials are placed in separate layers on top of each other. Here, we focus on BHJ in which the AL consists of a blend of an electron donor and an acceptor material.

There are two possible OPD architectures with respect to the direction of the incident light: a device structure with a transparent bottom contact (typically Indium-Tin-Oxide, ITO) and an opaque top contact and a device structure with an opaque bottom contact and a semitransparent top contact (typically thin metal). We refer to these two structures as “bottom type” and “top type”, respectively. Both architectures are illustrated in Figure 1. In the scenario of the possible optoplasmonic module architecture in which the OPD is monolithically fabricated on top of the OLET source electrode (see deliverable D1.3), the bottom-type OPD configuration is considered as a benchmark for testing materials such as the donor, acceptor, HTL and ETL materials in the OPD layer stacking. This device architecture is less sensitive to the exact layer thicknesses since the optical micro-cavity is less effective compared to the top-type architecture. Therefore, the bottom-type is a good platform for testing whether the overall layer stacking is well suited for the OPD functionality. However, bottom-type architecture is not suited for the implementation into the opto-plasmonic module due to the demands of the monolithic integration. The OPD has to be realized on top of the source electrode of the OLET. Therefore, top-type architecture is optimized in a second step (see infra).

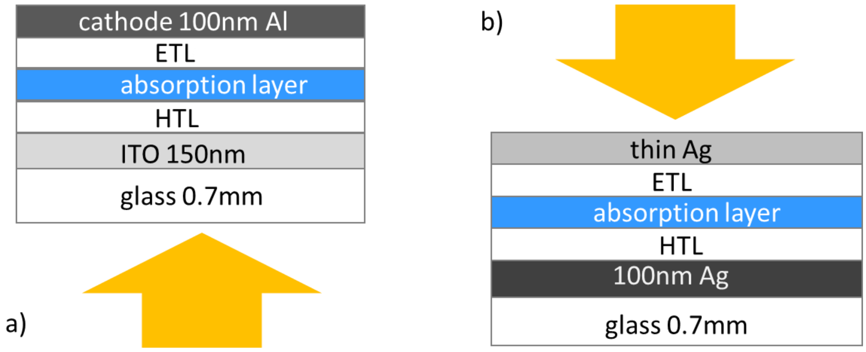

Figure 1 Basic OPD device architectures according to the side of incident light: a) "bottom-type", b) "top-type". Yellow arrows show the direction of incident light.

A layer stack comprising HTL, AL and ETL was chosen in both cases (bottom-type and top-type). In the case of bottom-type OPDs, a 100 nm thick aluminium layer and a 150 nm thick Indium-tin-oxide layer were used as top and bottom electrodes, respectively. In case of top-type OPDs, a semi-transparent thin silver layer and a 100 nm-thick silver layer were used as top and bottom electrodes, respectively. The HTL is a mixture of hole transport material and a p-dopant. Specifically, in the present work, buckminster fullerene (C60) is used as ETL. The AL is a blend of specific phthalocyanines and C60: manly this layer is optimized in terms of material choice and fabrication conditions in the following of the document.

The deposition of the organic and metal layers of the OPD was carried out by vacuum thermal evaporation (VTE). Patterning of these layers was realized by using fin metal masks (FMM).

3 OPD development for MOLOKO application

The spectral sensitivity of the OPD needs to be optimized with respect to the emission spectrum of the OLET light source and with respect to the spectral response of the nanoplasmonic grating. The OLET emission spectrum is centred at 766 nm as discussed in deliverable 2.1 (see Figure 2). The response of the plasmonic grating is described by the so-called reflectance ratio which compares the reflectivity of the grating in case of a solution/analyte of interest with respect to a blank reference (see D1.2). The plasmonic grating is optimized for maximum signal modulation at the OLET maximum emission at 766 nm. Thus, the objective of the OPD optimization is achieving maximized sensitivity at a wavelength of 766 nm.

