

# Supporting Information

## A TADF emitting Zn(II)-benzoporphyrin: an indicator for simultaneous sensing of oxygen and temperature

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## Experimental Section

**Materials:** Chemicals were purchased from various commercial suppliers (Fluka, Sigma Aldrich, Acros Organics, Roth, ABCR), solvents were purchased from VWR. Polystyrene (**PSAN**), av. MW  $\approx$ 185.000 Da, was purchased from Acros Organics.

**Instrumentation:** NMR spectra were recorded on a Bruker AVANCE III spectrometer equipped with an autosampler (300.36 MHz  $^1\text{H}$ -NMR, 75.53 MHz  $^{13}\text{C}$ -NMR).

**MS:** Mass spectrometry was performed in a positive reflector on a Micromass ToFSpec 2E time-of-flight (TOF) mass spectrometer or on a Matrix-Assisted Laser Desorption/ Ionization (MALDI)-TOF/TOF spectrometer (Bruker UltrafleXtreme).

**Photophysical Properties:** UV-vis spectra were recorded on a VARIAN CARY 50 conc using Hellma Analytics ([www.hellma-analytics.com](http://www.hellma-analytics.com)) optical glass 10 mm precision cuvettes. **Luminescence spectra** were recorded on FluoroLog 3 spectrofluorometer from Horiba Scientific equipped with a R2658 photomultiplier from Hamamatsu ([www.hamamatsu.com](http://www.hamamatsu.com)). **Luminescence decays** were obtained via time correlated single photon counting on a FluoroLog 3 spectrofluorometer equipped with a DeltaHub module controlling a SpectraLED-460 (456 nm) and using DAS-6 Analysis software for data analysis. Data were fitted using a biexponential decay model. **Average lifetimes  $\tau$**  were calculated from the relative amplitudes (B1, B2) and lifetimes (T1, T2) of the individual components from the biexponential model using the equation  $\tau = (B1 \cdot T1 + B2 \cdot T2)$ . A “Quanta- $\phi$ ” integrating sphere-based set-up on a FluoroLog 3 spectrofluorometer (Horiba Scientific) was used to determine absolute quantum yields.

