Electronic Supporting Information

High performance optical sensing nanocomposites for low and ultra-low oxygen concentrations using phase-shift measurements

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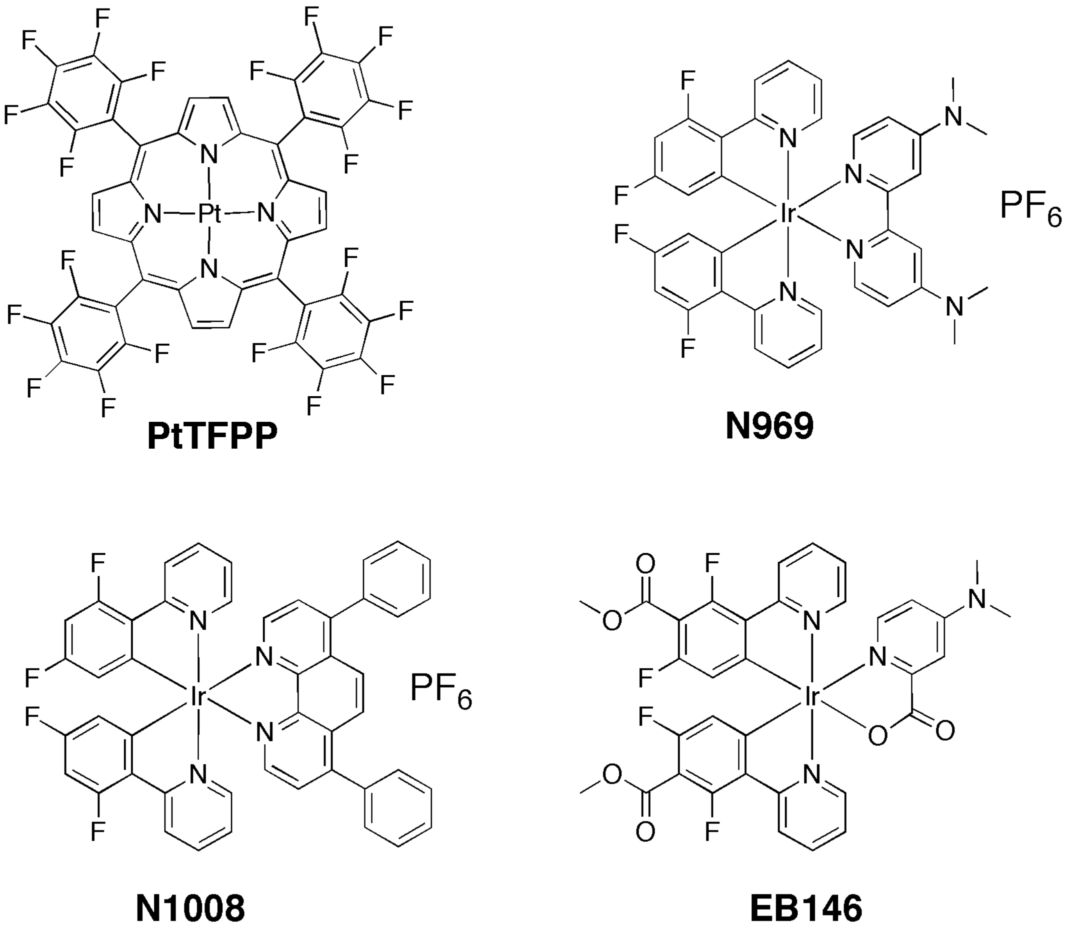

Figure ESI-1. Chemical structure of the complexes.

PtTFPP: Platinum(II) 5,10,15,20-meso-tetrakis-(2,3,4,5,6-pentafluorophenyl)-porphyrin)
N969: [Ir(2-(2,4-difluorophenyl)pyridine)$_2$(4,4’-dimethylamino-2,2’-bipyridine)](PF_6)
N1008: [Ir(2-(2,4-difluorophenyl)pyridine)$_2$(4,7-diphenyl-1,10-phenanthroline)](PF_6)
EB146: [Ir(2-(2,4-difluoro-3-methylesterphenyl)pyridine)$_2$(4-(*N*,*N*-dimethylamino)picolinate)].

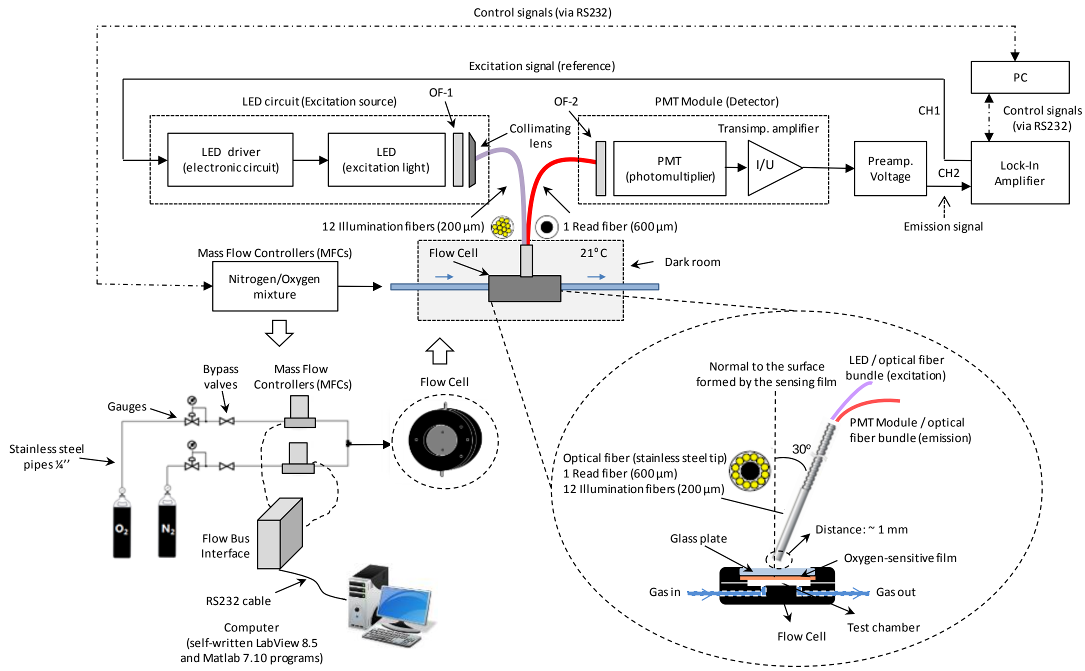

Figure ESI-2. Schematic diagrams of the designed experimental setup for phase-shift measurements and the flow cell used.

Details of the homemade system to control oxygen and for lifetime measurements

The control of oxygen and lifetime measurements was carried out with a homemade system (see Figure ESI-1). For it, a flow-through cell, which functions as a gas chamber, was designed in our laboratories to hold the sensing films. The flow cell was made of black PTFE to prevent stray reflections and also to assure the chemical inertness. It was not thermostated since it was to be used in a constant temperature (in this case, all measurements were performed at room temperature of 21 ºC). The temperature was continuously monitored using a commercial temperature sensor (MicroLite, Fourtec-Fourier Technologies, www.fouriersystems.com) located at an external point close to the flow cell. Different mixtures of nitrogen and oxygen at a constant flow rate of 200 mL/min were passed through the flow cell to perform the calibration of the sensing films. For gas mixing, two mass flow controllers (MFCs) (EL-FLOW Select F-201CV, Bronkhorst High-Tech, www.bronkhorst.com, Ruurlo, Netherlands) were connected to copper and stainless steel tubing. These tubes connected the MFCs and the flow cell. The gas station was completely controlled from a PC using an ad hoc computer program developed in LabView 8.5 (www.ni.com) and MATLAB 7.10 (www.mathworks.com) software. For it, the PC was connected to a Flow-Bus Interface (Bronkhorst High-Tech) that fully controls the MFCs via a RS-232 serial port.

For the study of the effect of relative humidity, one more MFC for nitrogen was added. Thus, nitrogen was split into two lines before two mass-flow controllers. One branch was humidified by guiding the nitrogen over water in a 2-neck glass flask, thus avoiding the formation of water droplets. A relative humidity (RH) of up to 80% was obtained. This was monitored with a hygrometer (Rotronic, Bassersdorf, www.rotronic.ch) coupled after the measurement cell. The two lines of nitrogen were merged to provide the desired carrier gas stream, to which an additional line carrying oxygen is connected.

For the study of the sensing response for concentrations lower than 0.25%, oxygen was replaced by synthetic air (21% O_2 balanced in N_2).

The luminescence phase shifts were measured with a dual-phase lock-in amplifier (SR830, Stanford Research Systems, www.thinksrs.com, USA).

The sensing films containing the iridium(III) complexes were excited with an ultraviolet light-emitting diode (LED) (λ_{max} 375 nm, angle of illumination 15º, LED diameter 5 mm, luminous power 6800 µW (max.) at 15 mA, LED Supply, www.ledsupply.com, USA) filtered through an optical bandpass filter ($\lambda_{central}$ 390 nm, MF390-18, Thorlabs GmbH, www.thorlabs.com) which was sinusoidally modulated at a frequency of 94100 Hz (in the case of N969 and EB146) or at a frequency of 30100 Hz (in the case of N1008). The sensing film containing PtTFPP was excited with an ultraviolet LED (λ_{max} 395 nm, angle of illumination 15º, LED diameter 5 mm, luminous power 25 µW) filtered through an optical bandpass filter ($\lambda_{central}$ 390 nm, MF390-18, Thorlabs GmbH) which was sinusoidally modulated at a frequency of 40100 Hz.

A bifurcated fibre bundle (wavelength range 200-800 nm UV-VIS, 12 illumination fibres 200 µm core diameter, 1 read fibre 600 µm core diameter, N.A. 0.22, FCR-7xx200-2, Avantes Inc., www.avantes.com) was used to guide the excitation light to the film and to guide back the luminescence after passing an optical longpass filter (λ_{cut-on} 450 nm, NT62-975, Edmund Optics) in the case of Ir(III) complexes, or an optical bandpass filter ($\lambda_{central}$ 630 nm, BW 30 nm, A10033-03, Hamamatsu Photonics) in the case of PtTFPP. The luminescence was detected with a photomultiplier tube (BW DC-1 MHz, H10723-20, Hamamatsu Photonics). The voltage signal provided by the PMT (of few tens of millivolts) was amplified with a commercial low-noise programmable voltage preamplifier (SIM911 BJT, Stanford Research Systems) before being applied to the lock-in amplifier. Both the flow cell and PMT were housed in a dark room (XE25C1, Thorlabs GmbH) to prevent interference from stray light.

Fundamentals of oxygen sensing measured by phase-resolved method (frequency domain).

The oxygen quenching process is described by the Stern-Volmer equation (Equation ESI-1):

$$\frac{\tau_0}{\tau} = 1 + K_{SV}[O_2] \qquad \text{(Equation ESI} - 1)$$

where τ_0 and τ are the unquenched and quenched excited state lifetimes, K_{SV} is the Stern-Volmer constant, and $[O_2]$ is the concentration of quencher (oxygen).

However, in many cases it is usual to find some deviation from linearity of the response due to the heterogeneity of the matrix where the dyes are immobilized.[1] This deviation is explained by the presence of different oxygen quenching sites within the matrix,[2, 3] and therefore a multi-site model with each site having a linear behaviour can be applied. The simplest one is the two-site model proposed by Demas et al.,[4] the so-called Demas model. This model assumes localization of the indicator in two regions of different microenvironment and explains the deviation from the linearity in the Stern-Volmer plot. Thus, the experimental data can be nicely fitted with the following Equation ESI-2:

$$\frac{\tau_0}{\tau} = \left[\frac{x_1}{1 + K_{SV1}[O_2]} + \frac{x_2}{1 + K_{SV2}[O_2]}\right]^{-1} \qquad \text{(Equation ESI} - 2)$$

where x_1 and x_2 are the fractions of the total emission for each component respectively (with x_1+x_2 being 1), and K_{SV1} and K_{SV2} are the Stern-Volmer quenching constants for each component.

Other two-site model was proposed by Lehrer,[5] where only one of the two microenvironments is accessible to the quencher (K_{SV2}=0). In this case, the experimental data can be fitted with the following Equation ESI-3:

$$\frac{\tau_0}{\tau} = \left[\frac{x_0}{1 + K_{SV}[O_2]} + (1 - x_0)\right]^{-1} \qquad \text{(Equation ESI} - 3)$$

where x_0 denotes the fraction of the total luminophores population that the quencher is able to access, and K_{SV} is the Stern-Volmer quenching constant associated with the accessible fraction of luminophores.

In phase-resolved method (frequency domain), the sample is excited with a sinusoidally modulated light at a fixed frequency that consequently causes a modulated luminescence emission at the identical frequency. Due to the emission lifetime of the luminescent material, the emission signal exhibits a phase shift (i.e., time delay) with respect to the excitation signal. The input excitation signal is used as a reference to establish the zero-phase position, and the lifetime is obtained indirectly by measuring the phase shift between excitation and emission signals.[6] If the luminescence emission is directly proportional to the intensity of the excitation light, and assuming that the luminescence decay is monoexponential (i.e., according to Equation ESI-1), the relationship between the phase shift, ϕ, and the emission lifetime, τ, is given by Equation ESI-3:[7, 8]

$$\tan(\phi) = 2\pi f \tau \qquad \text{(Equation ESI} - 4)$$

where ϕ is the phase shift, f is the exciting light modulation frequency, and τ is the decay time (or lifetime).

Characterization of the oxygen-sensing films

Excitation and emission spectra were recorded with a Varian Cary-Eclipse luminescence spectrometer. The parameter settings for spectroscopic characterization were: slit-width$_{exc/em}$ 10/10 nm, delay time 0.1 ms, gate time 5 ms, constant flow rate of 200 mL min^{-1}, and detector voltage 560 V (EB146), 550 V (N1008), 590 V (N969) and 440 V (PtTFPP). All measurements were performed in the absence (100% N_2) and in the presence (100% O_2) of oxygen and at 21 ºC.

Luminescence lifetimes were determined in frequency domain, and they were calculated indirectly with the experimental setup represented in Figure ESI-1 by measuring the phase shift between the excitation and emission signals (see equation ESI-4).

A disadvantage of phase luminometry is that the SNR (signal to noise ratio) decreases with increasing modulation frequency (i.e., the amplitude of the optical signal (optical power) decreases with increasing of the modulation frequency of the LED), and since the phase sensitivity increases with modulation frequency,[7] an optimal frequency has to be selected.[9, 10] Furthermore, the choice of the optimal modulation frequency also depends on the sensing application (i.e., measurement range of interest) because the changes of the phase shift within a certain oxygen concentrations range depend on the excitation modulation frequency.[11] One choice to achieve maximum dynamic range for measuring the phase shift (or lifetime, see equation ESI-4) is to adjust the modulation frequency such that the phase difference between the extremes of the oxygen measurement range is maximized.[11, 12] This strategy was used in this work to select the optimal modulation frequency for a given range of oxygen concentrations (between 0 and 1% O_2 and between 0 and 10% O_2).

Time trace curves were used to recorder the luminescence phase shifts at 14 different oxygen partial pressures between 0 and 100 kPa (or 0-100 vol. % pO_2). These phase-shift measurements were used to obtain the typical calibration curves (i.e., Stern-Volmer Plots (SVP)). Fitting was performed using MATLAB 7.10 software between 0 and 1 kPa (or 0-1 vol. % pO_2).0 and 0 and 10 kPa (or 0-10 vol. % pO_2). Furthermore, typical response-time curves were also obtained to determine the response times of the sensing films (i.e., rise and fall times to t_{95}). All measurements were done in the absence of ambient light and at 21 ºC.

The oxygen concentration of the gas passing through the flow cell was calculated in real-time from the measured oxygen/nitrogen flows provided by the MFCs. A total gas flow rate of 200 mL min^{-1} was maintained in all gas measurements, assuming a constant environment pressure of 1000 mbar. Before starting the experiments, the MFCs were calibrated using a flow sensor.

