Electronic Supplementary Information (ESI)

Luminescence lifetime-based capillary oxygen sensor utilizing monolithically integrated organic photodiodes

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Sensor configuration and setup

The organic photodiodes show a layered structure, where 100 nm thin organic active layers are sandwiched between two different metal electrodes: a 7 nm thin semitransparent sputtered gold bottom electrode and a silver top electrode with a thickness of 150 nm. Classical Tang-type pn-heterojunction devices consist of p-type conducting copper phthalocyanine (CuPc) and n-type perylene tetracarboxylic bisbenzimidazole (PTCBI). We used a 20 nm thin CuPc layer and a 30 nm thin PTCBI layer. We optimized this device design by introducing a molybdenum oxide (MoOx) as well as a Bphen (4,7-diphenyl-1,10-phenanthroline) layer in the OPD layer stack. A 30 nm thick Bphen layer serves as a transparent electron conducting material[i]. A 5 nm thin MoO_x layer acts as a hole-injection layer[ii]. The deposition of the organic as well as the metal layers is done by room-temperature vacuum sublimation (evaporation pressure < $3x10^{-5}$ mbar). For reproducible growth conditions the organic source materials are sublimed from effusion cells. During the evaporation process the capillaries were rotated to achieve good coverage and thickness uniformity all over the glass wall. Film thickness and deposition rate are monitored by a quartz crystal monitor during film deposition. All the structuring is done via conventional shadow masks. The completed devices are not packaged in an inert atmosphere as oxygen and moisture only weakly affect their performance. For electrical wiring the OPD is contacted with small conducting clamps.

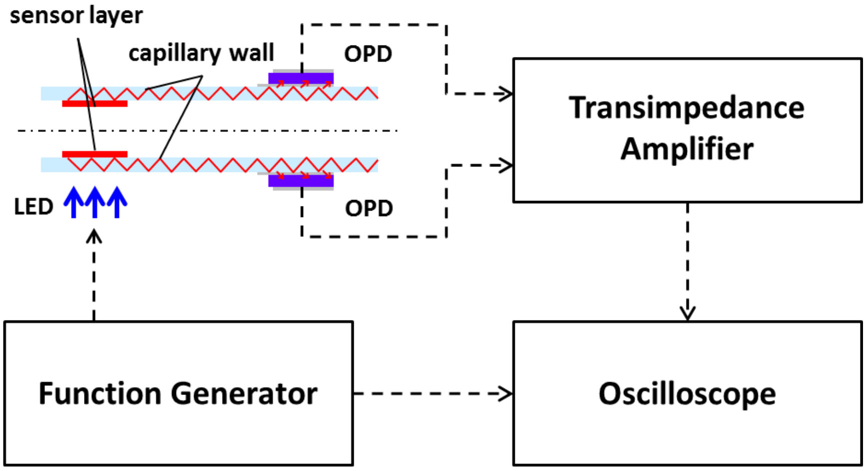
Platinum(II)-5,10,15,20-tetrakis-(2,3,4,5,6-pentafluorphenyl)-porphyrin (PtTFPP) was purchased from Frontier Scientific, Macrolex Fluorescent Yellow 10GN (MFY) from Simon & Werner GmbH (Floersheim am Main, Germany), polystyrene (PS, av. mol. wt. 45,000), and anisole (99.7 %) from Sigma Aldrich (Munich, Germany). Oxygen sensitive coatings on the glass capillaries were fabricated by dipcoating from a solution of 1% PtTFPP, 2% MFY, and 25% (w/w) PS in anisole.

The dip coating procedure yielded visually homogeneous well adhering sensor coatings but none of these coating processes was extensively optimized in terms of thickness homogeneity and reproducibility. Thickness variations of the sensor coatings would influence the response times of the sensors. With the current preparation method response times in the range of seconds were obtained in gas phase what is similar to screen printed sensor layers of 10 µm thickness

Characterization of the capillary oxygen sensor by luminescence decay time measurement

Emission Spectra at the end faces of the glass capillary were recorded using an Ocean Optics HR 4000 fiber optic spectrometer coupled to an Olympus BX51 fluorescence microscope. Excitation spectra of sensing layers were recorded using a Tecan Infinite Pro M200 fluorescence microplate reader.

