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Organic optoelectronics for lab-on-chip fluorescence detection

Organische Optoelektronik für Lab-on-Chip-Fluoreszenzdetektion

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Abstract: We present two designs of organic optoelectronics for compact lab-on-chip fluorescence detection. In the first configuration, organic light emitting diode (OLED) and organic photo diode (OPD) are fabricated on separate substrates. Transmission fluorescence measurements are performed using a dichroic colour filter to suppress parts of the OLED emission spectrum overlapping with the spectral OPD sensitivity. Fluorescence of Acid Yellow 73 in water is measured for concentrations down to 0.52 µM. For the second configuration, OLED and OPD are processed in cylindrical geometry on a single substrate for a more compact system operated in reflection.

Keywords: Organic optoelectronics, fluorescence, lab-on-chip, OLED, OPD, sensor.

Zusammenfassung: Wir präsentieren zwei Designs organischer Optoelektronik für ein kompaktes Lab-on-Chip System zur Fluoreszenzdetektion werden kann. In dem ersten Ansatz werden organische Leuchtdiode (OLED) und organische Fotodiode (OPD) auf separaten Substraten hergestellt. Fluoreszenzmessungen werden in Transmission unter Verwendung eines dichroitischen Farbfilters durchgeführt. Durch diesen Filter werden Teile des OLED Spektrums unterdrückt, die mit der OPD Sensitivität überlappen. Die Fluoreszenz von Acid Yellow 73 in Wasser wird für Konzentration bis 0.52 µM gemessen. Im dem zweiten Ansatz werden OLED und OPD in einer zylindrischen Geometrie zusammen auf ein Substrat für ein noch kompakteres System prozessiert, das in Reflektion betrieben wird.

Schlüsselwörter: Organische Optoelektronik, Fluoreszenz, Lab-on-Chip, OLED, OPD, Sensor.

1 Introduction

The demand for compact and fast operating systems has been increasing in the field of life sciences over the last years. Previously, we demonstrated biosensor systems based on optical refractive index measurements employing nanostructured transducer surfaces and compact light-emitting diode (LED) and camera/photodiode detection systems [1, 2]. Lab-on-chip systems promise short analysis times and are applicable at the point of care [3]. Fluorescence measurements are a wide-spread method to detect cells [4] and antigens [5]. Fluorescence dyes are coupled in preparation steps to the substance of interest. Fluorescence under laser excitation marks the presence of the substance of interest and the signal amplitude gives information on the substance concentration. Traditionally, these measurements are performed in central laboratories. Organic light emitting diodes (OLED) and organic photo detectors (OPD) may be processed on a wide variety of substrates. Thus, they hold the promise for integrating the optoelectronic detection system with the microfluidic chip. First fluorescence measurements with organic optoelectronics have been demonstrated [6, 7, 8]. We demonstrated the fabrication of OLED and OPD on a single substrate using cost-efficient wet processing [9]. Here, we present two designs of organic optoelectronics for compact lab-on-chip fluorescence detection – one operated in transmission and one operated in reflection.

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2 Transmission system

2.1 Device fabrication

In a first system, we fabricated four OLEDs and four OPDs separately on 25 x 25 mm² large glass substrates. Each optoelectronic device has a functional area of 5 x 5 mm². Via UV (ultraviolet) lithography and wet etching, the 120-nm thick indium tin oxide (ITO) layer is structured to form anode contact pads. For this purpose, the glass coated with ITO is cleaned first in acetone and then in isopropanol in an ultrasonic bath for 15 minutes, each. After dehydrating the sample for 10 minutes at 150°C on a hotplate the sample surface is activated by oxygen plasma treatment (2 minutes, 8 sccm O_2 and 300 W RF power) such that the surface becomes hydrophilic for better adhesion of the photo resist (AZ1518, *MicroChemicals*). The resist is spin coated at 2850 rpm for 30 seconds and is preheated on a hotplate at 100°C for 60 seconds. With a mask aligner the resist is excited with UV light to form the design of the anode pads. After resist development (30 seconds with developer AZ726 MIF, *MicroChemicals*, stopped with deionised (DI) water) the resist is hardened at 120°C for 50 seconds. To remove the excess ITO and form the ITO anode pads the sample is etched with 30% hydrochloric acid for 10 minutes. After stopping the etching process with DI water, the photo resist is stripped of the sample by using acetone and isopropanol in an ultrasonic bath for 7 minutes, each. Before the OLED and OPD are processed the samples are again dehydrated and treated with oxygen plasma.