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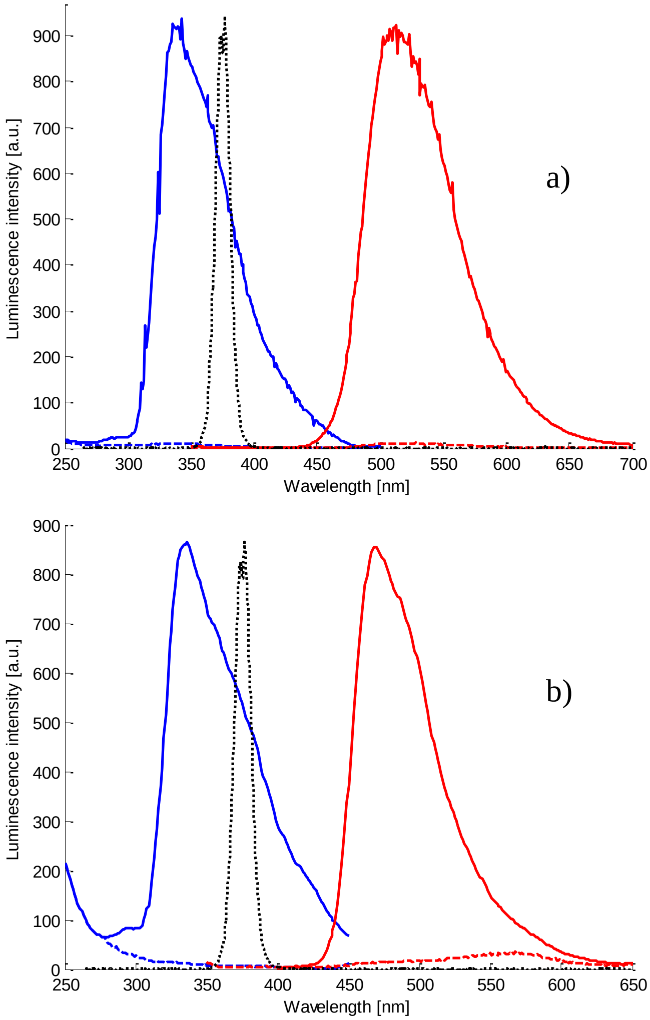

Figure ESI-3. Excitation (blue lines) and emission (red lines) spectra of in the absence (solid line) and in the presence (dashed line) of oxygen of a) N1008 and b) EB146 immobilized into AP200/19. The black dotted line (····) corresponds with the emission spectrum of the LED used for excited the sensing film. [Dye]=1.5 mg mL^{-1}, λ_{exc}=340 nm for N1008 and 335 nm for EB146, λ_{em}=512 nm for N1008 and 470 nm for EB146, slits-width$_{exc/em}$=10/10 nm, delay time=0.1 ms, gate time=5 ms, detector voltage=550 V for N1008 and 560 V for EB146, flow-rate 200 mL min^{-1}.

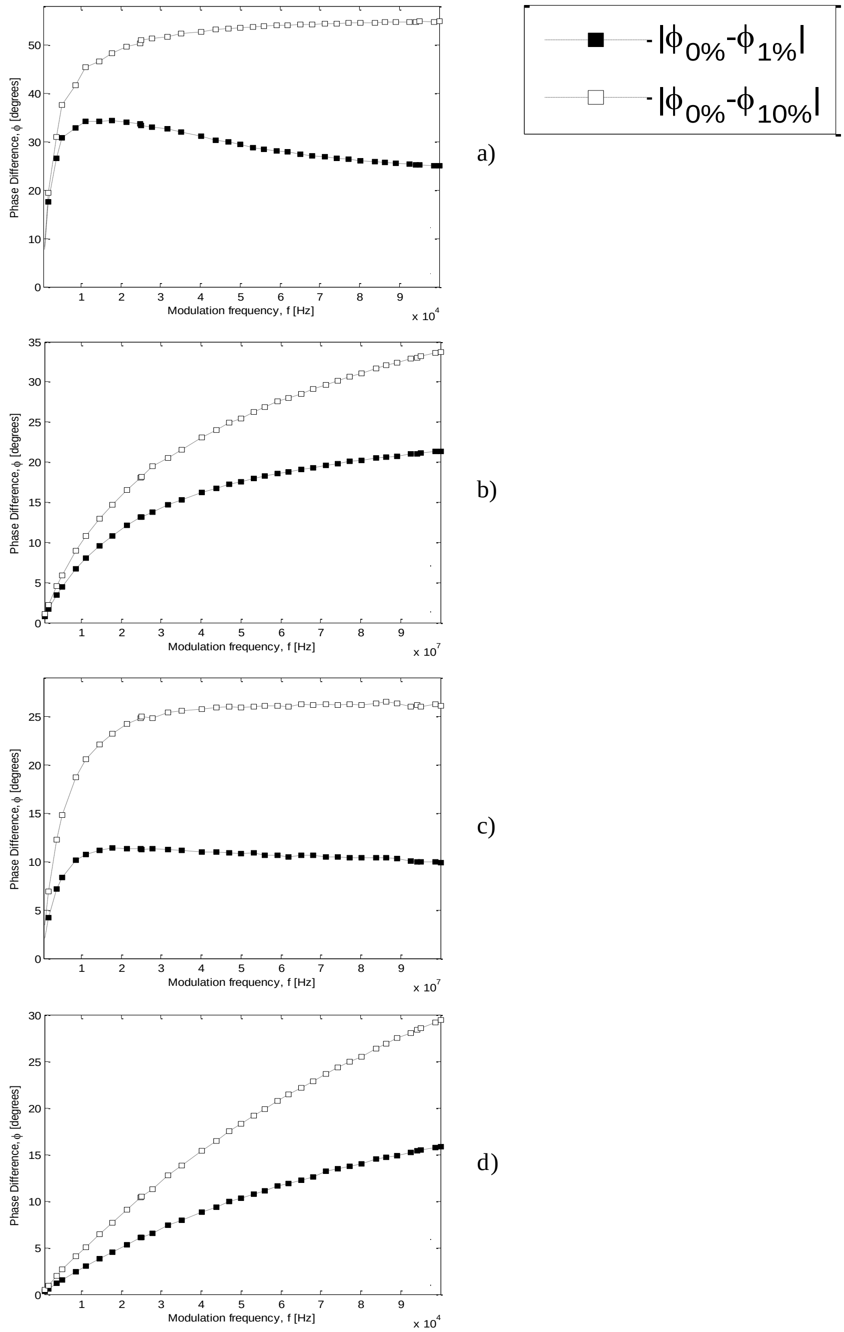

Figure ESI-4. Effect of the modulation frequency on the phase difference at several oxygen concentrations (■ from 0 to 1% O_2 and □ from 0 to 10% O_2) for a) PtTFPP, b) N969, c) N1008 and d) EB146 incorporated into AP200/19 using a multifrequency phase-resolved method. (see reference Sens. Actuators B 176 (2013) 1110-1120). See Table ESI-1 for the data.

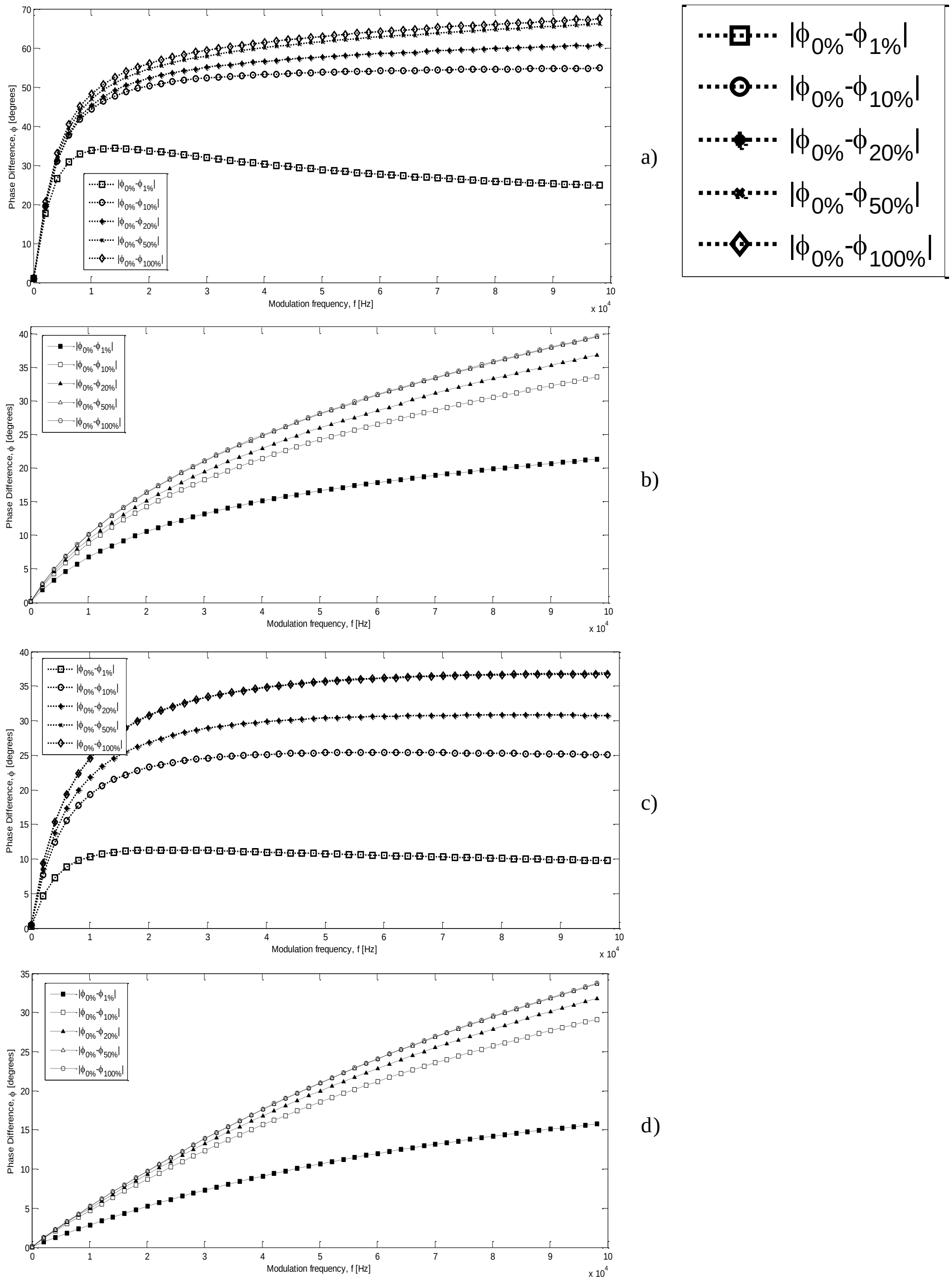

Figure ESI-5. Effect of the modulation frequency on the phase difference at several oxygen concentrations (■ from 0 to 1% O_2, , □ from 0 to 10% O_2, ▲ from 0 to 20% O_2, △ from 0 to 50% O_2, ○ from 0 to 100% O_2) for a) PtTFPP, b) N969, c) N1008 and d) EB146 incorporated into AP200/19 measured with the setup described in Fig 1. See Tables ESI-2 to ESI-5 for the data.

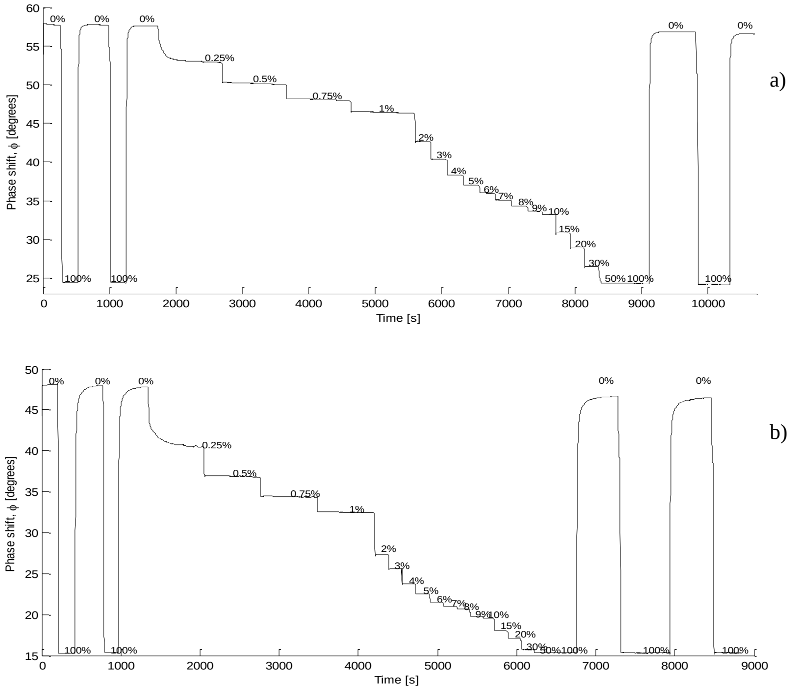

Figure ESI-6. Variation of the phase shift of a) N1008 and b) EB146 incorporated into AP200/19 with the oxygen concentration.

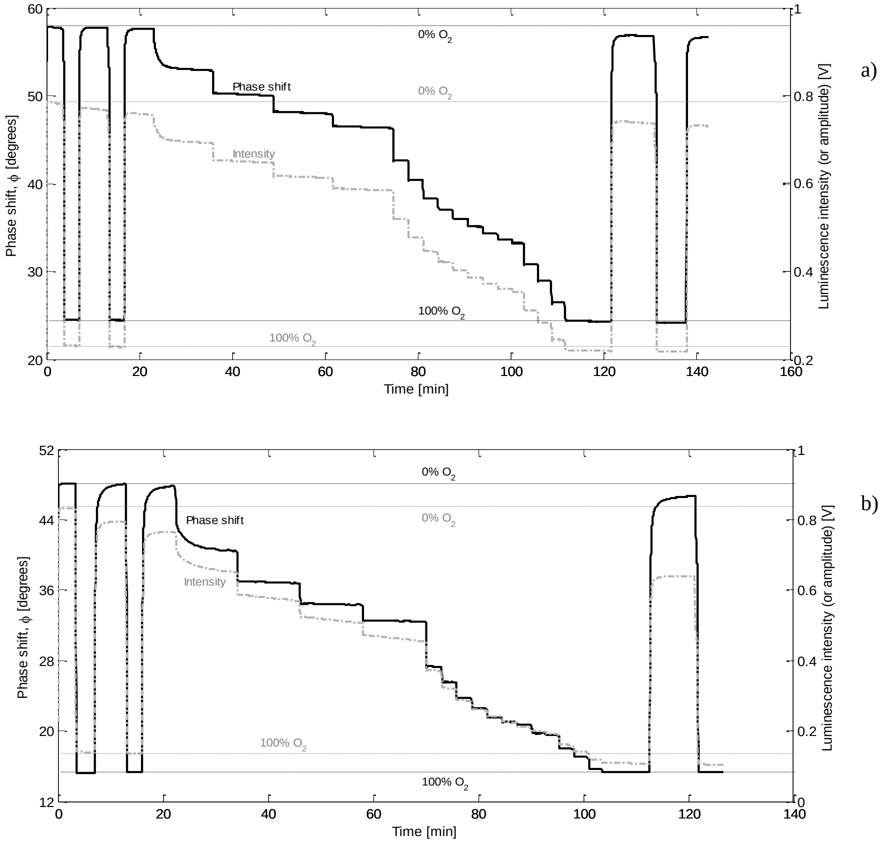

Figure ESI-7. Stability of the phase shift (dark bold line) and amplitude (doted light line) for a) N1008 and b) EB146 incorporated into AP200/19 at 21 ºC.

Table ESI-1. Average phase differences ($|\Phi_{0\%\ O_2} - \Phi_{x\%\ O_2}|$) in degrees for several oxygen concentrations at different modulation frequencies obtained with the multifrequency phase-resolved method reported in Sens. Actuators B 176 (2013) 1110-1120. All the values correspond to the average value of 20 phase-shift measurements.