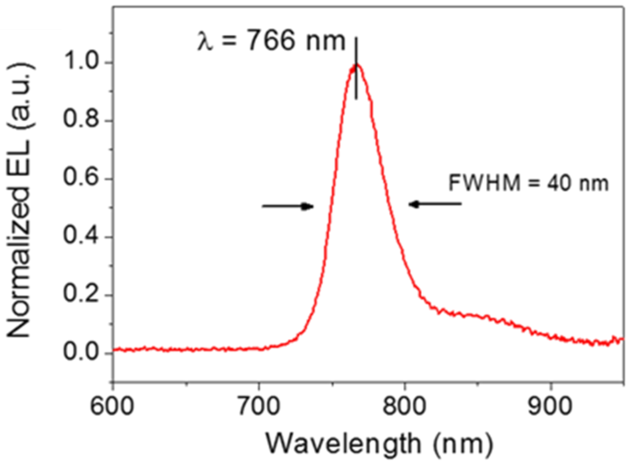

Figure 2 Electroluminescence spectrum of Alq_3: Pt(tpbp)- based OLETs.

Two different phthalocyanine species were investigated as absorber material: ZnPc and ClAlPc. The molecular structures of both molecules are given in Figure 3. The absorptance spectra of 50 nm thin films of mixed layers of ZnPc:C60 and ClAlPc:C60 (ratio 1:1), respectively, are shown in Figure 4. Both layers show maximum absorptance below the target value of 766 nm but the materials are still absorbing in the spectral range of interest.

The target of the OPD development is to maximize the OPD sensitivity at the specific wavelength range by the optimization of the layer OPD stack in the top-side architecture which is needed for monolithic integration.

A basic test sample layout, as shown Figure 5, was used for the OPD stack development. There are four devices on a 35 mm x 50 mm glass substrate (active areas marked by yellow dashed lines in Figure 5). The active area of each device is 22.2 mm2. The devices are encapsulated with a cavity glass lid filled with nitrogen.

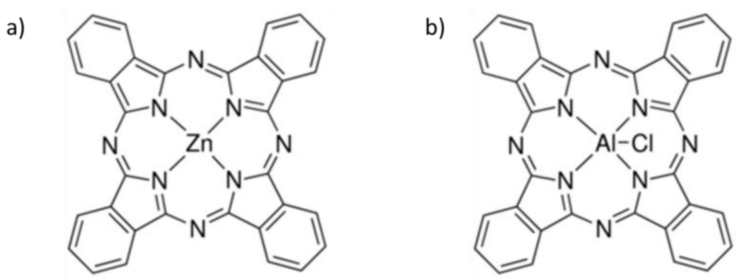

Figure 3. Absorbing molecules which are chosen for OPD development: a) ZnPc (Zinc-Phthalocyanine) b) ClAlPc (Chlor-Aluminium-Phthalocyanine).

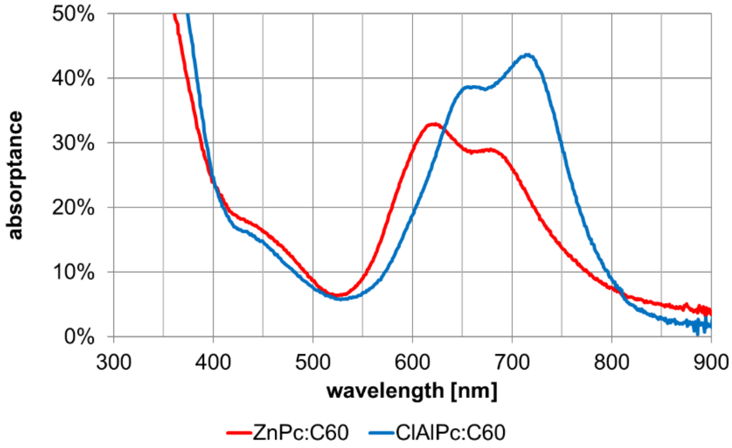

Figure 4. Absorptance spectra of 50 nm thin films of mixed layers of ZnPc:C60 (red curve) and ClAlPc:C60 (blue curve) on bare glass. Mixing ratio is 1:1 for both cases.

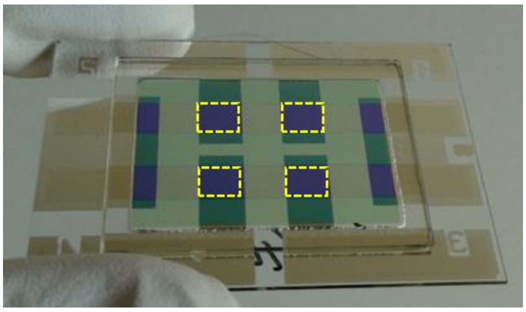

Figure 5. OPD Test device configuration.