### NMR and MS spectra of the indicator dye Zn-OS

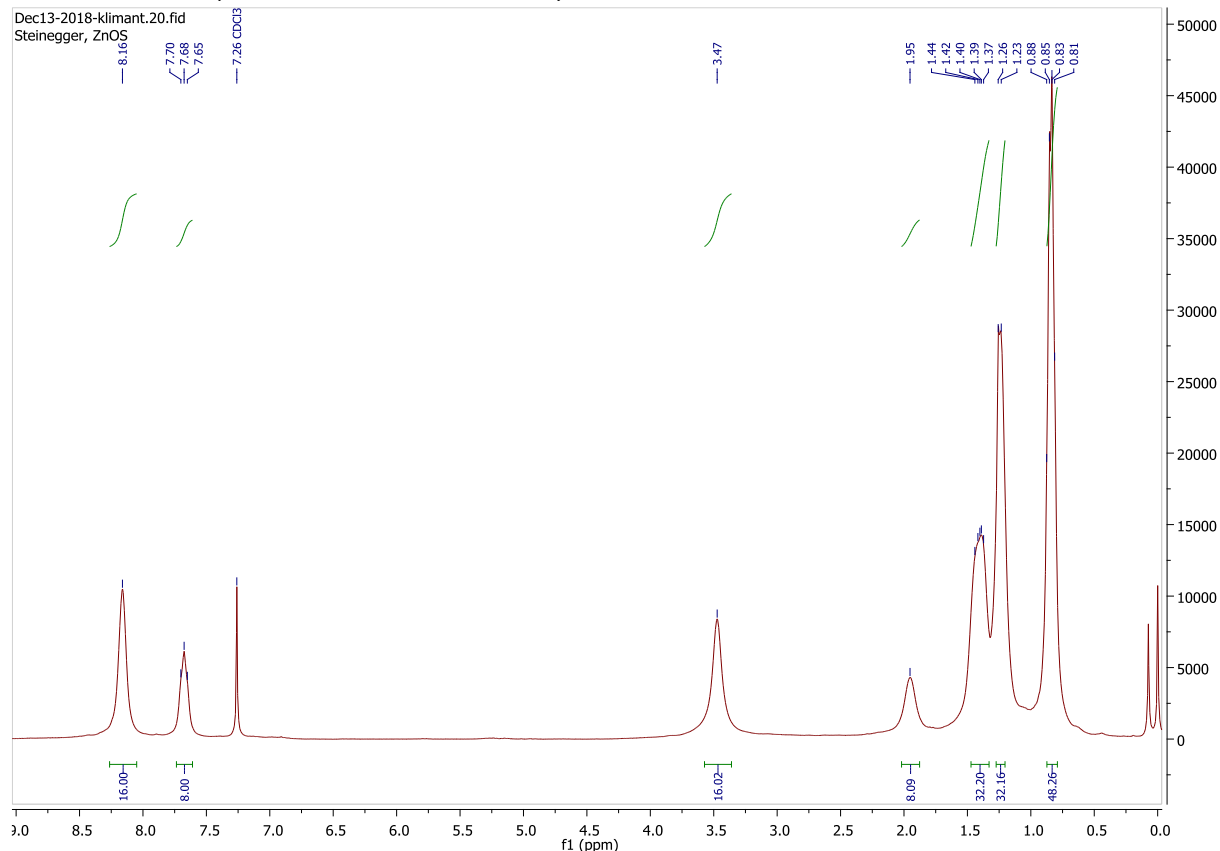


Figure S1.  $^1\text{H}$ -NMR spectrum of Zn-OS in  $\text{CDCl}_3$ .

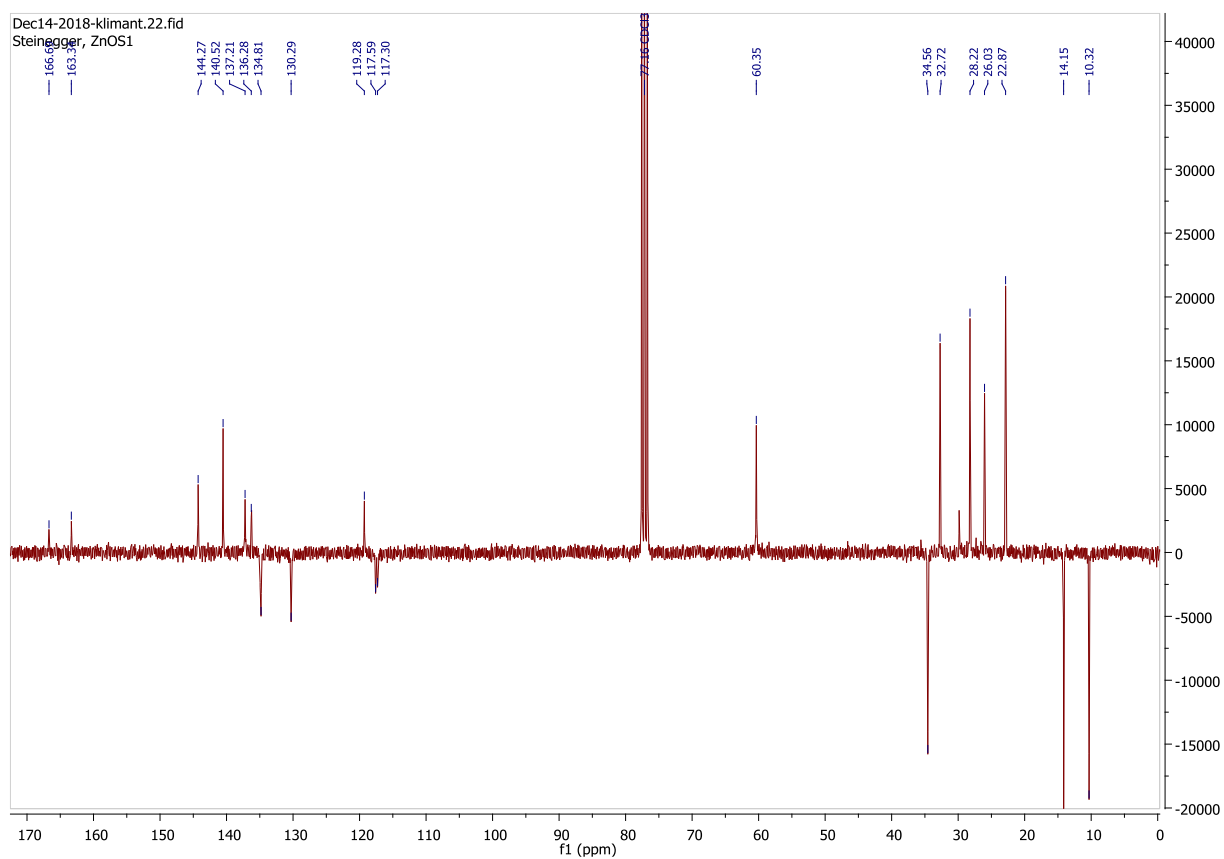


Figure S2. APT-NMR spectrum of Zn-OS in  $\text{CDCl}_3$ .