For the OPDs poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) is spin coated (1 min, 3500 rpm) on top of the ITO achieving a layer thickness of 90 nm. After baking the sample (150°C, 5 min) the mixture of 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C61 and poly(3-hexylthiophene) (PCBM: P3HT, each 30 mg) dissolved in 2 ml dichlorobenzene is spin coated as active layer (1 min, 2000 rpm).

By thermal evaporation the cathode pads consisting of lithium fluoride (LiF) and aluminium (Al) are deposited on top using a shadow mask (figure 1a and c).

Every layer of the blue emitting OLED is deposited by thermal evaporation on top of the ITO anode pads, as it is shown in figure 1c. Here, molybdenum trioxide (MoO_3) is used as hole injection layer (HIL), N,N'-Bis(naphthalen-1-yl)-N,N' -bis(phenyl) benzidine (NPB) as hole transport layer (HTL), and 4,4'-Bis(9-ethyl-3-carbazovinylene)-1,1'-biphenyl (BPhen) as electron transport layer (ETL) as well as hole blocking layer (HBL). For the emitter layer 4,4'-Bis(2,2-diphenylvinyl)-1,1'-biphenyl (DBVBi) is doped with 5% of 4,4'-Bis(9-ethyl-3-carbazovinylene)-1,1'-biphenyl (BCzVBi) to generate a narrowband emission spectrum in the blue spectral range matched with the fluorescence absorption. Finally, all devices are encapsulated with two-component adhesives and a glass plate.

2.2 Measurement system and results

For good excitation, the absorption spectrum of the fluorescence dye and the OLED emission spectrum should be aligned such that the spectral overlap is maximized or the spectral maxima lie on top of each other. For the following fluorescence measurements, the fluorescence dye Acid Yellow 73 (*Sigmal Aldrich*) with an absorption maximum at 430 nm is used (figure 2).

Additionally, for a good signal-to-noise ratio the emission maximum (537 nm) of Acid Yellow 73 and the

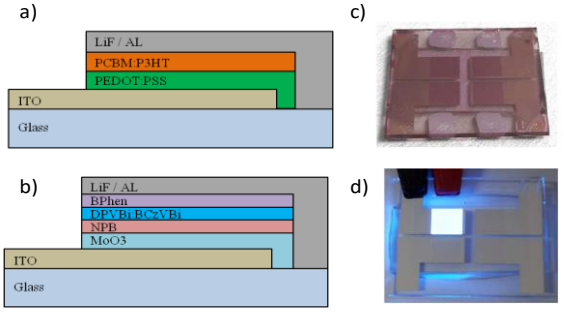

Figure 1: (a) Schematic of OPD stack (glass 1 mm, ITO 120 nm, PEDOT:PSS 90 nm, PCBM:P3HT 70 nm, LiF 0.8 nm, Al 150 nm). (b) Schematic of OLED stack (glass 1 mm, ITO 120 nm, MoO_3 10 nm, NPB 20 nm, DPVBi:BCzVBi 21nm (95%:5%), BPhen 30 nm, LiF 1nm, Al 151 nm).

