

1 Supplementary Information

1.1 Reference fibre

The structure of the fluorophore, which was used for the reference fibre is shown in Fig. 1. The spectral properties are: Max absorption/emission = 693/717 nm (toluene), $QY = 36\%$ (A. Gorman, J. Killoran, C. O'Shea, T. Kenna, W. M. Gallagher, und D. F. O'Shea, Journal of the American Chemical Society, 2004, 126, 1061910631).

1.2 Derivation of signal reconstruction

Of course, each component of the used measurement system will distort the signal generated by the DAC $s_{out}(t)$ to some degree due to bandwidth limitations. As both electronic circuits (represented by the transfer functions $H_{U/I}(j\omega)$ and $H_{I/U}(j\omega)$), which convert voltages into light and vice-versa, are designed to act linearly and time-invariant, the output of one system can be derived by performing the convolution of the impulse response with the input signal. As the excitation electronics feature a much higher bandwidth than the emission electronics, the system is simplified by assuming $h_{U/I}(t) = A_{U/I} \cdot \delta(t) \rightarrow s_{exc}(t) = A_{U/I} \cdot s_{out}(t)$. This means the output signal from the DAC is transformed without any distortion into the excitation light signal. The detected emission light $s_{em}(t)$ is convoluted with the impulse response of the emission electronics $h_{I/U}(t)$ to form the final signal $s_{in}(t)$, which is then sampled with the ADC. The above stated relations can be expressed in the frequency domain, where the convolutions transform to simple multiplications:

$$S_{in}(j\omega) = S_{em}(j\omega) \cdot H_{I/U}(j\omega) \quad (1)$$

By using a reference sensor with a very fast emission light decay, its impulse response $h_{ref}(t)$ can be characterized more simply by a dirac-delta distribution $\delta(t)$ with amplitude A_{ref} .

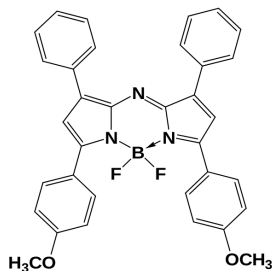


Fig. 1 The chemical structure of the used reference: BF_2 chelate of [5-(4-Methoxyphenyl)-3-phenyl-1H-pyrrol-2-yl][5-(4-methoxyphenyl)-3-phenylpyrrol-2-ylidene]amine

The Fourier-transformation of this impulse response is the constant A_{ref} , and simplifies equation 1 to:

$$S_{in}^{ref}(j\omega) = S_{out}(j\omega) \cdot \alpha \cdot H_{ref}(j\omega) \cdot H_{I/U}(j\omega) \quad (2)$$

$$= \alpha \cdot A_r \cdot S_{out}(j\omega) \cdot H_{I/U}(j\omega) \quad (3)$$

By choosing the right output signal, it is possible to accurately determine the transfer function of the electronic measurement chain, $H_{I/U}(j\omega)$. Of course, the measured signal $\hat{S}_{in}^{ref}(j\omega)$ will have an added noise term, which is assumed to be white noise with a constant noise power with respect to frequency. Therefore the noise density $N_{in}(j\omega) = p_n$ is constant. In order to keep the error term $E(j\omega)$ small, the denominator in the following formula has to be large compared to the noise term for the frequency of interest.

$$\hat{S}_{in}^{ref} = S_{in}^{ref}(j\omega) + p_n \quad (4)$$

$$\frac{\hat{S}_{in}^{ref}(j\omega)}{\alpha \cdot A_r \cdot S_{out}(j\omega)} = \underbrace{\frac{S_{in}^{ref}(j\omega)}{\alpha \cdot A_r \cdot S_{out}(j\omega)}}_{H_{I/U}(j\omega)} + \underbrace{\frac{p_n}{\alpha \cdot A_r \cdot S_{out}(j\omega)}}_{E(j\omega)} \quad (5)$$

A pulse with a width of one DAC-sampling period of the sampling frequency f_s and an amplitude of A_{out} features the signal transfer function as in Eqn. 6. The sinc term falls off slightly for higher frequencies, however, as the highest frequency component in the measurement system is lower than the Nyquist frequency $f_s/2$, the maximum reduction is only 36%. Thus, this function can be used to investigate the electronic system over the whole Nyquist-band, whilst keeping the error term $E(j\omega)$ small enough to be negligible.