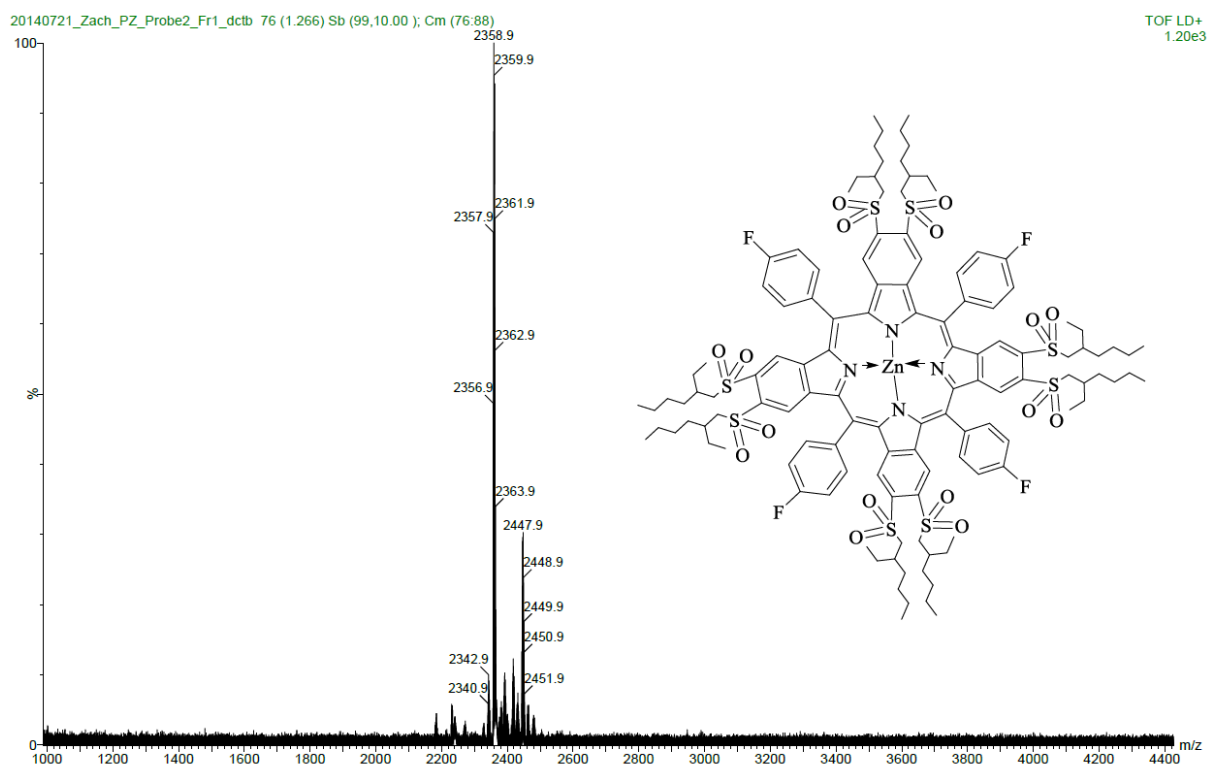


Figure S3. MS spectrum of Zn-OS

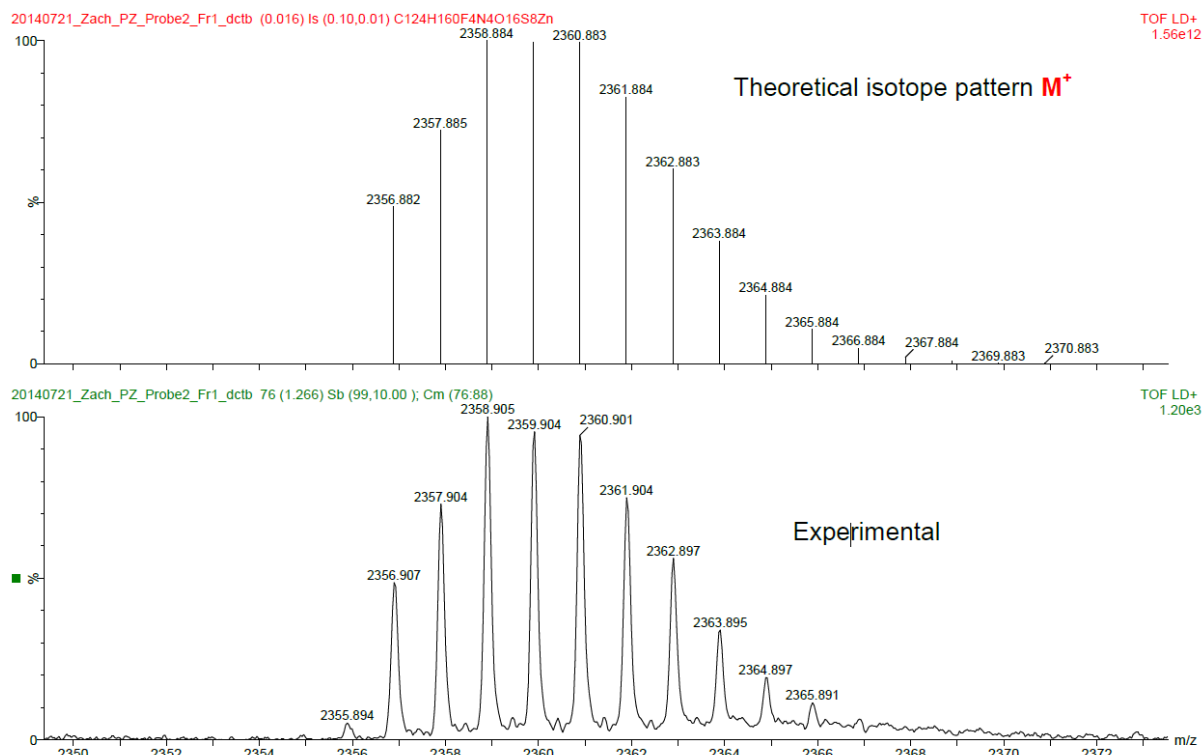


Figure S4. Isotope pattern from the MS spectrum of Zn-OS

## Data Analysis

### Mathematical derivation of the modified dual lifetime referencing (m-DLR) method

In the frequency domain spectroscopy, a dual optical sensor is described as a superposition of two single sine wave functions. As a result, the phase angle and the amplitude obtained at a single modulation frequency are determined by the decay time and the ratio of the intensity of both luminophores.<sup>1</sup> In order to determine all four parameters of the dual optical sensor and to identify the single unique solution, a set of four linear and independent equations has to be set up or some assumptions must be made to simplify the mathematical system.

The overall phase angle and the overall amplitude obtained at a single modulation frequency can be described by the general interference equation for two wave functions (cf. S1 and S2).

$$A = \sqrt{a_{PF}^2 + a_{DF}^2 + 2 \cdot a_{PF} \cdot a_{DF} \cdot \cos(\varphi_{PF} - \varphi_{DF})} \quad (S1)$$