	PtTFPP-AP200/19		N1008-AP200/19		N969-AP200/19		EB146-AP200/19	
Freq. (Hz)	$\lvert\Phi_{0\%-1\%\ O_2}\rvert$	$\lvert\Phi_{0\%-10\%\ O_2}\rvert$	$\lvert\Phi_{0\%-1\%\ O_2}\rvert$	$\lvert\Phi_{0\%-10\%\ O_2}\rvert$	$\lvert\Phi_{0\%-1\%\ O_2}\rvert$	$\lvert\Phi_{0\%-10\%\ O_2}\rvert$	$\lvert\Phi_{0\%-1\%\ O_2}\rvert$	$\lvert\Phi_{0\%-10\%\ O_2}\rvert$
769	7.78	8.29	2.06	3.41	0.77	1.02	0.32	0.50
1709	17.60	19.50	4.17	6.92	1.67	2.19	0.59	0.94
3761	26.52	31.02	7.14	12.27	3.45	4.55	1.14	1.97
5145	30.77	37.62	8.34	14.80	4.48	5.89	1.52	2.63
8713	32.80	41.69	10.15	18.72	6.71	8.91	2.40	4.10
11257	34.20	45.43	10.75	20.52	8.06	10.78	3.00	5.04
14639	34.20	46.63	11.16	22.08	9.57	12.93	3.79	6.45
17881	34.27	48.23	11.39	23.18	10.82	14.72	4.48	7.66
21499	33.97	49.66	11.29	24.18	12.12	16.55	5.29	9.06
24917	33.68	50.34	11.29	24.77	13.12	18.07	6.06	10.39
25111	33.36	50.90	11.21	24.96	13.15	18.15	6.09	10.45
27847	32.99	51.32	11.29	24.77	13.77	19.46	6.55	11.27
31849	32.61	51.67	11.20	25.42	14.68	20.55	7.39	12.75
35129	31.89	52.31	11.18	25.53	15.32	21.55	7.96	13.80
40277	31.20	52.74	10.94	25.71	16.17	23.06	8.79	15.36
43777	30.23	53.20	11.01	25.93	16.69	23.98	9.36	16.43
47143	29.98	53.33	10.90	25.94	17.22	24.88	9.95	17.50
50023	29.37	53.55	10.82	25.94	17.56	25.47	10.33	18.25
53309	28.83	53.74	10.85	25.99	17.91	26.24	10.74	19.15
56087	28.35	53.91	10.68	26.11	18.21	26.82	11.14	19.87
59183	28.12	54.01	10.68	26.08	18.52	27.54	11.61	20.78
62011	27.94	54.06	10.48	26.00	18.81	27.99	11.86	21.48
65071	27.45	54.16	10.65	26.26	19.08	28.54	12.20	22.14
68071	27.03	54.24	10.62	26.17	19.30	29.06	12.56	22.86
71327	26.89	54.27	10.45	26.22	19.63	29.61	13.21	23.66
74257	26.59	54.42	10.44	26.14	19.84	30.15	13.48	24.34
77291	26.43	54.50	10.37	26.20	20.11	30.68	13.74	24.95
80191	26.06	54.46	10.34	26.13	20.19	31.02	14.02	25.50
83843	25.91	54.51	10.40	26.28	20.48	31.64	14.50	26.37
86413	25.65	54.61	10.43	26.53	20.62	32.04	14.71	26.85
89231	25.53	54.65	10.33	26.30	20.77	32.40	14.88	27.45
92647	25.31	54.69	10.08	25.96	21.01	32.91	15.18	28.06
94111	25.17	54.72	9.96	26.19	21.03	32.97	15.43	28.40
95101	25.16	54.79	9.95	25.96	21.10	33.20	15.48	28.56
98809	24.97	54.73	9.97	26.21	21.34	33.66	15.72	29.17
99991	24.95	54.86	9.83	26.06	21.34	33.75	15.83	29.39

Table ESI-2. Average phase differences ($\left|\Phi_{0\%\,O_2} - \Phi_{x\%\,O_2}\right|$) for several oxygen concentrations at different modulation frequencies obtained for PtTFPP immobilized into AP200/19 measured with the setup described in Figure 1. All the values correspond to the average value of 100 phase-shift measurements.

Freq. (Hz)	$\left|\Phi_{0\%-x\%\,O_2}\right|$ (degrees)					Freq. (Hz)	$\left|\Phi_{0\%-x\%\,O_2}\right|$ (degrees)				
	x=1% O_2	x=10% O_2	x=20% O_2	x=50% O_2	x=100% O_2		x=1% O_2	x=10% O_2	x=20% O_2	x=50% O_2	x=100% O_2
100	0.953	0.952	1.019	1.070	1.173	50100	28.836	53.745	57.715	61.603	62.955
2100	17.606	19.506	19.524	20.133	20.697	52100	28.585	53.864	57.880	61.869	63.191
4100	26.527	31.028	31.236	32.232	33.129	54100	28.356	53.912	58.061	62.066	63.483
6100	30.775	37.629	38.087	39.356	40.419	56100	28.126	54.011	58.235	62.333	63.746
8100	32.803	41.691	42.438	43.860	45.081	58100	27.942	54.068	58.493	62.645	64.025
10100	33.810	44.418	45.360	47.019	48.264	60100	27.688	54.143	58.594	62.793	64.210
12100	34.206	46.339	47.479	49.301	50.636	62100	27.458	54.164	58.674	62.963	64.268
14100	34.277	47.738	49.104	51.042	52.409	64100	27.272	54.155	58.841	63.222	64.582
16100	34.178	48.844	50.381	52.545	53.917	66100	27.034	54.241	58.886	63.329	64.705
18100	33.976	49.663	51.418	53.689	55.084	68100	26.895	54.276	59.133	63.537	64.934
20100	33.685	50.346	52.238	54.651	56.099	70100	26.718	54.283	59.272	63.759	65.189
22100	33.367	50.902	52.969	55.493	56.910	72100	26.593	54.426	59.383	64.036	65.400
24100	32.999	51.327	53.561	56.232	57.625	74100	26.434	54.503	59.498	64.188	65.585
26100	32.618	51.673	54.107	56.958	58.273	76100	26.227	54.462	59.627	64.387	65.719
28100	32.301	52.040	54.601	57.451	58.906	78100	26.064	54.467	59.670	64.548	65.889
30100	31.890	52.311	55.002	57.935	59.329	80100	25.914	54.517	59.903	64.661	66.001
32100	31.552	52.556	55.387	58.403	59.817	82100	25.791	54.625	59.948	64.910	66.224
34100	31.203	52.749	55.726	58.933	60.312	84100	25.659	54.612	60.130	64.988	66.311
36100	30.894	52.922	56.042	59.325	60.740	86100	25.539	54.652	60.149	65.197	66.443
38100	30.571	53.090	56.312	59.729	61.100	88100	25.392	54.668	60.295	65.374	66.668
40100	30.232	53.207	56.603	60.020	61.362	90100	25.314	54.697	60.298	65.450	66.804
42100	29.984	53.331	56.835	60.431	61.795	92100	25.179	54.727	60.470	65.704	66.939
44100	29.662	53.454	57.098	60.727	62.118	94100	25.169	54.799	60.593	65.833	67.230
46100	29.373	53.554	57.279	60.976	62.399	96100	24.972	54.731	60.518	65.989	67.167
48100	29.106	53.672	57.575	61.355	62.677	98100	24.951	54.867	60.804	66.113	67.461

Table ESI-3. Average phase differences ($\left|\Phi_{0\%\ O_2} - \Phi_{x\%\ O_2}\right|$) for several oxygen concentrations at different modulation frequencies obtained for N969 immobilized into AP200/19 measured with the setup described in Figure 1. All the values correspond to the average value of 100 phase-shift measurements.

Freq. (Hz)	$\left\|\Phi_{0\%-x\%\ O_2}\right\|$ (degrees)					Freq. (Hz)	$\left\|\Phi_{0\%-x\%\ O_2}\right\|$ (degrees)				
	x=1% O_2	x=10% O_2	x=20% O_2	x=50% O_2	x=100% O_2		x=1% O_2	x=10% O_2	x=20% O_2	x=50% O_2	x=100% O_2
100	0.135	0.168	0.181	0.189	0.183	50100	16.612	24.190	25.948	27.987	28.116
2100	1.874	2.394	2.570	2.764	2.782	52100	16.868	24.667	26.487	28.569	28.709
4100	3.321	4.272	4.565	4.925	4.950	54100	17.125	25.155	27.014	29.155	29.283
6100	4.592	5.941	6.347	6.836	6.880	56100	17.366	25.629	27.538	29.704	29.845
8100	5.718	7.439	7.936	8.553	8.605	58100	17.616	26.091	28.054	30.276	30.408
10100	6.729	8.803	9.388	10.116	10.170	60100	17.849	26.532	28.550	30.815	30.934
12100	7.636	10.047	10.700	11.536	11.605	62100	18.076	26.971	29.035	31.351	31.480
14100	8.460	11.189	11.919	12.852	12.934	64100	18.285	27.386	29.586	31.871	31.995
16100	9.213	12.260	13.057	14.069	14.158	66100	18.495	27.818	30.236	32.368	32.512
18100	9.912	13.272	14.133	15.235	15.327	68100	18.710	28.229	30.692	32.883	33.013
20100	10.561	14.210	15.133	16.319	16.415	70100	18.910	28.629	31.146	33.381	33.499
22100	11.157	15.100	16.084	17.336	17.449	72100	19.109	29.022	31.595	33.851	33.978
24100	11.714	15.951	16.995	18.325	18.434	74100	19.293	29.394	32.016	34.328	34.447
26100	12.232	16.744	17.855	19.250	19.362	76100	19.487	29.786	32.468	34.800	34.906
28100	12.711	17.502	18.663	20.128	20.242	78100	19.683	30.161	32.890	35.243	35.370
30100	13.169	18.238	19.456	20.984	21.094	80100	19.850	30.531	33.304	35.707	35.817
32100	13.605	18.941	20.222	21.809	21.919	82100	20.022	30.877	33.696	36.130	36.244
34100	14.013	19.601	20.942	22.590	22.700	84100	20.190	31.238	34.104	36.580	36.690
36100	14.391	20.248	21.635	23.335	23.458	86100	20.373	31.591	34.493	37.031	37.116
38100	14.756	20.875	22.318	24.077	24.193	88100	20.546	31.951	34.915	37.454	37.563
40100	15.107	21.468	22.972	24.773	24.890	90100	20.712	32.277	35.294	37.878	37.975
42100	15.427	22.043	23.597	25.445	25.579	92100	20.878	32.637	35.712	38.304	38.413
44100	15.733	22.602	24.201	26.112	26.235	94100	21.033	32.972	36.077	38.711	38.823
46100	16.046	23.148	24.798	26.751	26.888	96100	21.184	33.279	36.446	39.119	39.209
48100	16.328	23.678	25.391	27.384	27.517	98100	21.342	33.595	36.804	39.533	39.620

Table ESI-4. Average phase differences ($\left|\Phi_{0\%\ O_2} - \Phi_{x\%\ O_2}\right|$) for several oxygen concentrations at different modulation frequencies obtained for N1008 immobilized into AP200/19 measured with the setup described in Figure 1. All the values correspond to the average value of 100 phase-shift measurements.

Freq. (Hz)	$\left|\Phi_{0\%-x\%\ O_2}\right|$ (degrees)					Freq. (Hz)	$\left|\Phi_{0\%-x\%\ O_2}\right|$ (degrees)				
	x=1% O_2	x=10% O_2	x=20% O_2	x=50% O_2	x=100% O_2		x=1% O_2	x=10% O_2	x=20% O_2	x=50% O_2	x=100% O_2
100	0.271	0.428	0.471	0.508	0.507	50100	10.747	25.343	30.383	35.707	35.649
2100	4.667	7.703	8.507	9.448	9.389	52100	10.688	25.355	30.442	35.815	35.770
4100	7.258	12.394	13.784	15.361	15.289	54100	10.640	25.368	30.498	35.930	35.868
6100	8.797	15.522	17.369	19.438	19.359	56100	10.595	25.383	30.567	36.037	35.983
8100	9.747	17.720	19.944	22.405	22.321	58100	10.543	25.384	30.603	36.118	36.066
10100	10.354	19.330	21.871	24.665	24.580	60100	10.502	25.379	30.640	36.212	36.150
12100	10.739	20.538	23.361	26.424	26.344	62100	10.463	25.382	30.676	36.277	36.228
14100	10.991	21.470	24.538	27.849	27.772	64100	10.415	25.378	30.705	36.352	36.277
16100	11.141	22.197	25.481	29.005	28.931	66100	10.366	25.361	30.737	36.414	36.355
18100	11.235	22.780	26.250	29.973	29.899	68100	10.318	25.352	30.748	36.465	36.394
20100	11.283	23.249	26.898	30.794	30.730	70100	10.276	25.343	30.766	36.526	36.455
22100	11.301	23.628	27.427	31.481	31.426	72100	10.239	25.323	30.775	36.563	36.489
24100	11.305	23.940	27.888	32.085	32.023	74100	10.215	25.331	30.812	36.622	36.548
26100	11.287	24.201	28.283	32.596	32.545	76100	10.162	25.308	30.807	36.643	36.573
28100	11.255	24.410	28.611	33.043	33.000	78100	10.124	25.280	30.809	36.684	36.611
30100	11.223	24.596	28.905	33.455	33.403	80100	10.090	25.269	30.817	36.718	36.622
32100	11.180	24.739	29.150	33.803	33.747	82100	10.043	25.261	30.824	36.750	36.662
34100	11.131	24.859	29.365	34.117	34.068	84100	10.009	25.213	30.818	36.772	36.689
36100	11.079	24.963	29.555	34.404	34.341	86100	9.965	25.197	30.822	36.782	36.672
38100	11.032	25.064	29.726	34.652	34.605	88100	9.922	25.166	30.811	36.811	36.713
40100	10.987	25.130	29.869	34.883	34.824	90100	9.911	25.168	30.830	36.830	36.738
42100	10.932	25.185	30.000	35.071	35.029	92100	9.884	25.136	30.799	36.854	36.737
44100	10.886	25.236	30.115	35.246	35.204	94100	9.833	25.098	30.781	36.844	36.731
46100	10.843	25.281	30.215	35.421	35.366	96100	9.800	25.091	30.776	36.863	36.750
48100	10.790	25.314	30.306	35.568	35.519	98100	9.779	25.057	30.770	36.859	36.748

Table ESI-5. Average phase differences ($\left|\Phi_{0\%\,O_2} - \Phi_{x\%\,O_2}\right|$) for several oxygen concentrations at different modulation frequencies obtained for EB146 immobilized into AP200/19 measured with the setup described in Figure 1. All the values correspond to the average value of 100 phase-shift measurements.