$$S_{out}(j\omega) = A_{out} \text{sinc}(f/f_s) \cdot e^{-j\pi f/f_s} \quad (6)$$

The luminescence emission signal $s_{em}(t)$ is generated by a complex set of physical processes when exciting the sensor with a known signal $s_{out}(t)$. It is then detected and converted with exactly the same measurement electronics used for the reference sensor, thus allowing the reconstruction of the exact shape of the emission signal for a known input signal.

$$\frac{S_{in}^{em}(j\omega)}{H_{I/U}(j\omega)} = S_{em}(j\omega) \xrightarrow{\mathcal{F}^{-1}} s_{em}(t) \quad (7)$$

In the case of a non-linear luminescence sensor, it is not longer valid to simplify the emission light signal as done in Eqn. 2. Therefore the use of fast excitation electronics (to render their influence negligible) and the detailed knowledge of the shape of the excitation signal from the DAC is crucial.

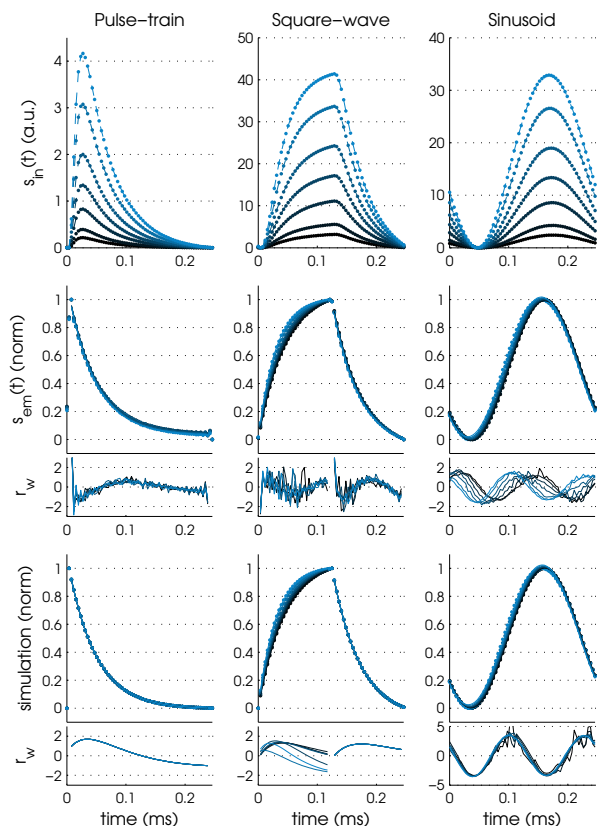


Fig. 2 Signals from a sensor coated with 1 % PtTPTBPF in PS in the absence of oxygen, for different excitation signals. The hue of the lines changes with increasing light intensities from black to blue. Mono-exponential and sinusoidal fits and weighted residuals (r_w) are included in the middle and bottom plots.

1.3 Sampled signals from Pt(II)-based sensor

Electronic distortions of the uncorrected signals from a Pt(II)-based sensor are much more visible due to the shorter luminescence lifetime (see top plots in Fig. 2 and Fig. 3). The shorter lifetime also reduced the amount of sampling points per repetition period compared to the sampled curves of Pd(II) based sensors, as the maximum ADC sampling frequency was limited to be smaller than 300 kHz.

The reconstructed signals (middle plots in Fig. 2 and Fig. 3) show a less significant distortion compared to Pd(II)-based sensors. The residuals for cases when the sensor is flushed with nitrogen indicate that the mono-exponential fit is much more appropriate for the measured data compared to Pd(II) based sensors.

Measurements in air show less distortions as excited luminophores are deactivated much faster due to quenching. The residuals indicate that a multi-exponential fit would represent the data better.