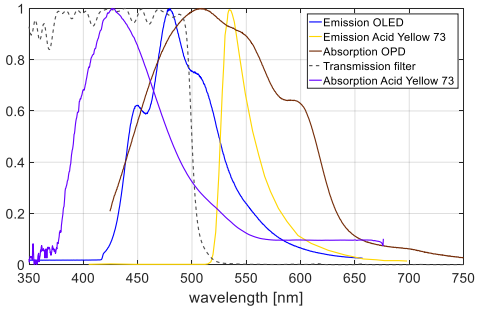

Figure 2: Emission spectra of OLED and the fluorescence dye Acid Yellow 73 as well as the absorption spectra of the OPD material and Acid Yellow 73 are shown. The grey dashed line represents the transmission spectra of the dichroic colour filter.

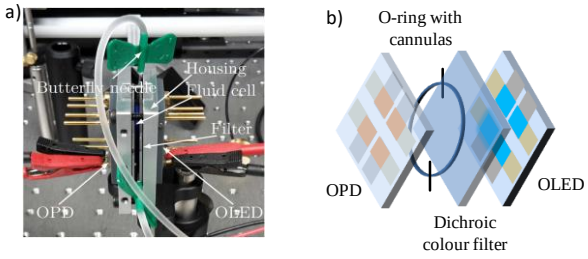

Figure 3: (a) Picture and (b) schematic of transmission measurement setup.

absorption maximum of the OPD material should be in a good spectral agreement. The dichroic colour filter suppresses parts of the OLED emission spectrum overlapping with the spectral OPD sensitivity to reduce the background signal and just let the fluorescence signal to the OPD.

Fluorescence measurements are performed by diluting Acid Yellow 73 in distilled water in various concentrations. As depict in figure 3a and b, for these transmission measurements an o-ring is pierced with two butterfly cannulas for analyte exchange and then is sandwiched between the OPD on the left side and a dichroic colour filter in front of the OLED on the right side. For the measurement results shown in figure 4, distilled water is filled inside the fluid cell to generate a baseline signal. Then, the water is replaced by the Acid Yellow 73 water solution and an increase of the photo current is obtained due to the fluorescence signal.

After washing again with water, the signal decreases to its baseline level. Afterwards the Acid Yellow 73 concentration is reduced continuously. Although, the spectra are not perfectly aligned to each other, the different concentrations are observed as levels in the photo current signal.

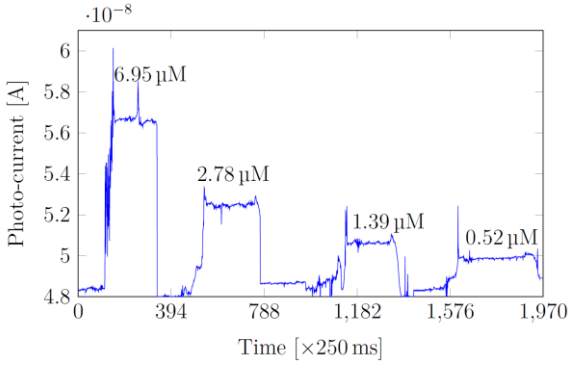

Figure 4: Fluorescence measurement with different concentrations of the fluorescent dye Acid Yellow 73 in water.

3 Reflection system

3.1 Concept and device fabrication

For further miniaturization a reflection system with OLED and OPD on a single substrate is investigated. The system furthermore avoids filter components. As depicted in figure 5, we now choose the fluorescence dye DY-480XL (Dyomics GmbH) because it possesses a large Stokes shift and the absorption and emission bands are separated spectrally. This leads to a reduction of the overlap between the OLED and the dye emission spectrum or the spectral sensitivity of the OPD. Because of this the background signal during fluorescence detection is reduced.

In this second system, we employ only small-molecule organic devices deposited by thermal evaporation. A cylindrical geometry is realized as shown in figure 6, where the anode pads are fabricated as described before via UV lithography. The blue emitting OLED with DPVBi as emitter material is fabricated around the OPD using separate shadow masks. This emitter material is aligned to the absorption spectrum of the fluorescence dye (figure 5) and thus promising for better fluorescence excitation compared to the first approach.