In a first step, bottom-type devices were prepared based on ZnPc:C60 and ClAlPc:C60 absorption layers. The expected output of these experiments is to demonstrate that the OPD stacks are effectively working and that the state-of-the-art performance using ZnPc:C60 and ClAlPc:C60 materials can be achieved. As a second step, top-type device with ClAlPc:C60 absorptance layers were prepared and optimized with respect to maximum sensitivity at 766 nm. By considering only the absorbance profile, ClAlPc:C60 is expected to be the better tailored for the coupling with the OLET whose emission spectrum is reported in Figure 2. However, photophysical processes as charge transfer and charge transport that master the photocurrent generation and collection in OPD devices are to be considered and optimized. In order not to exclude a-priori possible interesting results in a real-working device, it is ongoing therefore the investigation of the use of ZnPc:C60 material in a top-type architecture as well (data not reported here).

The most important parameter of the OPD with respect to the application in the optoplasmonic module is the EQE. This value describes the number of charge carriers extracted from the device with respect to the number of incident photons in a specific wavelength range. In principle, photocurrent can be measured in reverse bias or at zero bias. Due to measurement settlements of the characterization system at the Fraunhofer FEP, all measurements herein reported ate carried out at zero voltage (20 mV modulation voltage).

Figure shows the EQE data of a bottom-type ZnPc:C60 based device. The OPD shows strong sensitivity in the range of 550-750 nm with maximum EQE up to 50%, however, a remarkable drop of EQE is then observed for increasing light-collection wavelengths. The dashed line plotted in Figure reports the simulation of layer absorptance, *i.e.* the percentage of photons which are absorbed in the AL relative to the total number of incident photons at a specific wavelength. The layer absorptance was calculated using commercial simulation software SETFOS [4]. The optical constants of all organic materials in the stacks were determined based on ellipsometry measurements on single organic layers. The simulated shape of the EQE curve shows good agreement with measured data. Absolute values cannot be compared since the calculation is a pure optical simulation.

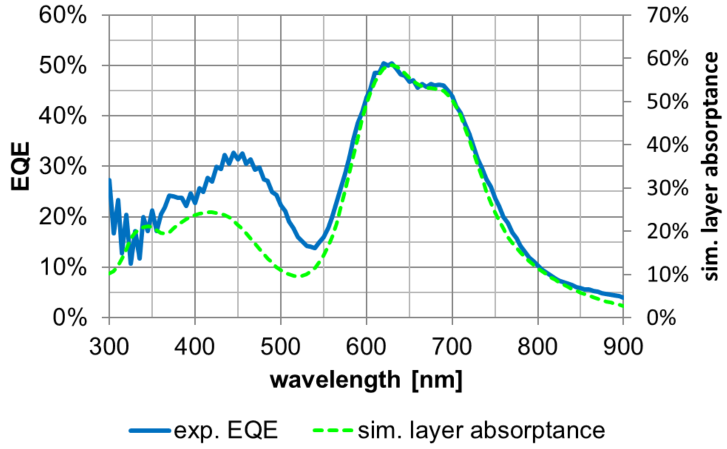

Figure 6. External quantum efficiency of bottom-type ZnPc-based OPDs. The solid blue line shows experimental data, the dashed green line shows the simulated layer absorptance.

In order to compare the performance of the as-realized devices with respect to the state of the art, density - voltage (J-V) curves were measured under AM1.5 illumination (sun spectrum, 1000W/m^2). As a general exemplum of the achieved benchmark, we report the J-V curve of the bottom-type ZnPc-based OPD in Figure A power conversion efficiency of 3.03% was determined from these curves which is in good agreement with literature data reported in literature, i.e. 2.3% [1] and 3.4% [2 Moreover, these data highlight the high device quality, which allows to efficiently drive the OPD at short circuit conditions without the need to operate under reverse bias to ensure high performance. However, the achieved EQE performance is under the expectations in view of the sensor engineering, other material system has been probed.