Freq. (Hz)	$\left|\Phi_{0\%-x\%\,O_2}\right|$ **(degrees)**					**Freq. (Hz)**	$\left|\Phi_{0\%-x\%\,O_2}\right|$ **(degrees)**				
	x=1% O_2	**x=10% O_2**	**x=20% O_2**	**x=50% O_2**	**x=100% O_2**		**x=1% O_2**	**x=10% O_2**	**x=20% O_2**	**x=50% O_2**	**x=100% O_2**
100	0.038	0.051	0.051	0.005	0.035	50100	10.662	18.571	19.996	21.003	21.029
2100	0.727	1.140	1.211	1.244	1.241	52100	10.938	19.115	20.596	21.643	21.657
4100	1.297	2.080	2.210	2.312	2.289	54100	11.214	19.646	21.191	22.268	22.293
6100	1.842	2.982	3.176	3.297	3.304	56100	11.485	20.176	21.768	22.870	22.912
8100	2.363	3.854	4.104	4.273	4.267	58100	11.736	20.695	22.328	23.467	23.517
10100	2.871	4.709	5.019	5.236	5.220	60100	11.996	21.192	22.890	24.073	24.102
12100	3.371	5.546	5.913	6.182	6.157	62100	12.247	21.693	23.439	24.672	24.713
14100	3.857	6.365	6.788	7.082	7.088	64100	12.482	22.175	23.983	25.235	25.268
16100	4.335	7.172	7.649	8.000	7.988	66100	12.712	22.638	24.493	25.778	25.838
18100	4.793	7.961	8.499	8.896	8.883	68100	12.939	23.109	25.017	26.338	26.379
20100	5.245	8.737	9.339	9.751	9.750	70100	13.152	23.561	25.517	26.871	26.933
22100	5.686	9.491	10.147	10.619	10.608	72100	13.367	23.999	26.005	27.400	27.457
24100	6.116	10.243	10.947	11.461	11.445	74100	13.576	24.434	26.489	27.918	28.006
26100	6.517	10.963	11.733	12.273	12.270	76100	13.784	24.868	26.978	28.443	28.506
28100	6.920	11.678	12.495	13.087	13.087	78100	13.975	25.293	27.445	28.939	29.015
30100	7.316	12.379	13.254	13.883	13.873	80100	14.165	25.705	27.904	29.424	29.520
32100	7.695	13.061	13.991	14.650	14.647	82100	14.366	26.107	28.368	29.930	29.994
34100	8.065	13.735	14.711	15.413	15.415	84100	14.557	26.513	28.822	30.415	30.492
36100	8.429	14.386	15.428	16.172	16.169	86100	14.738	26.899	29.261	30.879	30.971
38100	8.777	15.025	16.124	16.892	16.907	88100	14.910	27.287	29.705	31.351	31.432
40100	9.113	15.646	16.803	17.617	17.623	90100	15.096	27.672	30.133	31.809	31.904
42100	9.443	16.254	17.470	18.313	18.338	92100	15.265	28.052	30.566	32.276	32.360
44100	9.747	16.842	18.109	19.010	18.999	94100	15.432	28.415	30.971	32.734	32.824
46100	10.064	17.438	18.764	19.694	19.690	96100	15.599	28.782	31.389	33.183	33.273
48100	10.373	18.012	19.386	20.352	20.370	98100	15.751	29.126	31.784	33.609	33.715

Table ESI-6. Phase-shift measurements for different oxygen concentrations of PtTFPP immobilized into AP200/19 in triplicate at 21ºC. Modulation frequency of 40100 Hz.

pO_2(%)	Replica #1		Replica #2		Replica #3		Average results		Φ_0/Φ_x [e]	Phase difference $(\Phi_{0\%\,pO_2} - \Phi_{x\%})$				
	mean (º)[a]	s (º)[b]	mean (º)[a]	s (º)[b]	mean (º)[a]	s (º)[b]	mean (º)[c]	s (º)[d]		Rep. #1 (º)[f]	Rep. #2 (º)[f]	Rep. #3 (º)[f]	mean (º)[g]	s (º)[h]
0.00	87.743	0.047	87.593	0.049	87.645	0.050	87.660	0.076	1.000	0.000	0.000	0.000	0.000	0.000
0.25	74.635	0.168	74.492	0.095	74.258	0.059	74.462	0.190	1.176	13.108	12.901	13.387	13.132	0.243
0.50	66.347	0.535	66.150	0.033	66.548	0.037	66.348	0.198	1.320	21.396	21.243	21.097	21.245	0.149
0.75	60.076	0.074	60.475	0.047	60.091	0.035	60.214	0.226	1.454	27.667	26.918	27.553	27.380	0.403
1	57.113	0.034	57.458	0.031	57.512	0.033	57.361	0.216	1.527	30.630	29.935	30.132	30.232	0.358
2	47.420	0.034	47.698	0.036	47.769	0.030	47.629	0.184	1.839	40.323	39.695	39.875	39.964	0.323
3	43.430	0.034	43.610	0.031	43.832	0.034	43.624	0.201	2.007	44.312	43.783	43.812	43.969	0.297
4	41.044	0.045	41.272	0.044	41.516	0.044	41.277	0.235	2.122	46.699	46.121	46.129	46.316	0.331
5	39.115	0.047	39.080	0.043	39.521	0.040	39.238	0.245	2.232	48.628	48.313	48.123	48.355	0.254
6	37.811	0.043	37.587	0.046	38.053	0.030	37.817	0.232	2.316	49.932	49.806	49.592	49.776	0.172
7	36.770	0.041	36.515	0.058	37.016	0.038	36.767	0.250	2.382	50.973	50.878	50.628	50.826	0.178
8	36.334	0.042	36.233	0.044	36.687	0.046	36.418	0.238	2.405	51.409	51.159	50.957	51.175	0.226
9	35.172	0.038	35.362	0.048	35.701	0.045	35.412	0.268	2.473	52.571	52.031	51.943	52.182	0.339
10	34.602	0.037	34.447	0.046	34.108	0.053	34.386	0.252	2.547	53.141	52.946	53.536	53.207	0.300
15	32.271	0.062	32.270	0.046	32.732	0.053	32.424	0.266	2.701	55.472	55.123	54.913	55.169	0.282
20	30.711	0.057	30.977	0.054	31.264	0.053	30.984	0.276	2.827	57.031	56.416	56.381	56.609	0.366
30	28.973	0.065	29.353	0.065	29.518	0.076	29.281	0.279	2.991	58.770	58.040	58.126	58.312	0.398
50	27.339	0.053	27.552	0.074	27.854	0.076	27.581	0.258	3.175	60.404	59.841	59.790	60.012	0.340
100	26.039	0.073	26.517	0.069	26.143	0.069	26.233	0.251	3.339	61.704	60.876	61.501	61.361	0.431

[a] Average value (mean) of 100 phase-shift measurements (in degrees) calculated as: $\bar{\phi} = \frac{1}{n}\sum_{i=1}^{n}\phi_i$; [b] Standard deviation value (s) of 100 phase-shift measurements (in degrees) calculated as: $s = \left(\frac{1}{n-1}\sum_{i=1}^{n}(\phi_i - \bar{\phi})^2\right)^{1/2}$; [c] Mean of the average phase-shift values ($\bar{\phi}$, in degrees) obtained for each replica, calculated as: $\bar{\phi}_{avg} = \frac{1}{3}\sum_{i=1}^{3}\bar{\phi}_i$; [d] Standard deviation value (s) of the average phase-shift values ($\bar{\phi}_i$, in degrees) obtained for each replica, calculated as: $s = \left(\frac{1}{3-1}\sum_{i=1}^{3}(\bar{\phi}_i - \bar{\phi}_{avg})^2\right)^{1/2}$; [e] Ratio between the average phase-shift value, $\bar{\phi}_{avg}$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\phi}_{avg\,(0\%\,pO_2)}/\bar{\phi}_{avg\,(x\%\,pO_2)}$); [f] Average phase difference (in degrees) between the average phase-shift value, $\bar{\phi}_i$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\phi}_{i\,(0\%\,pO_2)} - \bar{\phi}_{i\,(x\%\,pO_2)}$); [g] Average value (mean) of the 3 average phase difference values obtained for each replica (in degrees); [h] Standard deviation value (s) of the 3 average phase difference values obtained for each replica (in degrees).

Table ESI-7. Luminescence lifetime measurements for different oxygen concentrations of PtTFPP immobilized into AP200/19 in triplicate at 21º C. Modulation frequency of 40100 Hz.

pO_2(%)	Replica #1		Replica #2		Replica #3		Average results		τ_0/τ_x [e]	Luminescence lifetime difference $(\tau_{x\%\,pO_2} - \tau_{0\%\,pO_2})$				
	mean (µs)[a]	s (µs)[b]	mean (µs)[a]	s (µs)[b]	mean (µs)[a]	s (µs)[b]	mean (µs)[c]	s (µs)[d]		Rep. #1 (µs)[f]	Rep. #2 (µs)[f]	Rep. #3 (µs)[f]	mean (µs)[g]	s (µs)[h]
0	100.779	2.132	94.493	1.965	96.493	2.009	97.255	3.211	1.000	0.000	0.000	0.000	0.000	0.000
0.25	14.446	0.166	14.304	0.092	14.080	0.055	14.277	0.184	6.812	86.333	80.189	82.412	82.978	3.111
0.5	9.066	0.231	8.978	0.014	9.148	0.016	9.064	0.085	10.729	91.713	85.515	87.344	88.191	3.184
0.75	6.895	0.020	7.008	0.013	6.899	0.010	6.934	0.063	14.024	93.884	87.485	89.593	90.321	3.260
1	6.138	0.008	6.220	0.007	6.233	0.008	6.197	0.051	15.693	94.641	88.273	90.260	91.058	3.258
2	4.319	0.005	4.361	0.005	4.372	0.004	4.351	0.028	22.351	96.460	90.132	92.120	92.904	3.236
3	3.757	0.004	3.780	0.004	3.810	0.004	3.782	0.026	25.709	97.022	90.713	92.682	93.472	3.228
4	3.455	0.005	3.483	0.005	3.513	0.005	3.484	0.028	27.913	97.324	91.010	92.979	93.771	3.230
5	3.227	0.005	3.223	0.005	3.274	0.004	3.241	0.028	30.002	97.552	91.270	93.218	94.014	3.215
6	3.079	0.004	3.055	0.005	3.106	0.003	3.080	0.025	31.570	97.699	91.438	93.386	94.175	3.204
7	2.965	0.004	2.938	0.006	2.992	0.004	2.965	0.027	32.793	97.813	91.555	93.500	94.289	3.203
8	2.919	0.004	2.908	0.004	2.957	0.005	2.928	0.025	33.213	97.860	91.585	93.536	94.327	3.211
9	2.796	0.003	2.816	0.005	2.852	0.004	2.821	0.028	34.464	97.982	91.677	93.641	94.433	3.226
10	2.738	0.003	2.722	0.004	2.688	0.005	2.716	0.025	35.804	98.041	91.771	93.805	94.539	3.198
15	2.506	0.006	2.506	0.004	2.551	0.005	2.521	0.025	38.575	98.273	91.987	93.942	94.734	3.216
20	2.357	0.005	2.382	0.005	2.409	0.005	2.383	0.026	40.805	98.422	92.111	94.083	94.872	3.228
30	2.197	0.006	2.232	0.006	2.247	0.007	2.225	0.025	43.697	98.582	92.261	94.245	95.029	3.232
50	2.052	0.004	2.070	0.006	2.097	0.006	2.073	0.022	46.907	98.727	92.423	94.395	95.182	3.225
100	1.939	0.006	1.980	0.006	1.948	0.006	1.955	0.021	49.725	98.840	92.513	94.545	95.299	3.230

[a] Average value (mean) of 100 luminescence lifetime measurements (in microseconds) calculated as: $\bar{\tau} = \frac{1}{n}\sum_{i=1}^{n}\tau_i$; [b] Standard deviation value (s) of 100 luminescence lifetime measurements (in microseconds) calculated as: $s = \left(\frac{1}{n-1}\sum_{i=1}^{n}(\tau_i - \bar{\tau})^2\right)^{1/2}$; [c] Mean of the average luminescence-lifetime values ($\bar{\tau}$, in microseconds) obtained for each replica, calculated as: $\bar{\mu}_{avg} = \frac{1}{3}\sum_{i=1}^{3}\bar{\tau}_i$; [d] Standard deviation value (s) of the average luminescence-lifetime values ($\bar{\tau}_i$, in microseconds) obtained for each replica, calculated as: $s = \left(\frac{1}{3-1}\sum_{i=1}^{3}(\bar{\tau}_i - \bar{\tau}_{avg})^2\right)^{1/2}$; [e] Ratio between the average luminescence-lifetime value, $\bar{\tau}_{avg}$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\tau}_{avg\,(0\%\,pO_2)}/\bar{\tau}_{avg\,(x\%\,pO_2)}$); [f] Average lifetime difference (in microseconds) between the average luminescence-lifetime value, $\bar{\tau}_i$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\tau}_{i\,(0\%\,pO_2)} - \bar{\tau}_{i\,(x\%\,pO_2)}$); [g] Average value (mean) of the 3 average lifetime difference values obtained for each replica (in microseconds); [h] Standard deviation value (s) of the 3 average lifetime difference values obtained for each replica (in microseconds).

Table ESI-8. Phase-shift measurements for different oxygen concentrations of N969 immobilized into AP200/19 in triplicate at 21º C. Modulation frequency of 94100 Hz.

pO_2(%)	Replica #1		Replica #2		Replica #3		Average results		Φ_0/Φ_x[e]	Phase difference $(\Phi_{0\%\,pO_2} - \Phi_{x\%})$				
	mean (º)[a]	s (º)[b]	mean (º)[a]	s (º)[b]	mean (º)[a]	s (º)[b]	mean (º)[c]	s (º)[d]		Rep. #1 (º)[f]	Rep. #2 (º)[f]	Rep. #3 (º)[f]	mean (º)[g]	s (º)[h]
0	65.642	0.018	65.608	0.020	65.829	0.018	65.693	0.119	1.000	0.000	0.000	0.000	0.000	0.000
0.25	53.126	0.029	52.820	0.023	53.179	0.060	53.041	0.193	1.238	12.516	12.787	12.650	12.651	0.135
0.5	49.111	0.006	48.706	0.004	48.894	0.006	48.903	0.202	1.343	16.531	16.902	16.935	16.789	0.224
0.75	46.608	0.004	46.249	0.006	46.427	0.005	46.428	0.179	1.414	19.033	19.359	19.402	19.265	0.201
1	44.801	0.008	44.489	0.004	44.691	0.006	44.660	0.158	1.470	20.841	21.119	21.137	21.032	0.166
2	40.355	0.007	40.402	0.006	40.698	0.006	40.485	0.186	1.622	25.287	25.205	25.130	25.207	0.078
3	38.167	0.005	38.140	0.005	38.510	0.005	38.273	0.206	1.716	27.475	27.467	27.319	27.420	0.087
4	36.555	0.006	36.633	0.006	36.940	0.006	36.709	0.203	1.789	29.087	28.974	28.889	28.983	0.099
5	35.565	0.005	35.527	0.008	35.954	0.006	35.682	0.236	1.841	30.077	30.081	29.875	30.011	0.117
6	34.932	0.005	34.666	0.006	35.096	0.007	34.898	0.217	1.882	30.710	30.941	30.733	30.795	0.127
7	34.260	0.007	33.955	0.008	34.377	0.008	34.197	0.218	1.921	31.382	31.653	31.451	31.495	0.140
8	33.602	0.007	33.355	0.006	33.762	0.007	33.573	0.205	1.956	32.040	32.253	32.066	32.120	0.115
9	33.011	0.007	32.820	0.007	33.203	0.006	33.011	0.191	1.990	32.631	32.788	32.626	32.682	0.092
10	32.703	0.008	32.552	0.008	32.918	0.004	32.724	0.183	2.007	32.939	33.055	32.911	32.968	0.076
15	30.762	0.008	30.792	0.008	31.020	0.007	30.858	0.141	2.128	34.880	34.815	34.809	34.835	0.039
20	29.470	0.007	29.651	0.007	29.729	0.008	29.616	0.132	2.218	36.172	35.957	36.100	36.076	0.109
30	27.775	0.006	28.145	0.009	28.030	0.007	27.983	0.189	2.347	37.867	37.462	37.799	37.709	0.217
50	26.755	0.008	27.162	0.009	27.027	0.007	26.981	0.207	2.434	38.886	38.445	38.802	38.711	0.234
100	26.637	0.008	27.073	0.010	26.912	0.008	26.874	0.220	2.444	39.005	38.534	38.917	38.819	0.250

[a] Average value (mean) of 100 phase-shift measurements (in degrees) calculated as: $\bar{\phi} = \frac{1}{n}\sum_{i=1}^{n}\phi_i$; [b] Standard deviation value (s) of 100 phase-shift measurements (in degrees) calculated as: $s = \left(\frac{1}{n-1}\sum_{i=1}^{n}(\phi_i - \bar{\phi})^2\right)^{1/2}$; [c] Mean of the average phase-shift values ($\bar{\phi}$, in degrees) obtained for each replica, calculated as: $\bar{\phi}_{avg} = \frac{1}{3}\sum_{i=1}^{3}\bar{\phi}_i$; [d] Standard deviation value (s) of the average phase-shift values ($\bar{\phi}_i$, in degrees) obtained for each replica, calculated as: $s = \left(\frac{1}{3-1}\sum_{i=1}^{3}(\bar{\phi}_i - \bar{\phi}_{avg})^2\right)^{1/2}$; [e] Ratio between the average phase-shift value, $\bar{\phi}_{avg}$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\phi}_{avg\,(0\%\,pO_2)}/\bar{\phi}_{avg\,(x\%\,pO_2)}$); [f] Average phase difference (in degrees) between the average phase-shift value, $\bar{\phi}_i$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\phi}_{i\,(0\%\,pO_2)} - \bar{\phi}_{i\,(x\%\,pO_2)}$); [g] Average value (mean) of the 3 average phase difference values obtained for each replica (in degrees); [h] Standard deviation value (s) of the 3 average phase difference values obtained for each replica (in degrees).