$$\tan(\Phi) = \frac{a_{PF} \cdot \sin(\varphi_{PF}) + a_{DF} \cdot \sin(\varphi_{DF})}{a_{PF} \cdot \cos(\varphi_{PF}) + a_{DF} \cdot \cos(\varphi_{DF})} \quad (S2)$$

where  $a_{PF}$ ,  $a_{DF}$  are the amplitudes of the prompt and delayed fluorescent indicator;  $\varphi_{PF}$ ,  $\varphi_{DF}$  are the corresponding phase shifts.  $A$  is the superimposed amplitude and  $\Phi$  is the corresponding superimposed phase shift at a certain modulation frequency.

<sup>1</sup> ISBN 3-540-67779-8

At low modulation frequencies, meaning in the kHz range, the dye with prompt fluorescent causes no phase shift ( $\varphi_{PF} \approx 0$ )<sup>2</sup>, which simplifies the previous equations (S1 and S2) as follows:

$$A = \sqrt{a_{PF}^2 + a_{DF}^2 + 2 \cdot a_{PF}^2 \cdot a_{DF}^2 \cdot \cos(\varphi_{DF})} \quad (S3)$$

$$\tan(\Phi) = \frac{a_{DF} \cdot \sin(\varphi_{DF})}{a_{PF} + a_{DF} \cdot \cos(\varphi_{DF})} \quad (S4)$$

In order to simplify the linear equation system further, the amplitude is converted into the intensity using the demodulation factor. This transformation is crucial, since the intensity is independent of the modulation frequency in the kHz range. A general description is shown in equation S5.