Here, MoO3 is used as HIL, Tris(8-hydroxyquinolinato)aluminium (Alq3) as protection layer to avoid oxidation processes due to the MoO_3 within the OLED stack, NPB as HTL, BPhen as ETL as well as HBL.

The OPD has fullerene C60 and Copper(II) phthalocyanine (CuPC) as active materials and BPhen as ETL. Finally, LiF and Al are deposited on top of both stacks as cathode pads and everything is encapsulated by using a 2-component adhesive and a glass substrate. The

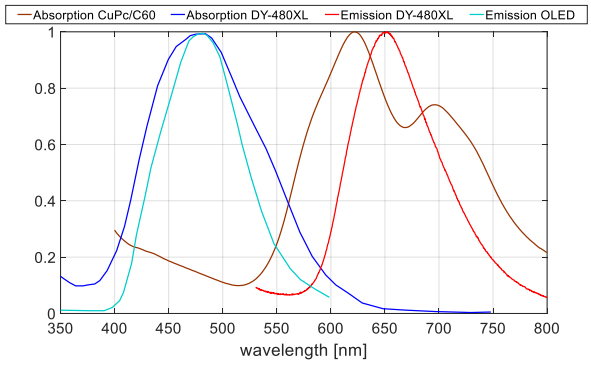

Figure 5: Emission spectra of OLED and the fluorescence dye DY-480XL as well as the absorption spectra of the OPD material and DY-480XL are shown.

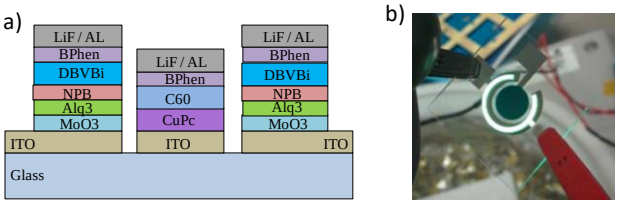

Figure 6: (a) Schematic of the processed OLED (glass 1 mm, ITO 120 nm, MoO_3 10 nm, Alq_3 1.5 nm, NPB 30 nm, DPVBi 20 nm, BPhen 30 nm, LiF 1 nm, Al 200 nm) and OPD (glass 1 mm, ITO 120 nm, CuPc 40 nm, C60 30 nm, BCP 12 nm, LiF 1 nm, Al 200 nm) stacks. (b) Picture of the processed device with OLED and OPD arranged in a cylindrical geometry.

picture in figure 6b shows the fabricated OLED-OPD sample and the luminous OLED. The OPD posses a fill factor of $FF = P_{max} \,/\, U_{OC} \cdot I_{SC} = 0.45$, with the maximal power $P_{max} = U_{MPP} \cdot I_{MPP}$ in the operating point (U: voltage, I: current, MPP: maximal power point), the open circuit voltage U_{OC} and the short circuit current I_{SC}. This arrangement of OLED and OPD is scalable and thus promising for miniaturized, multi-agent lab-on-chip systems.

Conclusion

We demonstrated two different designs of organic optoelectronics for lab-on-chip fluorescence detection and their fabrication. The first setup consists of OLED and OPD on separate substrates. Using an additional dichroic colour filter in front of the OLED transmission fluorescence measurements are performed successfully using the OLED as excitation source and the OPD for fluorescence detection. Different fluorescence dye concentrations down to 520 nM Acid Yellow 73 are clearly observed.

For the second approach, the OLED and OPD spectra are aligned to a fluorescence dye with a large Stokes shift to get a better separation of excitation and emission spectra. Additionally, OLED and OPD are processed successfully via thermal evaporation on one substrate for a more compact and filter free measurment setup. The next steps are to perform fluorescence measurements with varying concentrations of the fluorescent dye to investigate the behaviour of the photo current signal and to determine the limit of detection.

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