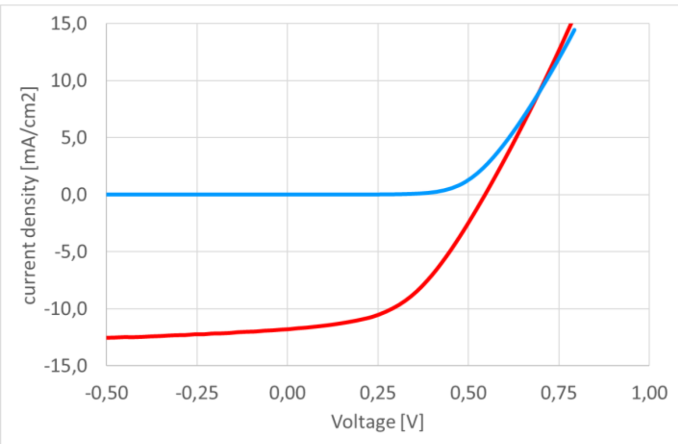

Figure 7. I-V-curve of a bottom-type ZnPc-based OPD (red: under illumination with AM 1.5, blue: dark measurement). Efficiency is 3.03%.

Figure shows the bottom-type OPD performance for devices based on the ClAlPc:C60 blend system. The graph shows the effect of the variation of the ClAlPc:C60 mixing ratio on EQE. The simulation of the layer absorptance is displayed as green dashed line. The shape of the simulated absorptance is in good correspondence with the measured EQE data.

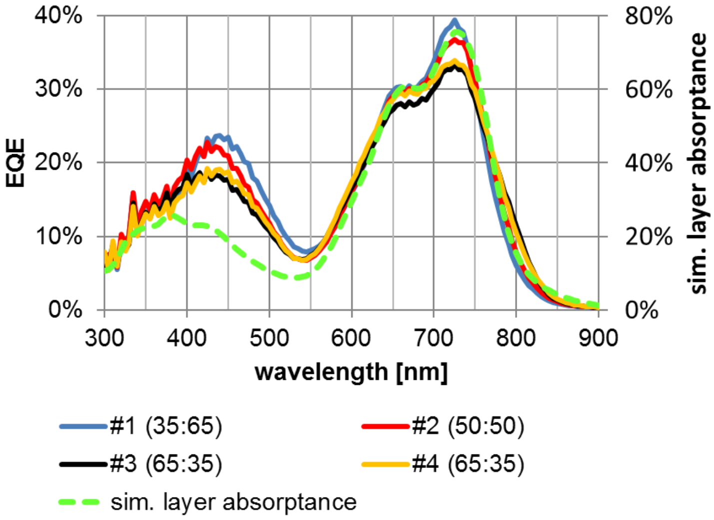

Figure 8. External quantum efficiency of bottom-type ClAlPc-based OPDs. The ClAlPc:C60 mixing ratio was varied in 3 steps (35:65, 50:50, 65:35). The dashed line shows the simulated layer absorptance in case of the 50:50 mixing ratio.

In the next step, top-type OPDs were prepared. As in the case of the bottom-type OPD, the device structure is comprised of bottom contact, HTL, AL, ETL and top contact. Moreover, in case of top-side absorbing devices which are considered in the M1 configuration of MOLOKO sensor (see D1.3), the use of an additional organic layer on top of the semi-transparent top contact which acts as a refractive index matching layer (IML) can improve the EQE. The corresponding EQE curve of top-type OPDs with index matching layer and ClAlPc:C60 absorptance layer is shown in Figure (solid blue line). The profile of the EQE spectrum shows a peak which is well-coupled the emission profile of the OLET emitter at 766 nm (Figure 2).

The measured EQE curve is compared to the calculated absorptance of the AL (dashed green line in in Figure). The maximum simulated absorptance at 765 nm is 66.7%. Experimental EQE at 766 nm is 18.6% which is higher than the ZnPc material-system in bottom-type OPD configuration.

The EQE values are lower compared to the expected layer absorptance: this evidence can be explained by the fact that the light absorption process is only the first step towards photocurrent collection, given that charge transfer and charge transport processes must be optimized.

However, both the experimental EQE and the simulated layer absorptance show maximum values at the target wavelength of 766 nm.