$$I = \frac{a}{dm} = \text{const.} \quad (S5)$$

where  $a$  is the amplitude and  $dm$  is the demodulation factor of the luminophore at a certain modulation frequency. Since the individual intensity of the luminophore is independent of the modulation frequency, also the ratio of both intensities is constant (see S6). Equation S6 can hereby further simplified, as in the kHz range, the amplitude demodulation of the fast fluorophore is very close to unity.

$$\frac{I_{PF}}{I_{DF}} = \frac{a_{PF} \cdot dm_{DF}}{a_{DF} \cdot dm_{PF}} \approx \frac{a_{PF}}{a_{DF}} \cdot dm_{DF}, \quad dm_{DF} = \frac{1}{\sqrt{1+(2 \cdot \pi \cdot f \cdot \tau)^2}} \quad (S6)$$

The demodulation of the delayed fluorophore is thereby determined by the modulation frequency and the luminescence decay time of the fluorophore.

To simplify the linear equation system further, equation S4 is solved for the amplitude of the fast luminophore and inserted into equation S6.

$$\frac{I_{PF}}{I_{DF}} = \frac{a_{PF}}{a_{DF}} \cdot dm_{DF} = \left[ \frac{\sin(\varphi_{DF})}{\tan(\Phi)} - \cos(\varphi_{DF}) \right] \cdot dm_{DF} = \left[ \frac{\sin(\varphi_{DF})}{\tan(\Phi)} - \cos(\varphi_{DF}) \right] \cdot \frac{1}{\sqrt{1+(2 \cdot \pi \cdot f \cdot \tau)^2}} \quad (S7)$$

Both trigonometric functions can be converted using trigonometric identities as they are described in equation S8 and S9.

$$\cos(\varphi_{DF}) = \cos(\arctan(2 \cdot \pi \cdot f \cdot \tau)) = \frac{1}{\sqrt{1+(2 \cdot \pi \cdot f \cdot \tau)^2}} \quad (S8)$$

$$\sin(\varphi_{DF}) = \sin(\arctan(2 \cdot \pi \cdot f \cdot \tau)) = \frac{2 \cdot \pi \cdot f \cdot \tau}{\sqrt{1+(2 \cdot \pi \cdot f \cdot \tau)^2}} \quad (S9)$$

After applying the trigonometric identities to equation S7, the reduced expression for the intensity ratio is obtained (see equation S10):

$$\frac{I_{PF}}{I_{DF}} = \left[ \frac{2 \cdot \pi \cdot f \cdot \tau}{\tan(\Phi) \cdot \sqrt{1+(2 \cdot \pi \cdot f \cdot \tau)^2}} - \frac{1}{\sqrt{1+(2 \cdot \pi \cdot f \cdot \tau)^2}} \right] \cdot \frac{1}{\sqrt{1+(2 \cdot \pi \cdot f \cdot \tau)^2}} = \frac{\omega \cdot \tau - \tan(\Phi)}{(1+(\omega \cdot \tau)^2) \cdot \tan(\Phi)}, \quad \omega = 2 \cdot \pi \cdot f \quad (S10)$$

The intensity ratio of the fast fluorophore and the delayed fluorophore is constant for different modulation frequencies and only dependent of the overall phase shift  $\Phi$  and the decay time  $\tau$  of the delayed fluorophore. The decay time of the fluorophore with delayed fluorescence is determined by the dual lifetime reference (DLR) technique published by Klimant et al.<sup>3</sup> as it is described in the main part (see equation 1). The linear equation set is therefore unique and the solution of the dual optical system can be identified.

<sup>2</sup> ISBN 3-540-67779-8

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## Correction of the oxygen partial pressures in the gas phase

To check the  $\tau_0$  ( $\tau$  at 0 hPa  $O_2$ ) values for correctness, Zn-OS in PSAN sensor spot were placed at the bottom of 3 mL Supelco vials filled with 2wt%  $Na_2SO_3$  aq. solution with cat.  $CoCl_2$ . After 1 day, overall luminescence phase shifts and overall luminescence amplitudes at both modulation frequencies were measured with a lock-in amplifier as described for the gas phase calibrations. Measurements were conducted at different temperatures (10 – 41 °C).