Table ESI-9. Luminescence lifetime measurements for different oxygen concentrations of N969 immobilized into AP200/19 in triplicate at 21° C. Modulation frequency of 94100 Hz.

pO_2(%)	Replica #1		Replica #2		Replica #3		Average results		τ_0/τ_x [e]	Luminescence lifetime difference $(\tau_{x\%\,pO_2} - \tau_{0\%\,pO_2})$				
	mean (µs)[a]	s (µs)[b]	mean (µs)[a]	s (µs)[b]	mean (µs)[a]	s (µs)[b]	mean (µs)[c]	s (µs)[d]		Rep. #1 (µs)[f]	Rep. #2 (µs)[f]	Rep. #3 (µs)[f]	mean (µs)[g]	s (µs)[h]
0	3.735	0.003	3.730	0.003	3.768	0.003	3.744	0.020	1.000	0.000	0.000	0.000	0.000	0.000
0.25	2.254	0.002	2.229	0.001	2.259	0.004	2.247	0.015	1.665	1.481	1.500	1.509	1.496	0.014
0.5	1.953	0.001	1.925	0.001	1.938	0.001	1.939	0.013	1.931	1.782	1.804	1.830	1.805	0.023
0.75	1.789	0.001	1.766	0.001	1.777	0.001	1.777	0.011	2.106	1.946	1.963	1.990	1.967	0.022
1	1.679	0.001	1.661	0.001	1.673	0.001	1.671	0.009	2.240	2.056	2.068	2.095	2.073	0.020
2	1.437	0.001	1.439	0.001	1.454	0.001	1.443	0.009	2.593	2.298	2.290	2.313	2.301	0.011
3	1.329	0.001	1.328	0.001	1.345	0.001	1.334	0.009	2.806	2.406	2.401	2.422	2.410	0.011
4	1.254	0.001	1.257	0.001	1.271	0.001	1.261	0.009	2.969	2.481	2.472	2.496	2.483	0.012
5	1.209	0.001	1.207	0.001	1.226	0.001	1.214	0.010	3.083	2.526	2.522	2.541	2.530	0.010
6	1.181	0.001	1.169	0.001	1.188	0.001	1.179	0.009	3.174	2.554	2.560	2.580	2.565	0.013
7	1.152	0.001	1.138	0.001	1.157	0.001	1.149	0.009	3.258	2.583	2.591	2.611	2.595	0.014
8	1.123	0.001	1.113	0.001	1.130	0.001	1.122	0.008	3.335	2.612	2.616	2.637	2.622	0.013
9	1.098	0.001	1.090	0.001	1.106	0.001	1.098	0.008	3.407	2.637	2.639	2.661	2.646	0.013
10	1.086	0.001	1.079	0.001	1.094	0.001	1.086	0.007	3.445	2.650	2.650	2.673	2.658	0.013
15	1.006	0.001	1.007	0.001	1.017	0.001	1.010	0.005	3.705	2.729	2.722	2.751	2.734	0.015
20	0.955	0.001	0.962	0.001	0.965	0.001	0.961	0.005	3.894	2.780	2.767	2.802	2.783	0.018
30	0.890	0.001	0.904	0.001	0.900	0.001	0.898	0.007	4.167	2.845	2.825	2.868	2.846	0.021
50	0.852	0.001	0.867	0.001	0.862	0.001	0.861	0.007	4.348	2.883	2.862	2.905	2.883	0.021
100	0.848	0.001	0.864	0.001	0.858	0.001	0.857	0.008	4.369	2.887	2.865	2.910	2.887	0.022

[a] Average value (mean) of 100 luminescence lifetime measurements (in microseconds) calculated as: $\bar{\tau} = \frac{1}{n}\sum_{i=1}^{n}\tau_i$; [b] Standard deviation value (s) of 100 luminescence lifetime measurements (in microseconds) calculated as: $s = \left(\frac{1}{n-1}\sum_{i=1}^{n}(\tau_i - \bar{\tau})^2\right)^{1/2}$; [c] Mean of the average luminescence-lifetime values ($\bar{\tau}$, in microseconds) obtained for each replica, calculated as: $\bar{\mu}_{avg} = \frac{1}{3}\sum_{i=1}^{3}\bar{\tau}_i$; [d] Standard deviation value (s) of the average luminescence-lifetime values ($\bar{\tau}_i$, in microseconds) obtained for each replica, calculated as: $s = \left(\frac{1}{3-1}\sum_{i=1}^{3}(\bar{\tau}_i - \bar{\tau}_{avg})^2\right)^{1/2}$; [e] Ratio between the average luminescence-lifetime value, $\bar{\tau}_{avg}$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\tau}_{avg\,(0\%\,pO_2)}/\bar{\tau}_{avg\,(x\%\,pO_2)}$); [f] Average lifetime difference (in microseconds) between the average luminescence-lifetime value, $\bar{\tau}_i$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\tau}_{i\,(0\%\,pO_2)} - \bar{\tau}_{i\,(x\%\,pO_2)}$); [g] Average value (mean) of the 3 average lifetime difference values obtained for each replica (in microseconds); [h] Standard deviation value (s) of the 3 average lifetime difference values obtained for each replica (in microseconds).

Table ESI-10. Phase-shift measurements for different oxygen concentrations of N1008 immobilized into AP200/19 in triplicate at 21º C. Modulation frequency of 30100 Hz.

pO_2(%)	Replica #1		Replica #2		Replica #3		Average results		Φ_0/Φ_x [e]	Phase difference $(\Phi_{0\%\,pO_2} - \Phi_{x\%})$				
	mean (º)[a]	s (º)[b]	mean (º)[a]	s (º)[b]	mean (º)[a]	s (º)[b]	mean (º)[c]	s (º)[d]		Rep. #1 (º)[f]	Rep. #2 (º)[f]	Rep. #3 (º)[f]	mean (º)[g]	s (º)[h]
0	57.904	0.015	58.028	0.024	57.561	0.014	57.831	0.241	1.000	0.000	0.000	0.000	0.000	0.000
0.25	52.640	0.047	53.122	0.030	52.861	0.035	52.874	0.241	1.093	5.264	4.906	4.700	4.956	0.285
0.5	50.015	0.016	50.598	0.043	50.351	0.007	50.321	0.292	1.149	7.889	7.430	7.210	7.509	0.346
0.75	47.883	0.011	48.331	0.028	48.280	0.008	48.165	0.245	1.200	10.021	9.696	9.281	9.666	0.370
1	46.326	0.010	46.772	0.016	46.726	0.008	46.608	0.245	1.240	11.578	11.255	10.835	11.223	0.372
2	42.534	0.006	43.023	0.013	42.804	0.006	42.787	0.245	1.351	15.370	15.004	14.757	15.044	0.308
3	40.121	0.004	40.616	0.011	40.262	0.003	40.333	0.255	1.433	17.783	17.411	17.299	17.498	0.253
4	38.199	0.005	38.570	0.012	38.525	0.005	38.431	0.202	1.504	19.705	19.458	19.036	19.400	0.338
5	36.970	0.005	37.410	0.010	37.002	0.004	37.127	0.245	1.557	20.934	20.618	20.559	20.704	0.201
6	35.898	0.005	36.304	0.009	35.843	0.005	36.015	0.251	1.605	22.006	21.724	21.718	21.816	0.164
7	34.992	0.006	35.361	0.008	34.855	0.005	35.069	0.262	1.649	22.912	22.666	22.706	22.762	0.131
8	34.196	0.005	34.531	0.008	34.081	0.004	34.269	0.233	1.687	23.708	23.496	23.480	23.561	0.127
9	33.474	0.004	33.875	0.009	33.381	0.005	33.577	0.262	1.722	24.430	24.153	24.180	24.254	0.152
10	33.124	0.004	33.515	0.008	33.060	0.005	33.233	0.246	1.740	24.780	24.512	24.501	24.598	0.157
15	30.629	0.004	30.993	0.006	30.559	0.004	30.727	0.233	1.882	27.275	27.035	27.002	27.104	0.148
20	28.852	0.005	29.204	0.006	28.739	0.004	28.932	0.242	1.998	29.051	28.824	28.822	28.899	0.131
30	26.332	0.006	26.787	0.007	26.231	0.005	26.450	0.296	2.186	31.572	31.241	31.330	31.381	0.171
50	24.281	0.007	24.718	0.005	24.208	0.005	24.402	0.275	2.369	33.623	33.310	33.353	33.429	0.169
100	24.241	0.006	24.734	0.007	24.317	0.006	24.431	0.265	2.367	33.663	33.294	33.244	33.400	0.228

[a] Average value (mean) of 100 phase-shift measurements (in degrees) calculated as: $\bar{\phi} = \frac{1}{n}\sum_{i=1}^{n}\phi_i$; [b] Standard deviation value (s) of 100 phase-shift measurements (in degrees) calculated as: $s = \left(\frac{1}{n-1}\sum_{i=1}^{n}(\phi_i - \bar{\phi})^2\right)^{1/2}$; [c] Mean of the average phase-shift values ($\bar{\phi}$, in degrees) obtained for each replica, calculated as: $\bar{\phi}_{avg} = \frac{1}{3}\sum_{i=1}^{3}\bar{\phi}_i$; [d] Standard deviation value (s) of the average phase-shift values ($\bar{\phi}_i$, in degrees) obtained for each replica, calculated as: $s = \left(\frac{1}{3-1}\sum_{i=1}^{3}(\bar{\phi}_i - \bar{\phi}_{avg})^2\right)^{1/2}$; [e] Ratio between the average phase-shift value, $\bar{\phi}_{avg}$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\phi}_{avg\,(0\%\,pO_2)}/\bar{\phi}_{avg\,(x\%\,pO_2)}$); [f] Average phase difference (in degrees) between the average phase-shift value, $\bar{\phi}_i$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\phi}_{i\,(0\%\,pO_2)} - \bar{\phi}_{i\,(x\%\,pO_2)}$); [g] Average value (mean) of the 3 average phase difference values obtained for each replica (in degrees); [h] Standard deviation value (s) of the 3 average phase difference values obtained for each replica (in degrees).

Table ESI-11. Luminescence lifetime measurements for different oxygen concentrations of N1008 immobilized into AP200/19 in triplicate at 21° C. Modulation frequency of 30100 Hz.

pO_2(%)	Replica #1		Replica #2		Replica #3		Average results		τ_0/τ_x [e]	Luminescence lifetime difference $\left(\tau_{x\%\,pO_2} - \tau_{0\%\,pO_2}\right)$				
	mean (μs)[a]	s (μs)[b]	mean (μs)[a]	s (μs)[b]	mean (μs)[a]	s (μs)[b]	mean (μs)[c]	s (μs)[d]		Rep. #1 (μs)[f]	Rep. #2 (μs)[f]	Rep. #3 (μs)[f]	mean (μs)[g]	s (μs)[h]
0	8.430	0.005	8.471	0.008	8.319	0.004	8.407	0.078	1.000	0.000	0.000	0.000	0.000	0.000
0.25	6.926	0.011	7.048	0.007	6.981	0.009	6.985	0.061	1.203	1.504	1.423	1.337	1.421	0.083
0.5	6.304	0.003	6.436	0.009	6.380	0.001	6.374	0.066	1.319	2.125	2.034	1.939	2.033	0.093
0.75	5.848	0.002	5.941	0.006	5.930	0.001	5.906	0.050	1.423	2.582	2.530	2.389	2.500	0.099
1	5.538	0.002	5.625	0.003	5.616	0.001	5.593	0.047	1.503	2.892	2.846	2.703	2.813	0.098
2	4.851	0.001	4.934	0.002	4.897	0.001	4.894	0.042	1.717	3.579	3.536	3.422	3.512	0.081
3	4.456	0.001	4.534	0.001	4.478	0.001	4.489	0.040	1.872	3.974	3.936	3.841	3.917	0.068
4	4.160	0.001	4.216	0.001	4.209	0.001	4.195	0.030	2.003	4.269	4.254	4.109	4.211	0.088
5	3.980	0.001	4.044	0.001	3.984	0.001	4.003	0.035	2.100	4.450	4.427	4.334	4.404	0.061
6	3.827	0.001	3.884	0.001	3.819	0.001	3.843	0.035	2.187	4.603	4.586	4.500	4.563	0.055
7	3.701	0.001	3.752	0.001	3.682	0.001	3.712	0.036	2.264	4.729	4.718	4.637	4.695	0.050
8	3.592	0.001	3.638	0.001	3.577	0.001	3.602	0.031	2.333	4.837	4.832	4.742	4.804	0.053
9	3.496	0.001	3.549	0.001	3.484	0.001	3.510	0.035	2.395	4.934	4.921	4.835	4.897	0.053
10	3.450	0.001	3.501	0.001	3.441	0.001	3.464	0.032	2.426	4.980	4.969	4.877	4.942	0.056
15	3.130	0.001	3.176	0.001	3.122	0.001	3.143	0.029	2.674	5.299	5.295	5.197	5.264	0.057
20	2.913	0.001	2.955	0.001	2.899	0.001	2.922	0.029	2.876	5.517	5.515	5.420	5.484	0.055
30	2.617	0.001	2.669	0.001	2.605	0.001	2.630	0.034	3.195	5.813	5.801	5.714	5.776	0.054
50	2.385	0.001	2.434	0.001	2.377	0.001	2.398	0.030	3.504	6.045	6.037	5.942	6.008	0.057
100	2.380	0.001	2.435	0.001	2.389	0.001	2.402	0.029	3.500	6.049	6.035	5.930	6.005	0.065

[a] Average value (mean) of 100 luminescence lifetime measurements (in microseconds) calculated as: $\bar{\tau} = \frac{1}{n}\sum_{i=1}^{n}\tau_i$; [b] Standard deviation value (s) of 100 luminescence lifetime measurements (in microseconds) calculated as: $s = \left(\frac{1}{n-1}\sum_{i=1}^{n}(\tau_i - \bar{\tau})^2\right)^{1/2}$; [c] Mean of the average luminescence-lifetime values ($\bar{\tau}$, in microseconds) obtained for each replica, calculated as: $\bar{\mu}_{avg} = \frac{1}{3}\sum_{i=1}^{3}\bar{\tau}_i$; [d] Standard deviation value (s) of the average luminescence-lifetime values ($\bar{\tau}_i$, in microseconds) obtained for each replica, calculated as: $s = \left(\frac{1}{3-1}\sum_{i=1}^{3}(\bar{\tau}_i - \bar{\tau}_{avg})^2\right)^{1/2}$; [e] Ratio between the average luminescence-lifetime value, $\bar{\tau}_{avg}$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\tau}_{avg\,(0\%\,pO_2)}/\bar{\tau}_{avg\,(x\%\,pO_2)}$); [f] Average lifetime difference (in microseconds) between the average luminescence-lifetime value, $\bar{\tau}_i$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\tau}_{i\,(0\%\,pO_2)} - \bar{\tau}_{i\,(x\%\,pO_2)}$); [g] Average value (mean) of the 3 average lifetime difference values obtained for each replica (in microseconds); [h] Standard deviation value (s) of the 3 average lifetime difference values obtained for each replica (in microseconds).