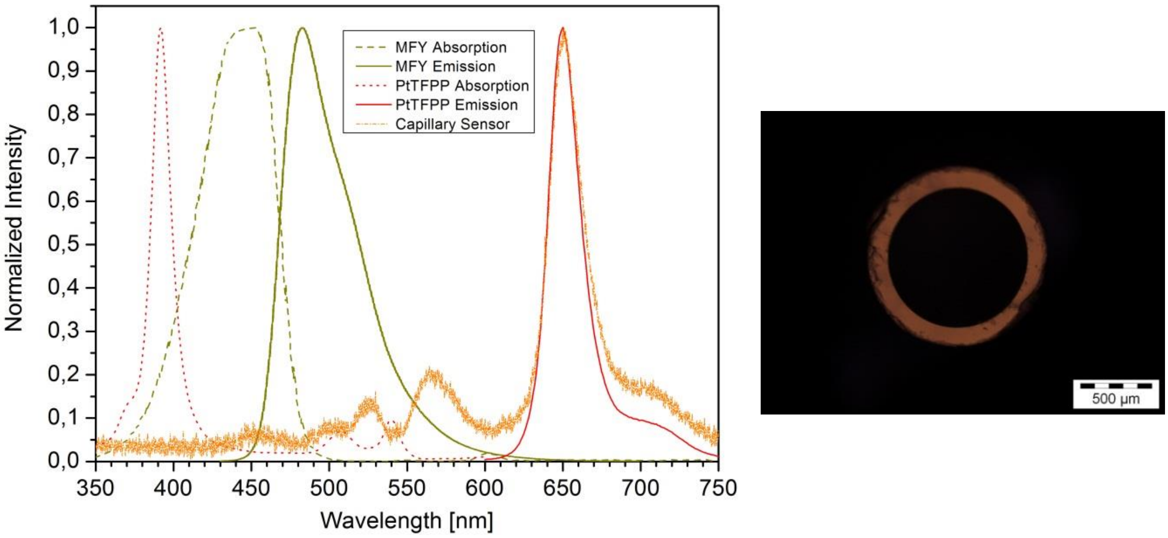
The used electronic measuring setup consists of a Pulse Function Generator 81150A (Agilent Technologies, Santa Clara, USA) and a blue high power LED (based on a thin GaN chip) for excitation, and a prototype printed circuit board (PCB) including a transimpedance amplifier which converts the rather small (10-100 nA range) photocurrent into a voltage. The voltage provided by the transimpedance amplifier stage (including a TIA and a further amplification stage) was recorded using an Infinii Vision MSO7104A oscilloscope from Agilent Technologies for the time resolved decay traces and with a Lock-In amplifier (model SR830 DSP) from Stanford Research Systems for the time trace sensorgram. The data was then processed using OriginPro 8.1 Software (OriginLab Corporation, Northampton, USA). The gas mixtures (O_2 in N_2) for the oxygen-dependent lifetime measurements were adjusted with mass flow controllers (red-y smart controller GSC, Vögtlin, Switzerland).



Supplementary Figure 1: Experimental setup for lifetime measurements

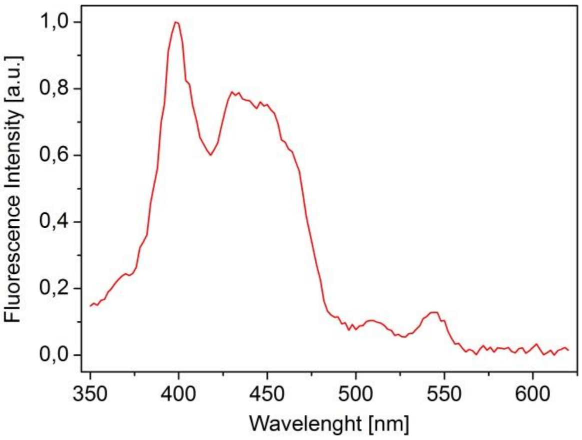
Signal analysis and fitting of decay functions

The acquired signal from the oscilloscope was processed in the following way. For decay time determination by fitting of the measured curves, the first five µs after switching off the LED was discarded in order to reduce interferences caused by the OPD fall times and from residual excitation light. This five µs delay corresponds to approximately four time constants (τ) of the used OPDs (1.3 µs) which means that the background signal has decayed by 98.2 %. Afterward, the data was cropped after three times the expected lifetime of the dye at the respective oxygen concentration. These signals were fitted to single exponential decay functions using the data analysis software Origin Pro 8.6. In order to remove interferences by transient overshooting of the signal the data curves were smoothed using Savitzky–Golay algorithm[iv] integrated into the Origin software package. Reported fluorescence lifetimes are taken as 1/e decrease of the initial signal intensities.



(a) (b)

Supplementary Figure 2: Emission spectrum (a) and fluorescence micrograph (b) measured at the end face of the glass capillary sensor upon excitation with a 450 nm blue LED, together with absorption and emission spectra of the used fluorophores and indicator dyes (MFY and PtTFPP) taken from literature[iii]



Supplementary Figure 3: Fluorescence excitation spectrum of the used sensing layer consisting of PtTFPP and MFY in PS recorded at an emission wavelength of 650 nm.

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[ii] Vishal Shrotriya, Gang Li, Yan Yao, Chih-Wei Chu, and Yang Yang, Appl. Phys. Lett. 88, 073508 (2006)

[iii] Fluorophores.org (http://www.fluorophores.tugraz.at/)

[iv] A. Savitzky, M. J. E. Golay, *Anal. Chem*. 36, 162 (1964)