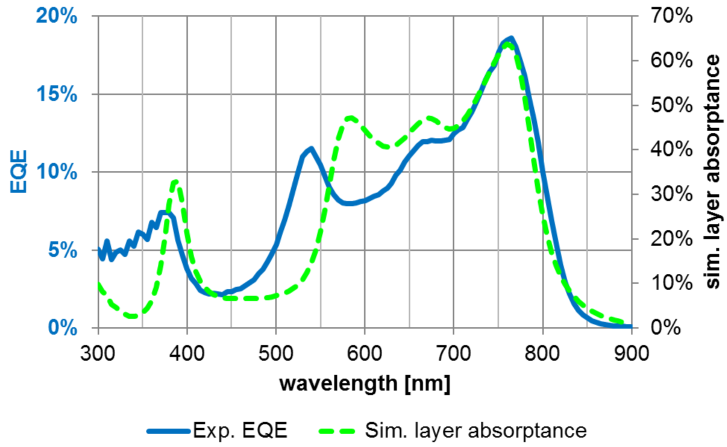

Figure 9. EQE and layer absorptance for the ClAlPc-based top-type device with optimized film thicknesses obtained by the simulations.

The effect of the index matching layer is illustrated by Figure where measured EQE spectra for identical OPDs with and without IML are reported. EQE at 765nm drops from 18.6% to 13.3% if no IML is deposited on the top contact. Thus, this optimization step in the fabrication process of OPD for the implementation into the MOLOKO sensor is mandatory.

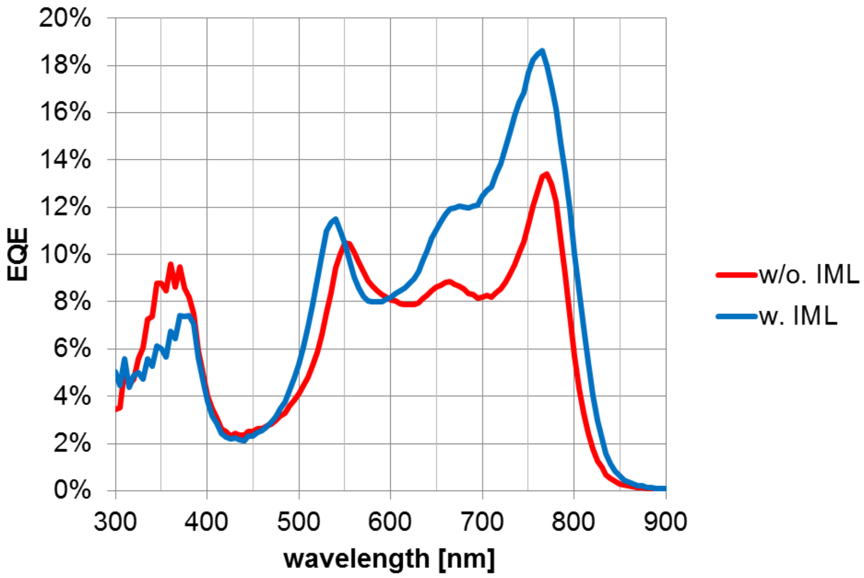

Figure 10. Measured EQE spectra for identical top-type OPDs with and without IML.

4 Conclusions

In a first step, bottom-type OPDs with state-of-the-art performance were prepared using two benchmark absorber layers, such as ZnPc:C60 and ClAlPc:C60. Within the MOLOKO project, the OPD has to be realized on top of the source electrode of the OLET. Therefore, top-type architectures were optimized by modifying the device structures for absorption from the glass-ITO substrate.

The layer stacking of the final top-type OPD is comprised by hole transport layer, absorption layer, electron-transport layer, top contact and refractive index-matching layer. An EQE of 18.6% was achieved at the target wavelength range around 766 nm using ClAlPc:C60 as absorption layer which is considered at this stage of development of WP2 the best material-system for the implementation in the MOLOKO sensor.

This device performance together with the simulated spatial light distribution reported in D1.3 will be taken as input parameter for the development of the layout of the monolithically integrated organic photonic module, and finally of the optolasmonic module once the nanoplasmonic grating reflectance efficiency is taken in consideration (please refer to upcoming D2.3 at M12).

It is planned to continue the optimization work of the top-type OPD. This includes further optimization of ZnPc:C60 based devices in top-type geometry (only preliminary tests have been performed by now) as well as continuing the search for commercially available absorber materials with higher absorbance at 766 nm.

5 References

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