Table ESI-12. Phase-shift measurements for different oxygen concentrations of EB146 immobilized into AP200/19 in triplicate at 21° C. Modulation frequency of 94100 Hz.

pO_2(%)	Replica #1		Replica #2		Replica #3		Average results		Φ_0/Φ_x [e]	Phase difference $(\Phi_{0\%\,pO_2} - \Phi_{x\%})$				
	mean (°)[a]	s (°)[b]	mean (°)[a]	s (°)[b]	mean (°)[a]	s (°)[b]	mean (°)[c]	s (°)[d]		Rep. #1 (°)[f]	Rep. #2 (°)[f]	Rep. #3 (°)[f]	mean (°)[g]	s (°)[h]
0	48.090	0.012	48.004	0.014	48.144	0.013	48.079	0.070	1.000	0.000	0.000	0.000	0.000	0.000
0.25	40.483	0.033	41.013	0.039	40.616	0.020	40.704	0.275	1.181	7.606	6.991	7.528	7.375	0.335
0.5	36.641	0.019	37.035	0.016	36.546	0.005	36.741	0.259	1.308	11.449	10.969	11.598	11.338	0.328
0.75	34.303	0.015	34.769	0.020	34.389	0.007	34.487	0.248	1.394	13.786	13.234	13.755	13.592	0.310
1	32.621	0.009	32.905	0.012	32.425	0.004	32.651	0.241	1.472	15.468	15.098	15.719	15.428	0.312
2	27.651	0.008	27.423	0.010	27.094	0.005	27.389	0.280	1.755	20.438	20.580	21.050	20.690	0.320
3	25.326	0.005	25.844	0.006	25.513	0.006	25.561	0.262	1.880	22.764	22.160	22.631	22.518	0.317
4	23.493	0.006	24.036	0.006	23.739	0.005	23.756	0.271	2.023	24.596	23.968	24.405	24.323	0.322
5	22.553	0.008	22.788	0.005	22.372	0.007	22.571	0.208	2.130	25.537	25.216	25.772	25.508	0.279
6	21.490	0.007	21.818	0.004	21.384	0.006	21.564	0.226	2.229	26.599	26.186	26.760	26.515	0.296
7	21.108	0.005	21.221	0.006	20.685	0.007	21.005	0.282	2.288	26.981	26.783	27.459	27.074	0.347
8	20.549	0.007	21.039	0.006	20.500	0.008	20.696	0.298	2.323	27.541	26.964	27.644	27.383	0.366
9	19.757	0.009	20.038	0.007	19.530	0.006	19.775	0.254	2.431	28.333	27.965	28.614	28.304	0.325
10	19.620	0.008	19.991	0.005	19.413	0.006	19.675	0.292	2.443	28.470	28.013	28.731	28.404	0.363
15	17.941	0.008	18.325	0.006	17.789	0.009	18.018	0.276	2.668	30.148	29.678	30.355	30.061	0.347
20	16.963	0.009	17.441	0.009	16.918	0.006	17.108	0.289	2.810	31.126	30.563	31.226	30.971	0.357
30	15.719	0.009	16.094	0.009	15.557	0.009	15.790	0.275	3.044	32.370	31.910	32.587	32.289	0.345
50	15.087	0.007	15.653	0.011	15.301	0.007	15.347	0.286	3.132	33.003	32.350	32.843	32.732	0.340
100	15.064	0.011	15.601	0.007	15.103	0.009	15.256	0.299	3.151	33.025	32.402	33.041	32.823	0.364

[a] Average value (mean) of 100 phase-shift measurements (in degrees) calculated as: $\bar{\phi} = \frac{1}{n}\sum_{i=1}^{n}\phi_i$; [b] Standard deviation value (s) of 100 phase-shift measurements (in degrees) calculated as: $s = \left(\frac{1}{n-1}\sum_{i=1}^{n}(\phi_i - \bar{\phi})^2\right)^{1/2}$; [c] Mean of the average phase-shift values ($\bar{\phi}$, in degrees) obtained for each replica, calculated as: $\bar{\phi}_{avg} = \frac{1}{3}\sum_{i=1}^{3}\bar{\phi}_i$; [d] Standard deviation value (s) of the average phase-shift values ($\bar{\phi}_i$, in degrees) obtained for each replica, calculated as: $s = \left(\frac{1}{3-1}\sum_{i=1}^{3}(\bar{\phi}_i - \bar{\phi}_{avg})^2\right)^{1/2}$; [e] Ratio between the average phase-shift value, $\bar{\phi}_{avg}$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\phi}_{avg\,(0\%\,pO_2)}/\bar{\phi}_{avg\,(x\%\,pO_2)}$); [f] Average phase difference (in degrees) between the average phase-shift value, $\bar{\phi}_i$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\phi}_{i\,(0\%\,pO_2)} - \bar{\phi}_{i\,(x\%\,pO_2)}$); [g] Average value (mean) of the 3 average phase difference values obtained for each replica (in degrees); [h] Standard deviation value (s) of the 3 average phase difference values obtained for each replica (in degrees).

Table ESI-13. Luminescence lifetime measurements for different oxygen concentrations of EB146 immobilized into AP200/19 in triplicate at 21º C. Modulation frequency of 94100 Hz.

pO_2(%)	Replica #1		Replica #2		Replica #3		Average results		τ_0/τ_x [e]	Luminescence lifetime difference $(\tau_{x\%\,pO_2} - \tau_{0\%\,pO_2})$				
	mean (µs)[a]	s (µs)[b]	mean (µs)[a]	s (µs)[b]	mean (µs)[a]	s (µs)[b]	mean (µs)[c]	s (µs)[d]		Rep. #1 (µs)[f]	Rep. #2 (µs)[f]	Rep. #3 (µs)[f]	mean (µs)[g]	s (µs)[h]
0	1.884	0.001	1.878	0.001	1.888	0.001	1.883	0.004	1.000	0.000	0.000	0.000	0.000	0.000
0.25	1.443	0.001	1.471	0.002	1.450	0.001	1.455	0.014	1.294	0.440	0.407	0.437	0.428	0.018
0.5	1.258	0.001	1.276	0.001	1.253	0.001	1.262	0.011	1.491	0.626	0.602	0.634	0.621	0.016
0.75	1.153	0.001	1.174	0.001	1.157	0.001	1.161	0.010	1.621	0.730	0.704	0.730	0.721	0.014
1	1.082	0.001	1.094	0.001	1.074	0.001	1.083	0.010	1.738	0.801	0.784	0.813	0.799	0.014
2	0.886	0.001	0.877	0.001	0.865	0.001	0.876	0.010	2.149	0.998	1.001	1.022	1.007	0.013
3	0.800	0.001	0.819	0.001	0.807	0.001	0.809	0.009	2.328	1.083	1.059	1.080	1.074	0.013
4	0.735	0.001	0.754	0.001	0.743	0.001	0.744	0.009	2.530	1.149	1.124	1.144	1.139	0.013
5	0.702	0.001	0.710	0.001	0.696	0.001	0.703	0.007	2.679	1.182	1.168	1.191	1.180	0.011
6	0.665	0.001	0.677	0.001	0.662	0.001	0.668	0.007	2.818	1.218	1.201	1.225	1.215	0.012
7	0.652	0.001	0.656	0.001	0.638	0.001	0.649	0.009	2.900	1.231	1.222	1.249	1.234	0.013
8	0.634	0.001	0.650	0.001	0.632	0.001	0.639	0.010	2.947	1.250	1.228	1.255	1.244	0.014
9	0.607	0.001	0.616	0.001	0.599	0.001	0.608	0.008	3.097	1.276	1.261	1.288	1.275	0.013
10	0.602	0.001	0.615	0.001	0.596	0.001	0.604	0.009	3.114	1.281	1.263	1.291	1.278	0.014
15	0.547	0.001	0.560	0.001	0.542	0.001	0.550	0.009	3.423	1.336	1.318	1.345	1.333	0.013
20	0.515	0.001	0.531	0.001	0.514	0.001	0.520	0.009	3.618	1.368	1.347	1.373	1.363	0.013
30	0.476	0.001	0.488	0.001	0.470	0.001	0.478	0.008	3.938	1.408	1.390	1.417	1.405	0.013
50	0.456	0.001	0.473	0.001	0.462	0.001	0.464	0.009	4.057	1.428	1.404	1.425	1.419	0.012
100	0.455	0.001	0.472	0.001	0.456	0.001	0.461	0.009	4.083	1.429	1.406	1.431	1.422	0.013

[a] Average value (mean) of 100 luminescence lifetime measurements (in microseconds) calculated as: $\bar{\tau} = \frac{1}{n}\sum_{i=1}^{n}\tau_i$; [b] Standard deviation value (s) of 100 luminescence lifetime measurements (in microseconds) calculated as: $s = \left(\frac{1}{n-1}\sum_{i=1}^{n}(\tau_i - \bar{\tau})^2\right)^{1/2}$; [c] Mean of the average luminescence-lifetime values ($\bar{\tau}$, in microseconds) obtained for each replica, calculated as: $\bar{\mu}_{avg} = \frac{1}{3}\sum_{i=1}^{3}\bar{\tau}_i$; [d] Standard deviation value (s) of the average luminescence-lifetime values ($\bar{\tau}_i$, in microseconds) obtained for each replica, calculated as: $s = \left(\frac{1}{3-1}\sum_{i=1}^{3}(\bar{\tau}_i - \bar{\tau}_{avg})^2\right)^{1/2}$; [e] Ratio between the average luminescence-lifetime value, $\bar{\tau}_{avg}$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\tau}_{avg\,(0\%\,pO_2)}/\bar{\tau}_{avg\,(x\%\,pO_2)}$); [f] Average lifetime difference (in microseconds) between the average luminescence-lifetime value, $\bar{\tau}_i$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\tau}_{i\,(0\%\,pO_2)} - \bar{\tau}_{i\,(x\%\,pO_2)}$); [g] Average value (mean) of the 3 average lifetime difference values obtained for each replica (in microseconds); [h] Standard deviation value (s) of the 3 average lifetime difference values obtained for each replica (in microseconds).

Table ESI-14. Phase-shift measurements for ultra-low oxygen concentrations between 0 and 0.26% O_2 of PtTFPP immobilized into AP200/19 in triplicate at 21ºC. Modulation frequency of 40100 Hz.

pO_2(%)	Replica #1		Replica #2		Replica #3		Average results		Φ_0/Φ_x [e]	Phase difference $(\Phi_{0\%\,pO_2} - \Phi_{x\%})$				
	mean (º)[a]	s (º)[b]	mean (º)[a]	s (º)[b]	mean (º)[a]	s (º)[b]	mean (º)[c]	s (º)[d]		Rep. #1 (º)[f]	Rep. #2 (º)[f]	Rep. #3 (º)[f]	mean (º)[g]	s (º)[h]
0.00	87.736	0.075	87.614	0.069	87.892	0.085	87.747	0.139	1.000	0.000	0.000	0.000	0.000	0.000
0.05	84.068	0.086	84.114	0.077	84.086	0.079	84.089	0.023	1.043	3.668	3.500	3.806	3.658	0.153
0.10	81.013	0.070	80.954	0.061	80.873	0.065	80.946	0.070	1.084	6.723	6.660	7.019	6.800	0.191
0.15	78.427	0.054	78.461	0.060	78.563	0.049	78.483	0.070	1.118	9.309	9.153	9.329	9.263	0.096
0.21	76.241	0.066	76.408	0.062	76.367	0.061	76.338	0.087	1.149	11.495	11.206	11.525	11.408	0.176
0.26	74.322	0.066	74.425	0.057	74.493	0.063	74.413	0.086	1.179	13.414	13.189	13.399	13.334	0.125

[a] Average value (mean) of 100 phase-shift measurements (in degrees) calculated as: $\bar{\phi} = \frac{1}{n}\sum_{i=1}^{n}\phi_i$; [b] Standard deviation value (s) of 100 phase-shift measurements (in degrees) calculated as: $s = \left(\frac{1}{n-1}\sum_{i=1}^{n}(\phi_i - \bar{\phi})^2\right)^{1/2}$; [c] Mean of the average phase-shift values ($\bar{\phi}$, in degrees) obtained for each replica, calculated as: $\bar{\phi}_{avg} = \frac{1}{3}\sum_{i=1}^{3}\bar{\phi}_i$; [d] Standard deviation value (s) of the average phase-shift values ($\bar{\phi}_i$, in degrees) obtained for each replica, calculated as: $s = \left(\frac{1}{3-1}\sum_{i=1}^{3}(\bar{\phi}_i - \bar{\phi}_{avg})^2\right)^{1/2}$; [e] Ratio between the average phase-shift value, $\bar{\phi}_{avg}$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\phi}_{avg\,(0\%\,pO_2)}/\bar{\phi}_{avg\,(x\%\,pO_2)}$); [f] Average phase difference (in degrees) between the average phase-shift value, $\bar{\phi}_i$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\phi}_{i\,(0\%\,pO_2)} - \bar{\phi}_{i\,(x\%\,pO_2)}$); [g] Average value (mean) of the 3 average phase difference values obtained for each replica (in degrees); [h] Standard deviation value (s) of the 3 average phase difference values obtained for each replica (in degrees).

Table ESI-15. Luminescence lifetime measurements for ultra-low oxygen concentrations between 0 and 0.26% O_2 of PtTFPP immobilized into AP200/19 in triplicate at 21° C. Modulation frequency of 40100 Hz.

pO_2(%)	Replica #1		Replica #2		Replica #3		Average results		τ_0/τ_x [e]	Luminescence lifetime difference $(\tau_{x\%\,pO_2} - \tau_{0\%\,pO_2})$				
	mean (µs)[a]	s (µs)[b]	mean (µs)[a]	s (µs)[b]	mean (µs)[a]	s (µs)[b]	mean (µs)[c]	s (µs)[d]		Rep. #1 (µs)[f]	Rep. #2 (µs)[f]	Rep. #3 (µs)[f]	mean (µs)[g]	s (µs)[h]
0.00	100.391	1.475	95.252	1.480	101.828	1.471	99.157	3.457	1.000	0.000	0.000	0.000	0.000	0.000
0.05	38.198	0.396	38.498	0.401	38.315	0.391	38.337	0.151	2.586	62.193	56.753	63.512	60.820	3.582
0.10	25.095	0.160	24.929	0.165	24.704	0.156	24.909	0.196	3.980	75.295	70.323	77.123	74.247	3.519
0.15	19.381	0.079	19.440	0.084	19.618	0.075	19.480	0.123	5.090	81.009	75.812	82.209	79.677	3.400
0.21	16.208	0.071	16.415	0.076	16.364	0.067	16.329	0.107	6.072	84.182	78.836	85.463	82.827	3.515
0.26	14.140	0.056	14.239	0.062	14.304	0.052	14.228	0.082	6.969	86.250	81.013	87.523	84.929	3.450

[a] Average value (mean) of 100 luminescence lifetime measurements (in microseconds) calculated as: $\bar{\tau} = \frac{1}{n}\sum_{i=1}^{n}\tau_i$; [b] Standard deviation value (s) of 100 luminescence lifetime measurements (in microseconds) calculated as: $s = \left(\frac{1}{n-1}\sum_{i=1}^{n}(\tau_i - \bar{\tau})^2\right)^{1/2}$; [c] Mean of the average luminescence-lifetime values ($\bar{\tau}$, in microseconds) obtained for each replica, calculated as: $\bar{\mu}_{avg} = \frac{1}{3}\sum_{i=1}^{3}\bar{\tau}_i$; [d] Standard deviation value (s) of the average luminescence-lifetime values ($\bar{\tau}_i$, in microseconds) obtained for each replica, calculated as: $s = \left(\frac{1}{3-1}\sum_{i=1}^{3}(\bar{\tau}_i - \bar{\tau}_{avg})^2\right)^{1/2}$; [e] Ratio between the average luminescence-lifetime value, $\bar{\tau}_{avg}$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\tau}_{avg\,(0\%\,pO_2)}/\bar{\tau}_{avg\,(x\%\,pO_2)}$); [f] Average lifetime difference (in microseconds) between the average luminescence-lifetime value, $\bar{\tau}_i$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\tau}_{i\,(0\%\,pO_2)} - \bar{\tau}_{i\,(x\%\,pO_2)}$); [g] Average value (mean) of the 3 average lifetime difference values obtained for each replica (in microseconds); [h] Standard deviation value (s) of the 3 average lifetime difference values obtained for each replica (in microseconds).