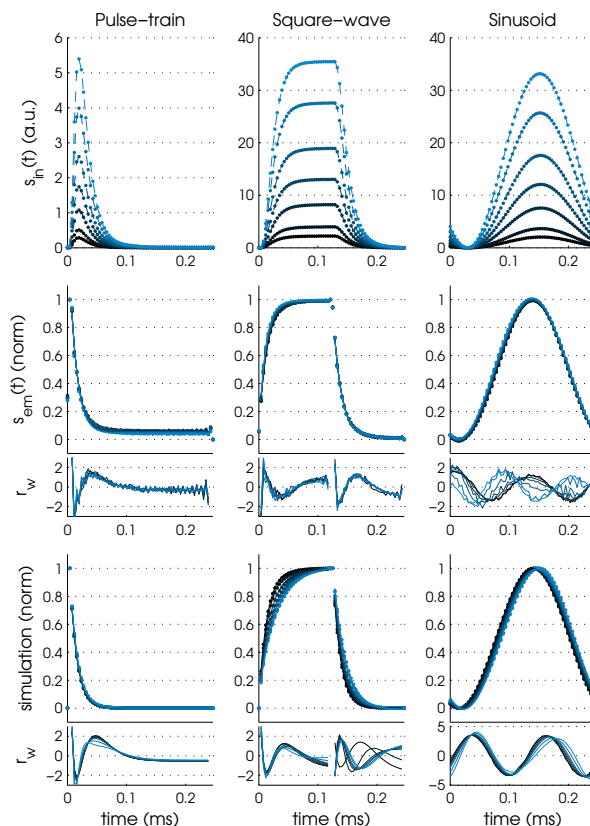


Fig. 3 Signals from a sensor coated with 1 % PtTPTBPF in PS in air, for different excitation signals. The hue of the lines changes with increasing light intensities from black to blue. Mono-exponential and sinusoidal fits and weighted residuals (r_w) are included in the middle and bottom plots.

The simulation results for the fibre flushed with nitrogen (see bottom plots in Fig. 2 and Fig. 3) are very similar compared to measurements. The simulation with quencher show a trend to longer lifetimes with increasing excitation light intensity. This is especially visible in the square wave excitation and cannot be seen in the measured data.

1.4 Determined lifetimes overview

The following graphs allow to compare the effect of the parameters measurement method and luminophore concentration for increasing light intensities against each other. The results of all measured fibres are shown as well as the simulation results. It is clearly visible that the Pd(II)-based sensors are more susceptible throughout all measurement methods to lifetime errors due to the longer lifetime of the triplet state compared to Pt(II)-based sensors.

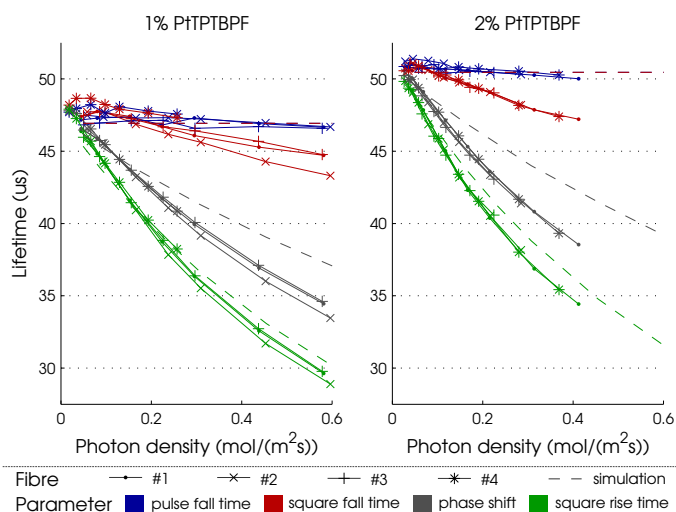


Fig. 4 Results of the different lifetime determination methods for a set of fibreoptic sensors based on 1% (left) and 2% (right) Pt(II) under nitrogen. The different fibres are marked with different symbols, the numerical simulation results are shown as dashed lines. Different lifetime determination methods are color coded.