When comparing the measurement data for 0 hPa  $O_2$  in the gas phase to deoxygenated aqueous sodium sulfite solution, it became apparent that the 0 hPa  $O_2$  concentration during gas phase calibration were not completely oxygen-free. To correct the oxygen concentrations, the values measured in sodium sulphite solution were added to the calibration data and the oxygen concentration are adjusted. This is done according to following procedure. The oxygen partial pressure in the Stern-Volmer equation (3) is substituted by:

$$pO_2 = x * 18.942 hPa + (1 - x) * c + c \quad (S11)$$

where  $x$  is the fraction of the test gas (2.00 vol% in nitrogen) in nitrogen (used by the gas mixing device for adjusting the oxygen partial pressure), 18.942 hPa is the oxygen partial pressure in the test gas adjusted for the altitude,  $c$  is the error in oxygen concentration. The oxygen error can be constant if it appears after the gas-mixing device or can be variable if it depends on the fraction of nitrogen (if the nitrogen gas is the source of oxygen error). It was assumed that the oxygen error originates to 50% from both sources. From the measurement in sodium sulfite solution, the new  $\tau_0$  values are used to calculate  $\tau_0/\tau$  values. Then, the dependency at 25 °C is fitted according to the Stern-Volmer equation (Figure S5) and gives  $c$  of 0.195 hPa. Finally, the corrected oxygen partial pressures are calculated according to eq. S11.

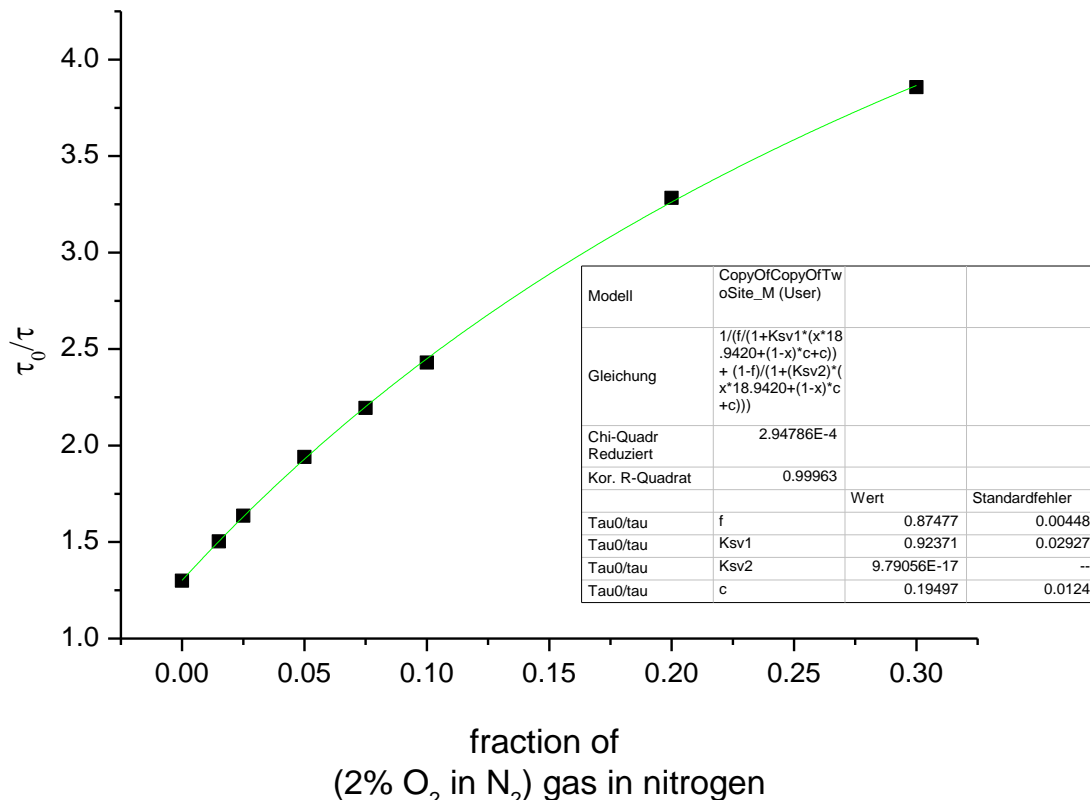


Figure S5. The Stern-Volmer fit used to correct the  $pO_2$  values for oxygen impurity in the calibration gas and the measurement set-up ( $T=25^\circ C$ ).

## Estimation of the singlet-triplet energy gap

For temperature calibrations, temperature was adjusted with a Cary SPV - 1X0 Single Cell Peltier Accessory Peltier element from Varian in combination with a cryostat from Avantor, Model 1150S (us.vwr.com). The PSAN sensor foil was placed diagonally in Hellma Analytics optical glass 10 mm precision cuvettes. The cuvettes were filled with aqueous 2wt% Na<sub>2</sub>SO<sub>3</sub> solution. After temperature adjustment, the cuvettes were thermally equilibrated for 10 min. Temperature was adjusted between 5 and 45 °C. The TADF lifetime was measured at each temperature with the same setup as for the photophysical characterization. The calibration cycle was repeated three times.