Table ESI-16. Phase-shift measurements for ultra-low oxygen concentrations between 0 and 0.26% O_2 of N969 immobilized into AP200/19 in triplicate at 21ºC. Modulation frequency of 94100 Hz.

pO_2(%)	Replica #1		Replica #2		Replica #3		Average results		Φ_0/Φ_x [e]	Phase difference $(\Phi_{0\%\,pO_2} - \Phi_{x\%})$				
	mean (º)[a]	s (º)[b]	mean (º)[a]	s (º)[b]	mean (º)[a]	s (º)[b]	mean (º)[c]	s (º)[d]		Rep. #1 (º)[f]	Rep. #2 (º)[f]	Rep. #3 (º)[f]	mean (º)[g]	s (º)[h]
0.00	65.678	0.026	65.699	0.024	65.767	0.025	65.714	0.046	1.000	0.000	0.000	0.000	0.000	0.000
0.05	61.748	0.008	61.614	0.008	61.757	0.007	61.706	0.080	1.065	3.930	4.085	4.010	4.008	0.077
0.10	58.807	0.007	58.891	0.009	58.837	0.007	58.845	0.042	1.116	6.871	6.808	6.930	6.869	0.061
0.15	56.550	0.009	56.439	0.009	56.596	0.009	56.528	0.080	1.162	9.128	9.260	9.171	9.186	0.067
0.21	54.649	0.007	54.640	0.006	54.724	0.007	54.671	0.046	1.202	11.029	11.059	11.043	11.043	0.015
0.26	53.000	0.007	52.951	0.005	52.875	0.005	52.942	0.063	1.241	12.678	12.748	12.892	12.772	0.109

[a] Average value (mean) of 100 phase-shift measurements (in degrees) calculated as: $\bar{\phi} = \frac{1}{n}\sum_{i=1}^{n}\phi_i$; [b] Standard deviation value (s) of 100 phase-shift measurements (in degrees) calculated as: $s = \left(\frac{1}{n-1}\sum_{i=1}^{n}(\phi_i - \bar{\phi})^2\right)^{1/2}$; [c] Mean of the average phase-shift values ($\bar{\phi}$, in degrees) obtained for each replica, calculated as: $\bar{\phi}_{avg} = \frac{1}{3}\sum_{i=1}^{3}\bar{\phi}_i$; [d] Standard deviation value (s) of the average phase-shift values ($\bar{\phi}_i$, in degrees) obtained for each replica, calculated as: $s = \left(\frac{1}{3-1}\sum_{i=1}^{3}(\bar{\phi}_i - \bar{\phi}_{avg})^2\right)^{1/2}$; [e] Ratio between the average phase-shift value, $\bar{\phi}_{avg}$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\phi}_{avg\,(0\%\,pO_2)}/\bar{\phi}_{avg\,(x\%\,pO_2)}$); [f] Average phase difference (in degrees) between the average phase-shift value, $\bar{\phi}_i$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\phi}_{i\,(0\%\,pO_2)} - \bar{\phi}_{i\,(x\%\,pO_2)}$); [g] Average value (mean) of the 3 average phase difference values obtained for each replica (in degrees); [h] Standard deviation value (s) of the 3 average phase difference values obtained for each replica (in degrees).

Table ESI-17. Luminescence lifetime measurements for ultra-low oxygen concentrations between 0 and 0.26% O_2 of N969 immobilized into AP200/19 in triplicate at 21° C. Modulation frequency of 94100 Hz.

pO_2 (%)	Replica #1		Replica #2		Replica #3		Average results		τ_0/τ_x [e]	Luminescence lifetime difference $(\tau_{x\%\,pO_2} - \tau_{0\%\,pO_2})$				
	mean (µs)[a]	s (µs)[b]	mean (µs)[a]	s (µs)[b]	mean (µs)[a]	s (µs)[b]	mean (µs)[c]	s (µs)[d]		Rep. #1 (µs)[f]	Rep. #2 (µs)[f]	Rep. #3 (µs)[f]	mean (µs)[g]	s (µs)[h]
0.00	3.742	0.004	3.745	0.004	3.757	0.002	3.748	0.008	1.000	0.000	0.000	0.000	0.000	0.000
0.05	3.147	0.003	3.129	0.002	3.148	0.001	3.142	0.010	1.193	0.594	0.615	0.608	0.606	0.010
0.10	2.793	0.003	2.802	0.003	2.796	0.001	2.797	0.004	1.339	0.948	0.942	0.960	0.950	0.009
0.15	2.560	0.002	2.549	0.002	2.564	0.001	2.558	0.007	1.465	1.181	1.196	1.192	1.190	0.007
0.21	2.384	0.002	2.383	0.002	2.390	0.001	2.386	0.004	1.570	1.357	1.362	1.366	1.362	0.004
0.26	2.244	0.002	2.240	0.001	2.234	0.001	2.239	0.005	1.673	1.497	1.505	1.523	1.508	0.013

[a] Average value (mean) of 100 luminescence lifetime measurements (in microseconds) calculated as: $\bar{\tau} = \frac{1}{n}\sum_{i=1}^{n}\tau_i$; [b] Standard deviation value (s) of 100 luminescence lifetime measurements (in microseconds) calculated as: $s = \left(\frac{1}{n-1}\sum_{i=1}^{n}(\tau_i - \bar{\tau})^2\right)^{1/2}$; [c] Mean of the average luminescence-lifetime values ($\bar{\tau}$, in microseconds) obtained for each replica, calculated as: $\bar{\mu}_{avg} = \frac{1}{3}\sum_{i=1}^{3}\bar{\tau}_i$; [d] Standard deviation value (s) of the average luminescence-lifetime values ($\bar{\tau}_i$, in microseconds) obtained for each replica, calculated as: $s = \left(\frac{1}{3-1}\sum_{i=1}^{3}(\bar{\tau}_i - \bar{\tau}_{avg})^2\right)^{1/2}$; [e] Ratio between the average luminescence-lifetime value, $\bar{\tau}_{avg}$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\tau}_{avg\,(0\%\,pO_2)}/\bar{\tau}_{avg\,(x\%\,pO_2)}$); [f] Average lifetime difference (in microseconds) between the average luminescence-lifetime value, $\bar{\tau}_i$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\tau}_{i\,(0\%\,pO_2)} - \bar{\tau}_{i\,(x\%\,pO_2)}$); [g] Average value (mean) of the 3 average lifetime difference values obtained for each replica (in microseconds); [h] Standard deviation value (s) of the 3 average lifetime difference values obtained for each replica (in microseconds).

Table ESI-18. Phase-shift measurements for ultra-low oxygen concentrations between 0 and 0.26% O_2 of N1008 immobilized into AP200/19 in triplicate at 21ºC. Modulation frequency of 30100 Hz.

pO_2 (%)	Replica #1		Replica #2		Replica #3		Average results		Φ_0/Φ_x [e]	Phase difference $(\Phi_{0\%\,pO_2} - \Phi_{x\%})$				
	mean (º)[a]	s (º)[b]	mean (º)[a]	s (º)[b]	mean (º)[a]	s (º)[b]	mean (º)[c]	s (º)[d]		Rep. #1 (º)[f]	Rep. #2 (º)[f]	Rep. #3 (º)[f]	mean (º)[g]	s (º)[h]
0.00	57.926	0.088	57.821	0.089	57.801	0.087	57.849	0.067	1.000	0.000	0.000	0.000	0.000	0.000
0.05	57.031	0.008	57.042	0.010	56.959	0.009	57.010	0.045	1.014	0.895	0.779	0.842	0.838	0.058
0.10	55.885	0.012	55.759	0.012	55.865	0.014	55.836	0.067	1.036	2.041	2.062	1.936	2.013	0.067
0.15	54.773	0.015	54.655	0.017	54.677	0.015	54.701	0.062	1.057	3.153	3.166	3.124	3.147	0.021
0.21	53.705	0.017	53.557	0.018	53.599	0.015	53.620	0.076	1.078	4.221	4.264	4.202	4.229	0.031
0.26	52.697	0.017	52.792	0.019	52.807	0.018	52.765	0.059	1.096	5.229	5.029	4.994	5.084	0.126

[a] Average value (mean) of 100 phase-shift measurements (in degrees) calculated as: $\bar{\phi} = \frac{1}{n}\sum_{i=1}^{n}\phi_i$; [b] Standard deviation value (s) of 100 phase-shift measurements (in degrees) calculated as: $s = \left(\frac{1}{n-1}\sum_{i=1}^{n}(\phi_i - \bar{\phi})^2\right)^{1/2}$; [c] Mean of the average phase-shift values ($\bar{\phi}$, in degrees) obtained for each replica, calculated as: $\bar{\phi}_{avg} = \frac{1}{3}\sum_{i=1}^{3}\bar{\phi}_i$; [d] Standard deviation value (s) of the average phase-shift values ($\bar{\phi}_i$, in degrees) obtained for each replica, calculated as: $s = \left(\frac{1}{3-1}\sum_{i=1}^{3}(\bar{\phi}_i - \bar{\phi}_{avg})^2\right)^{1/2}$; [e] Ratio between the average phase-shift value, $\bar{\phi}_{avg}$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\phi}_{avg\,(0\%\,pO_2)}/\bar{\phi}_{avg\,(x\%\,pO_2)}$); [f] Average phase difference (in degrees) between the average phase-shift value, $\bar{\phi}_i$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\phi}_{i\,(0\%\,pO_2)} - \bar{\phi}_{i\,(x\%\,pO_2)}$); [g] Average value (mean) of the 3 average phase difference values obtained for each replica (in degrees); [h] Standard deviation value (s) of the 3 average phase difference values obtained for each replica (in degrees).

Table ESI-19. Luminescence lifetime measurements for ultra-low oxygen concentrations between 0 and 0.26% O_2 of N1008 immobilized into AP200/19 in triplicate at 21º C. Modulation frequency of 30100 Hz.

pO_2 (%)	Replica #1		Replica #2		Replica #3		Average results		τ_0/τ_x [e]	Luminescence lifetime difference $(\tau_{x\%\,pO_2} - \tau_{0\%\,pO_2})$				
	mean (µs)[a]	s (µs)[b]	mean (µs)[a]	s (µs)[b]	mean (µs)[a]	s (µs)[b]	mean (µs)[c]	s (µs)[d]		Rep. #1 (µs)[f]	Rep. #2 (µs)[f]	Rep. #3 (µs)[f]	mean (µs)[g]	s (µs)[h]
0.00	8.437	0.007	8.403	0.006	8.396	0.005	8.412	0.021	1.000	0.000	0.000	0.000	0.000	0.000
0.05	8.151	0.006	8.155	0.005	8.129	0.004	8.145	0.014	1.032	0.286	0.248	0.267	0.267	0.019
0.10	7.805	0.005	7.768	0.004	7.799	0.004	7.790	0.019	1.079	0.632	0.635	0.597	0.621	0.021
0.15	7.488	0.005	7.455	0.004	7.461	0.005	7.468	0.017	1.126	0.949	0.948	0.935	0.944	0.007
0.21	7.199	0.004	7.160	0.003	7.171	0.004	7.176	0.020	1.172	1.238	1.243	1.225	1.235	0.009
0.26	6.940	0.005	6.964	0.005	6.967	0.006	6.957	0.014	1.209	1.497	1.439	1.429	1.455	0.036

[a] Average value (mean) of 100 luminescence lifetime measurements (in microseconds) calculated as: $\bar{\tau} = \frac{1}{n}\sum_{i=1}^{n}\tau_i$; [b] Standard deviation value (s) of 100 luminescence lifetime measurements (in microseconds) calculated as: $s = \left(\frac{1}{n-1}\sum_{i=1}^{n}(\tau_i - \bar{\tau})^2\right)^{1/2}$; [c] Mean of the average luminescence-lifetime values ($\bar{\tau}$, in microseconds) obtained for each replica, calculated as: $\bar{\mu}_{avg} = \frac{1}{3}\sum_{i=1}^{3}\bar{\tau}_i$; [d] Standard deviation value (s) of the average luminescence-lifetime values ($\bar{\tau}_i$, in microseconds) obtained for each replica, calculated as: $s = \left(\frac{1}{3-1}\sum_{i=1}^{3}(\bar{\tau}_i - \bar{\tau}_{avg})^2\right)^{1/2}$; [e] Ratio between the average luminescence-lifetime value, $\bar{\tau}_{avg}$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\tau}_{avg\,(0\%\,pO_2)}/\bar{\tau}_{avg\,(x\%\,pO_2)}$); [f] Average lifetime difference (in microseconds) between the average luminescence-lifetime value, $\bar{\tau}_i$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\tau}_{i\,(0\%\,pO_2)} - \bar{\tau}_{i\,(x\%\,pO_2)}$); [g] Average value (mean) of the 3 average lifetime difference values obtained for each replica (in microseconds); [h] Standard deviation value (s) of the 3 average lifetime difference values obtained for each replica (in microseconds).

Table ESI-20. Phase-shift measurements for ultra-low oxygen concentrations between 0 and 0.26% O_2 of EB146 immobilized into AP200/19 in triplicate at 21ºC. Modulation frequency of 94100 Hz.

pO_2(%)	Replica #1		Replica #2		Replica #3		Average results		Φ_0/Φ_x [e]	Phase difference $\left(\Phi_{0\%\,pO_2} - \Phi_{x\%}\right)$				
	mean (º)[a]	s (º)[b]	mean (º)[a]	s (º)[b]	mean (º)[a]	s (º)[b]	mean (º)[c]	s (º)[d]		Rep. #1 (º)[f]	Rep. #2 (º)[f]	Rep. #3 (º)[f]	mean (º)[g]	s (º)[h]
0.00	48.028	0.069	47.922	0.071	47.893	0.051	47.947	0.071	1.000	0.000	0.000	0.000	0.000	0.000
0.05	45.787	0.012	45.824	0.022	45.921	0.032	45.844	0.069	1.045	2.241	2.098	1.972	2.103	0.134
0.10	43.897	0.041	43.901	0.011	43.894	0.020	43.897	0.003	1.092	4.131	4.021	3.999	4.050	0.070
0.15	43.091	0.017	42.964	0.016	43.211	0.017	43.088	0.123	1.112	4.937	4.958	4.682	4.859	0.153
0.21	41.813	0.010	41.700	0.009	41.697	0.011	41.736	0.066	1.148	6.215	6.222	6.196	6.211	0.013
0.26	40.558	0.008	40.480	0.007	40.525	0.007	40.521	0.039	1.183	7.470	7.442	7.368	7.426	0.052

[a] Average value (mean) of 100 phase-shift measurements (in degrees) calculated as: $\bar{\phi} = \frac{1}{n}\sum_{i=1}^{n}\phi_i$; [b] Standard deviation value (s) of 100 phase-shift measurements (in degrees) calculated as: $s = \left(\frac{1}{n-1}\sum_{i=1}^{n}(\phi_i - \bar{\phi})^2\right)^{1/2}$; [c] Mean of the average phase-shift values ($\bar{\phi}$, in degrees) obtained for each replica, calculated as: $\bar{\phi}_{avg} = \frac{1}{3}\sum_{i=1}^{3}\bar{\phi}_i$; [d] Standard deviation value (s) of the average phase-shift values ($\bar{\phi}_i$, in degrees) obtained for each replica, calculated as: $s = \left(\frac{1}{3-1}\sum_{i=1}^{3}(\bar{\phi}_i - \bar{\phi}_{avg})^2\right)^{1/2}$; [e] Ratio between the average phase-shift value, $\bar{\phi}_{avg}$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\phi}_{avg\,(0\%\,pO_2)}/\bar{\phi}_{avg\,(x\%\,pO_2)}$); [f] Average phase difference (in degrees) between the average phase-shift value, $\bar{\phi}_i$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\phi}_{i\,(0\%\,pO_2)} - \bar{\phi}_{i\,(x\%\,pO_2)}$); [g] Average value (mean) of the 3 average phase difference values obtained for each replica (in degrees); [h] Standard deviation value (s) of the 3 average phase difference values obtained for each replica (in degrees).