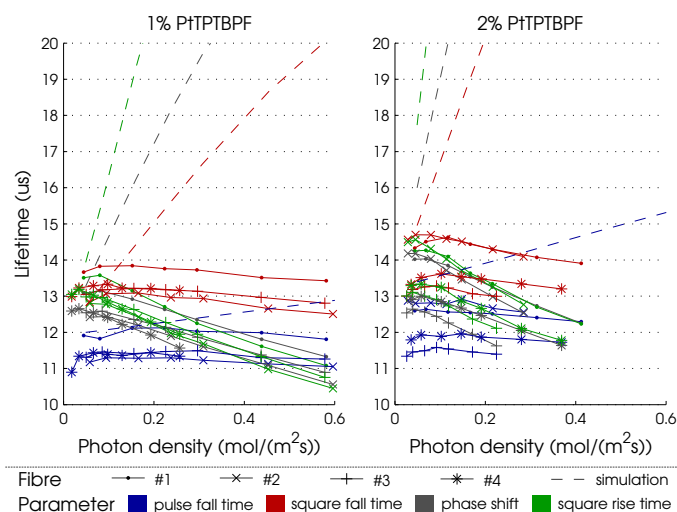


Fig. 6 Results of the different lifetime determination methods for a set of fibreoptic sensors based on 1% (left) and 2% (right) Pd(II) in air. The different fibres are marked with different symbols, the numerical simulation results are shown as dashed lines. Different lifetime determination methods are color coded.

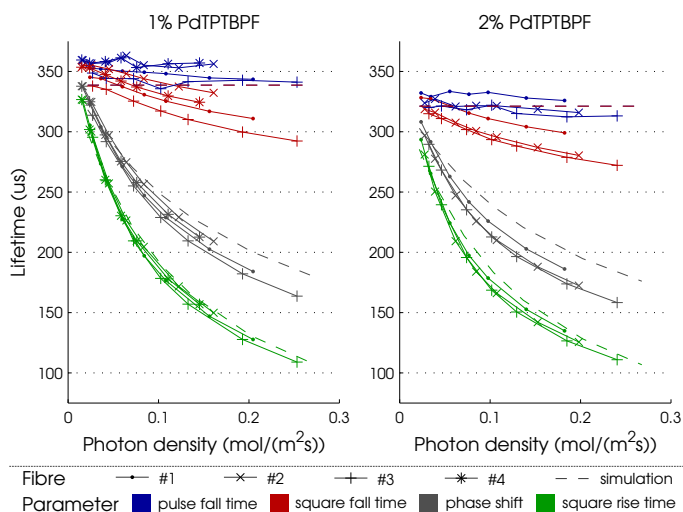


Fig. 5 Results of the different lifetime determination methods for a set of fibreoptic sensors based on 1% (left) and 2% (right) Pd(II) under nitrogen. The different fibres are marked with different symbols, the numerical simulation results are shown as dashed lines. Different lifetime determination methods are color coded.

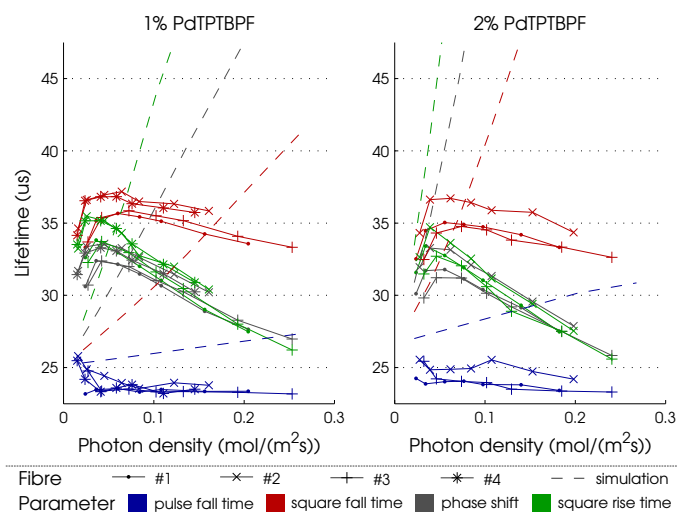


Fig. 7 Results of the different lifetime determination methods for a set of fibreoptic sensors based on 1% (left) and 2% (right) Pd(II) in air. The different fibres are marked with different symbols, the numerical simulation results are shown as dashed lines. Different lifetime determination methods are color coded.