Experimental data (Figure S6) was fitted with an Arrhenius type model<sup>4</sup>:

$$\tau = (k_0 + k_1 * e^{\frac{-\Delta E}{k_B T}})^{-1} \quad (S12)$$

where  $k_0$  is the temperature-independent decay rate for the excited-state deactivation,  $k_1$  is a pre-exponential factor,  $k_B$  the  $\Delta E$  the energy necessary for the reverse Intersystem Crossing (ISC), and  $T$  the absolute temperature.  $\Delta E$  corresponds to the singlet-triplet energy gap.

From the fit,  $\Delta E$  was estimated to be  $3.27 \times 10^{-20}$  J or  $1646 \text{ cm}^{-1}$ .

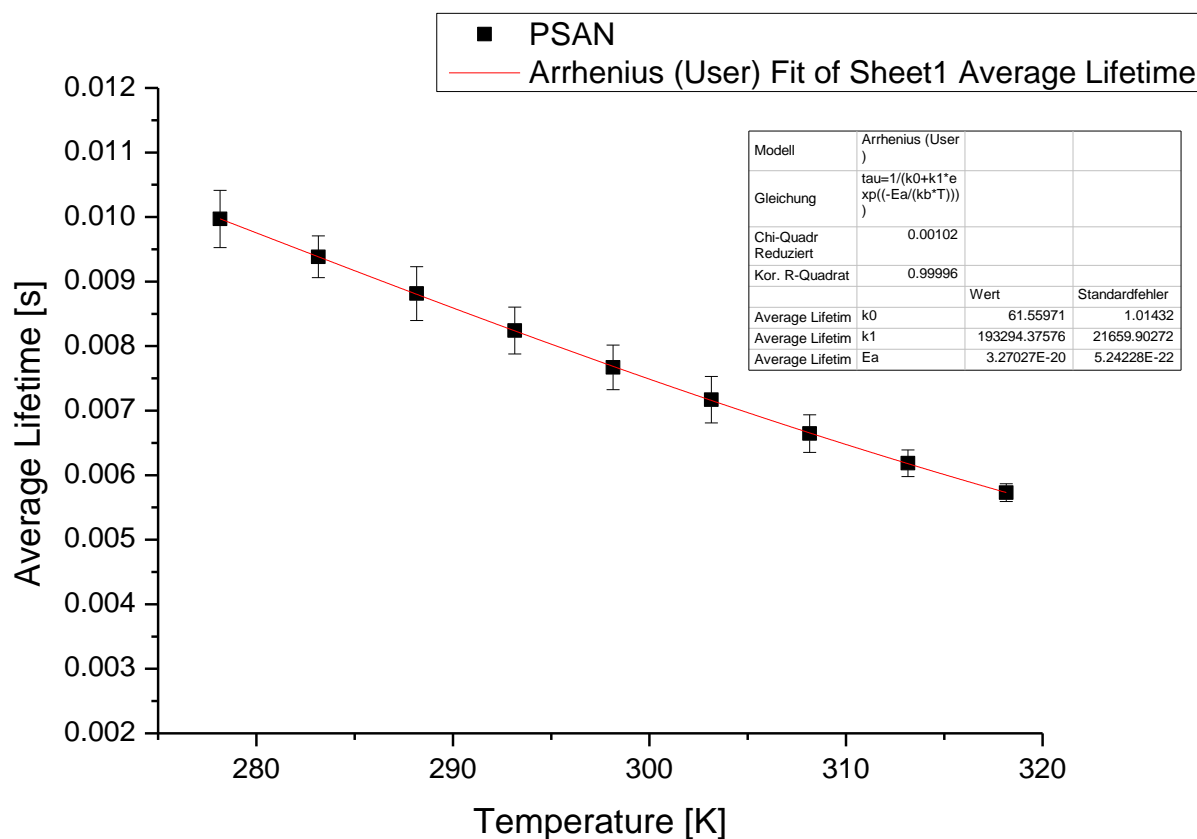


Figure S6. Temperature dependence of the average luminescence decay times of ZnOS immobilized in PSAN.

<sup>4</sup> G. Liebsch, I. Klimant, O. S. Wolfbeis, Adv. Mater. 1999, 11, 1296.