Table ESI-21. Luminescence lifetime measurements for ultra-low oxygen concentrations between 0 and 0.26% O_2 of EB146 immobilized into AP200/19 in triplicate at 21º C. Modulation frequency of 94100 Hz.

pO_2 (%)	Replica #1		Replica #2		Replica #3		Average results		τ_0/τ_x [e]	Luminescence lifetime difference $(\tau_{x\%\,pO_2} - \tau_{0\%\,pO_2})$				
	mean (µs)[a]	s (µs)[b]	mean (µs)[a]	s (µs)[b]	mean (µs)[a]	s (µs)[b]	mean (µs)[c]	s (µs)[d]		Rep. #1 (µs)[f]	Rep. #2 (µs)[f]	Rep. #3 (µs)[f]	mean (µs)[g]	s (µs)[h]
0.00	1.880	0.002	1.873	0.002	1.871	0.002	1.874	0.004	1.000	0.000	0.000	0.000	0.000	0.000
0.05	1.738	0.001	1.740	0.002	1.746	0.001	1.741	0.004	1.076	0.142	0.133	0.125	0.133	0.008
0.10	1.627	0.001	1.637	0.001	1.629	0.001	1.631	0.005	1.149	0.253	0.236	0.242	0.243	0.008
0.15	1.582	0.001	1.575	0.001	1.588	0.001	1.581	0.006	1.185	0.298	0.298	0.283	0.293	0.008
0.21	1.512	0.001	1.506	0.001	1.508	0.001	1.508	0.003	1.242	0.368	0.367	0.363	0.366	0.002
0.26	1.447	0.001	1.443	0.001	1.445	0.001	1.445	0.002	1.297	0.433	0.430	0.426	0.429	0.003

[a] Average value (mean) of 100 luminescence lifetime measurements (in microseconds) calculated as: $\bar{\tau} = \frac{1}{n}\sum_{i=1}^{n}\tau_i$; [b] Standard deviation value (s) of 100 luminescence lifetime measurements (in microseconds) calculated as: $s = \left(\frac{1}{n-1}\sum_{i=1}^{n}(\tau_i - \bar{\tau})^2\right)^{1/2}$; [c] Mean of the average luminescence-lifetime values ($\bar{\tau}$, in microseconds) obtained for each replica, calculated as: $\bar{\mu}_{avg} = \frac{1}{3}\sum_{i=1}^{3}\bar{\tau}_i$; [d] Standard deviation value (s) of the average luminescence-lifetime values ($\bar{\tau}_i$, in microseconds) obtained for each replica, calculated as: $s = \left(\frac{1}{3-1}\sum_{i=1}^{3}(\bar{\tau}_i - \bar{\tau}_{avg})^2\right)^{1/2}$; [e] Ratio between the average luminescence-lifetime value, $\bar{\tau}_{avg}$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\tau}_{avg\,(0\%\,pO_2)}/\bar{\tau}_{avg\,(x\%\,pO_2)}$); [f] Average lifetime difference (in microseconds) between the average luminescence-lifetime value, $\bar{\tau}_i$, at 0% oxygen and any oxygen concentration (i.e., $\bar{\tau}_{i\,(0\%\,pO_2)} - \bar{\tau}_{i\,(x\%\,pO_2)}$); [g] Average value (mean) of the 3 average lifetime difference values obtained for each replica (in microseconds); [h] Standard deviation value (s) of the 3 average lifetime difference values obtained for each replica (in microseconds).

Table ESI-22. Phase-shift measurements for different oxygen concentrations and several relative humidity of PtTFPP immobilized into AP200/19 at 21ºC. Modulation frequency of 40100 Hz.

pO_2 (%)	0% Hum.		10% Hum.		20% Hum.		40% Hum.		60% Hum.		80% Hum.	
	mean (º)[a]	s (º)[b]	mean (º)[a]	s (º)[b]	mean (º)[a]	s (º)[b]	mean (º)[a]	s (º)[b]	mean (º)[a]	s (º)[b]	mean (º)[a]	s (º)[b]
0.00	87.734	0.102	87.861	0.114	87.849	0.128	88.238	0.130	88.351	0.125	88.232	0.111
0.25	74.602	0.140	73.964	0.074	74.348	0.086	74.584	0.076	74.704	0.076	74.470	0.086
0.50	66.489	0.255	65.385	0.077	65.695	0.076	65.968	0.075	66.058	0.082	65.961	0.075
0.75	60.354	0.076	60.210	0.072	60.538	0.073	60.834	0.064	60.888	0.091	60.809	0.073
1	57.502	0.069	57.626	0.076	58.005	0.073	58.254	0.067	58.324	0.070	58.222	0.063
2	47.770	0.079	47.926	0.072	48.368	0.068	48.672	0.076	48.723	0.082	48.612	0.064
3	43.765	0.071	44.024	0.078	44.464	0.068	44.821	0.088	44.791	0.063	44.689	0.082
4	41.418	0.078	41.721	0.074	42.160	0.085	42.522	0.075	42.502	0.083	42.383	0.073
5	39.379	0.080	39.700	0.079	40.146	0.072	40.550	0.079	40.466	0.087	40.388	0.096
6	37.958	0.090	38.391	0.068	38.821	0.092	39.213	0.081	39.128	0.089	39.106	0.072
7	36.908	0.111	37.281	0.095	37.787	0.079	38.133	0.071	38.011	0.087	37.936	0.090
8	36.559	0.078	36.924	0.078	37.435	0.073	37.794	0.075	37.641	0.095	37.646	0.102
9	35.552	0.082	35.938	0.091	36.450	0.071	36.802	0.076	36.611	0.080	36.770	0.108
10	34.527	0.076	34.951	0.095	35.434	0.085	35.826	0.092	35.572	0.107	35.838	0.088
15	32.565	0.094	33.048	0.109	33.538	0.098	33.908	0.100	33.605	0.089	34.257	0.101
20	31.125	0.117	31.625	0.096	32.131	0.098	32.478	0.119	32.162	0.113	33.098	0.099
30	29.422	0.108	29.992	0.104	30.508	0.110	30.854	0.098	30.460	0.103	31.990	0.107
50	27.722	0.097	28.382	0.136	28.950	0.113	29.305	0.120	30.000	0.137	31.344	0.114
100	26.373	0.131	26.921	0.112	27.466	0.113	27.824	0.125	27.502	0.118	28.622	0.144

[a] Average value (mean) of 100 phase-shift measurements (in degrees) calculated as: $\bar{\phi} = \frac{1}{n}\sum_{i=1}^{n}\phi_i$; [b] Standard deviation value (s) of 100 phase-shift measurements (in degrees) calculated as: $s = \left(\frac{1}{n-1}\sum_{i=1}^{n}(\phi_i - \bar{\phi})^2\right)^{1/2}$.

Table ESI-23. Luminescence lifetime measurements for different oxygen concentrations and several relative humidity of PtTFPP immobilized into AP200/19 at 21ºC. Modulation frequency of 40100 Hz.

pO_2 (%)	0% Hum.		10% Hum.		20% Hum.		40% Hum.		60% Hum.		80% Hum.	
	mean (µs)[a]	s (µs)[b]	mean (µs)[a]	s (µs)[b]	mean (µs)[a]	s (µs)[b]	mean (µs)[a]	s (µs)[b]	mean (µs)[a]	s (µs)[b]	mean (µs)[a]	s (µs)[b]
0.00	100.315	1.207	106.273	1.437	105.714	1.238	129.085	1.339	137.933	1.428	128.647	1.677
0.25	14.411	0.013	13.808	0.023	14.165	0.015	14.394	0.019	14.512	0.011	14.282	0.014
0.50	9.123	0.017	8.663	0.005	8.788	0.005	8.901	0.005	8.938	0.005	8.898	0.005
0.75	6.973	0.005	6.933	0.005	7.026	0.005	7.111	0.004	7.127	0.006	7.104	0.005
1	6.230	0.004	6.260	0.005	6.352	0.005	6.414	0.004	6.432	0.004	6.407	0.004
2	4.372	0.005	4.396	0.005	4.465	0.004	4.513	0.005	4.521	0.005	4.503	0.004
3	3.801	0.004	3.836	0.005	3.895	0.004	3.944	0.006	3.940	0.004	3.926	0.005
4	3.501	0.005	3.538	0.005	3.593	0.005	3.639	0.005	3.637	0.005	3.622	0.005
5	3.257	0.005	3.295	0.005	3.347	0.005	3.395	0.005	3.385	0.006	3.376	0.006
6	3.096	0.006	3.144	0.004	3.193	0.006	3.238	0.005	3.228	0.006	3.226	0.005
7	2.980	0.007	3.021	0.006	3.077	0.005	3.115	0.005	3.102	0.006	3.093	0.006
8	2.943	0.005	2.982	0.005	3.038	0.005	3.078	0.005	3.061	0.006	3.061	0.007
9	2.836	0.005	2.877	0.006	2.931	0.005	2.969	0.005	2.948	0.005	2.965	0.007
10	2.730	0.005	2.774	0.006	2.824	0.005	2.865	0.006	2.838	0.007	2.866	0.006
15	2.534	0.006	2.582	0.007	2.630	0.006	2.667	0.007	2.637	0.006	2.703	0.007
20	2.396	0.008	2.444	0.006	2.492	0.006	2.526	0.008	2.495	0.007	2.587	0.006
30	2.238	0.007	2.290	0.007	2.338	0.007	2.371	0.006	2.334	0.007	2.479	0.007
50	2.085	0.006	2.144	0.009	2.195	0.007	2.227	0.008	2.291	0.009	2.417	0.007
100	1.967	0.009	2.015	0.007	2.063	0.007	2.094	0.008	2.066	0.008	2.166	0.010

[a] Average value (mean) of 100 luminescence lifetime measurements (in microseconds) calculated as: $\bar{\tau} = \frac{1}{n}\sum_{i=1}^{n}\tau_i$; [b] Standard deviation value (s) of 100 luminescence lifetime measurements (in microseconds) calculated as: $s = \left(\frac{1}{n-1}\sum_{i=1}^{n}(\tau_i - \bar{\tau})^2\right)^{1/2}$.

Table ESI-24. Phase-shift measurements for different oxygen concentrations and several relative humidity of N969 immobilized into AP200/19 at 21ºC. Modulation frequency of 94100 Hz.

pO_2 (%)	0% Hum.		10% Hum.		20% Hum.		40% Hum.		60% Hum.		80% Hum.	
	mean (º)[a]	s (º)[b]	mean (º)[a]	s (º)[b]	mean (º)[a]	s (º)[b]	mean (º)[a]	s (º)[b]	mean (º)[a]	s (º)[b]	mean (º)[a]	s (º)[b]
0.00	65.637	0.109	62.640	0.006	60.580	0.011	58.989	0.012	57.639	0.013	56.549	0.014
0.25	52.986	0.008	50.165	0.012	48.403	0.009	47.057	0.008	45.958	0.008	45.022	0.008
0.50	48.848	0.007	46.335	0.009	44.818	0.007	43.639	0.008	42.684	0.010	41.861	0.012
0.75	46.372	0.011	44.125	0.008	42.780	0.008	41.739	0.009	40.895	0.008	40.160	0.010
1	44.605	0.012	42.576	0.010	41.380	0.011	40.444	0.009	39.679	0.008	39.006	0.010
2	40.430	0.010	38.952	0.010	38.098	0.011	37.416	0.010	36.856	0.010	36.348	0.010
3	38.217	0.013	37.085	0.009	36.444	0.009	35.926	0.009	35.473	0.008	35.064	0.008
4	36.654	0.015	35.769	0.009	35.251	0.010	34.843	0.010	34.471	0.011	34.131	0.008
5	35.626	0.011	34.923	0.009	34.528	0.009	34.180	0.010	33.858	0.011	33.564	0.011
6	34.842	0.009	34.284	0.011	33.961	0.010	33.679	0.011	33.391	0.010	33.138	0.011
7	34.142	0.010	33.701	0.009	33.447	0.009	33.196	0.010	32.951	0.010	32.668	0.010
8	33.517	0.013	33.170	0.011	32.950	0.008	32.743	0.011	32.524	0.010	32.304	0.011
9	32.955	0.008	32.675	0.009	32.509	0.012	32.324	0.010	32.122	0.011	31.957	0.010
10	32.669	0.009	32.458	0.010	32.320	0.010	32.154	0.010	31.967	0.010	31.845	0.010
15	30.802	0.017	30.789	0.010	30.744	0.011	30.671	0.009	30.538	0.015	30.625	0.014
20	29.561	0.009	29.647	0.012	29.685	0.011	29.646	0.009	29.556	0.013	29.811	0.009
30	27.928	0.013	28.123	0.011	28.212	0.010	28.232	0.012	28.139	0.014	28.743	0.011
50	26.926	0.013	27.208	0.013	27.335	0.010	27.396	0.013	27.926	0.012	28.469	0.013
100	26.818	0.013	27.090	0.016	27.233	0.012	27.262	0.015	27.281	0.014	27.695	0.013

[a] Average value (mean) of 100 phase-shift measurements (in degrees) calculated as: $\bar{\phi} = \frac{1}{n}\sum_{i=1}^{n} \phi_i$; [b] Standard deviation value (s) of 100 phase-shift measurements (in degrees) calculated as: $s = \left(\frac{1}{n-1}\sum_{i=1}^{n}(\phi_i - \bar{\phi})^2\right)^{1/2}$.

Table ESI-25. Luminescence lifetime measurements for different oxygen concentrations and several relative humidity of N969 immobilized into AP200/19 at 21ºC. Modulation frequency of 94100 Hz.

pO_2 (%)	0% Hum.		10% Hum.		20% Hum.		40% Hum.		60% Hum.		80% Hum.	
	mean (µs)[a]	s (µs)[b]	mean (µs)[a]	s (µs)[b]	mean (µs)[a]	s (µs)[b]	mean (µs)[a]	s (µs)[b]	mean (µs)[a]	s (µs)[b]	mean (µs)[a]	s (µs)[b]
0.00	3.734	0.003	3.268	0.002	2.999	0.003	2.813	0.003	2.669	0.004	2.560	0.003
0.25	2.243	0.001	2.027	0.001	1.905	0.001	1.817	0.001	1.748	0.001	1.692	0.001
0.50	1.935	0.001	1.772	0.001	1.680	0.001	1.612	0.001	1.559	0.001	1.515	0.001
0.75	1.774	0.001	1.640	0.001	1.565	0.001	1.509	0.001	1.464	0.001	1.427	0.001
1	1.668	0.001	1.554	0.001	1.490	0.001	1.441	0.001	1.403	0.001	1.369	0.001
2	1.441	0.001	1.367	0.001	1.326	0.001	1.293	0.001	1.267	0.001	1.244	0.001
3	1.331	0.001	1.278	0.001	1.249	0.001	1.225	0.001	1.205	0.001	1.187	0.001
4	1.258	0.001	1.218	0.001	1.195	0.001	1.177	0.001	1.161	0.001	1.146	0.001
5	1.212	0.001	1.180	0.001	1.163	0.001	1.148	0.001	1.134	0.001	1.122	0.001
6	1.177	0.001	1.153	0.001	1.139	0.001	1.127	0.001	1.114	0.001	1.104	0.001
7	1.146	0.001	1.128	0.001	1.117	0.001	1.106	0.001	1.096	0.001	1.084	0.001
8	1.120	0.001	1.105	0.001	1.096	0.001	1.087	0.001	1.078	0.001	1.069	0.001
9	1.096	0.001	1.084	0.001	1.077	0.001	1.070	0.001	1.061	0.001	1.055	0.001
10	1.084	0.001	1.075	0.001	1.070	0.001	1.063	0.001	1.055	0.001	1.050	0.001
15	1.008	0.001	1.007	0.001	1.006	0.001	1.003	0.001	0.997	0.001	1.001	0.001
20	0.959	0.001	0.962	0.001	0.964	0.001	0.962	0.001	0.959	0.001	0.969	0.001
30	0.896	0.001	0.904	0.001	0.907	0.001	0.908	0.001	0.904	0.001	0.927	0.001
50	0.859	0.001	0.869	0.001	0.874	0.001	0.876	0.001	0.896	0.001	0.917	0.001
100	0.855	0.001	0.865	0.001	0.870	0.001	0.871	0.001	0.872	0.001	0.887	0.001

[a] Average value (mean) of 100 luminescence lifetime measurements (in microseconds) calculated as: $\overline{\tau} = \frac{1}{n}\sum_{i=1}^{n} \tau_i$; [b] Standard deviation value (s) of 100 luminescence lifetime measurements (in microseconds) calculated as: $s = \left(\frac{1}{n-1}\sum_{i=1}^{n}(\tau_i - \overline{\tau})^2\right)^{1/2}$.