## Results and Discussion

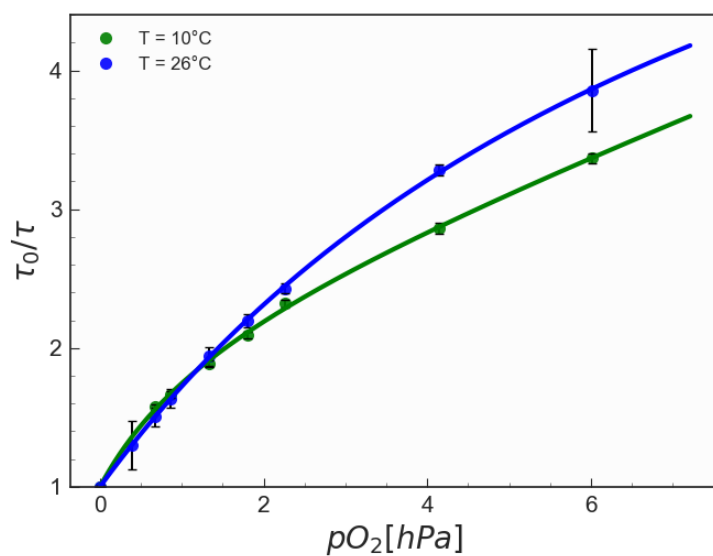


Figure S7. Response of the dual sensor (Zn-OS in PSAN) to oxygen exemplified for two temperatures.

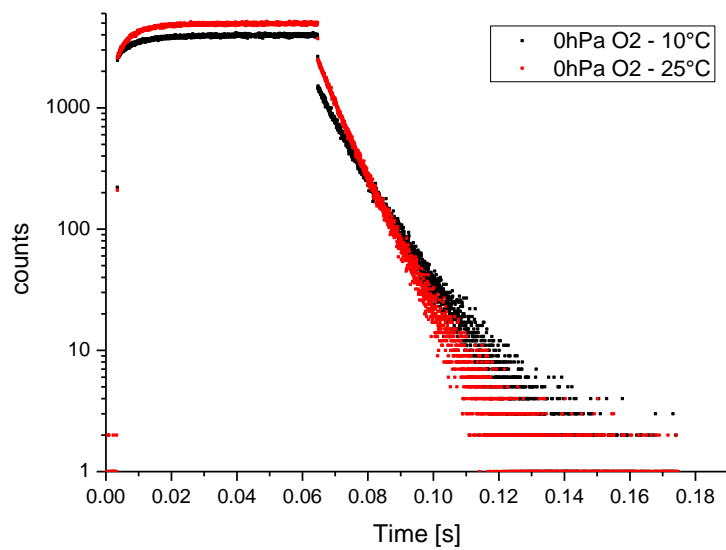


Figure S8. Influence of temperature at a constant oxygen concentration on the decay curve of the sensor foil (1 wt% Zn-OS incorporated in PVC).



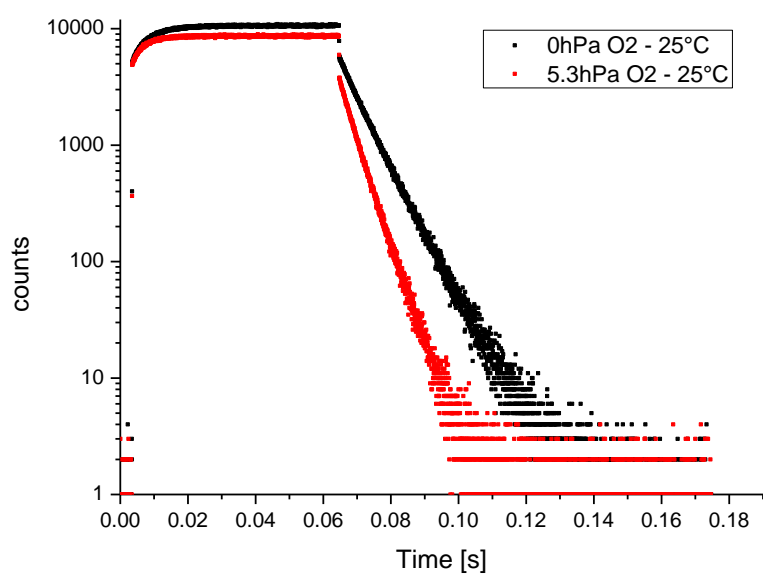


Figure S9. Influence of oxygen concentration at a constant temperature on the decay curve of the sensor foil (1 wt% Zn-OS incorporated in PVC).