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Oxygen Sensors

Optical Sensing and Imaging of Trace Oxygen with Record Response**

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Dioxygen is one of the key molecules on Earth. It plays an essential role in the atmosphere, the hydrosphere, the geosphere and not the least the biosphere.[1] Many physiological transformations, chemical reactions, and (bio)technological processes produce or consume O_2, while anoxic species, numerous chemical syntheses, and manufacturing protocols demand its complete absence. Its extraterrestrial presence hints at the potential presence of life in the form we know.[2] Trace oxygen detection is also important in aerospace research[3] and from a safety standpoint,[4] as oxygen leaks can cause fires and explosions and can be harmful in storage chambers and packaged food.[5]

Common trace oxygen sensors are based on amperometry (Clark electrodes). These instruments are sensitive and applicable over a wide temperature range but are difficult to miniaturize, invasive, and limited to discrete points.[6] Optical sensors overcome these limitations. Most are based on the quenching of the long-lived luminescence exhibited by polycyclic aromatic hydrocarbons, transition-metal complexes, and metalloporphyrins.[7] These compounds are typically placed in inert polymer membranes. Highly permeable matrices are employed in order to sense traces of O_2.[8] Herein we show that an as yet unmatched sensitivity combined with an unmatched brightness at high temperatures can be achieved by exploiting the extremely efficient quenching of the delayed fluorescence of the ellipsoidal fullerene C_{70} embedded in two highly permeable polymer membranes, an organosilica, and an ethyl cellulose.

The electronic states and transitions of C_{70} and other fullerenes, owing to the large number of π electrons, lie on the interface between discrete molecular orbitals and band structures.[9] The absorbance spectrum of C_{70} displays a peak at 470 nm ($\varepsilon \approx 20000\,\text{M}^{-1}\,\text{cm}^{-1}$; Figure 1). The luminescence of C_{70} is very atypical in several ways. The fluorescence occurs from two excited singlet states. Weak prompt fluorescence (Φ_F: 0.05 %, $\tau \approx 650$ ps) occurs in the red region (mainly 650–725 nm). Strong energy overlap and many low-lying excited states lead to a quantum yield of triplet formation close to one (reported: 0.994[9b]). Multiple weak phosphorescence bands are observed between 750 and 950 nm, displaying lifetimes of 20–25 ms at room temperature.[9]

Triplet-state lifetimes of this magnitude or even longer are observed for many molecules and are known to be efficiently

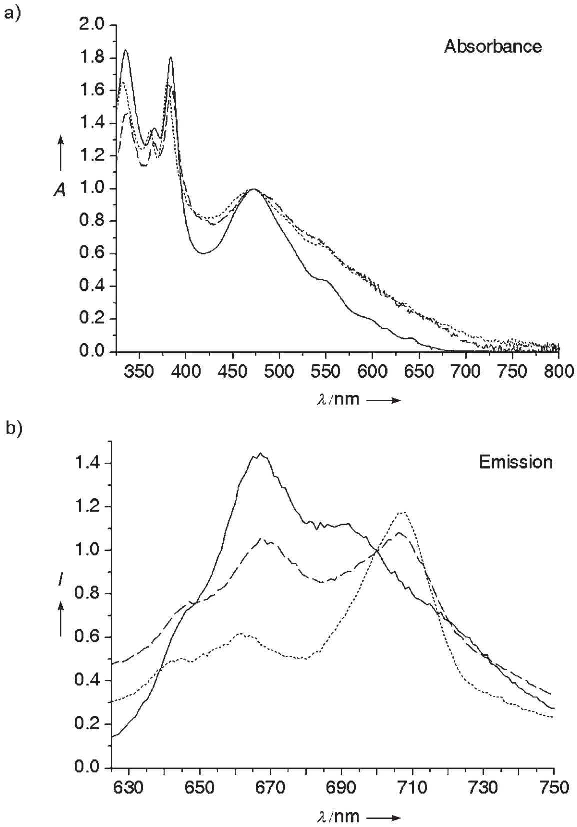

Figure 1. Spectral properties of the fullerene-doped polymer films used in this work and comparison with the spectra of C_{70} in toluene (——), organosilica (••••), and ethyl cellulose (-----); a) absorbance, normalized to the peak near 470 nm; b) emission spectra, normalized to the emission at 700 nm (λ_{exc}: 470 nm).

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quenched by molecular oxygen generating excited singlet oxygen. However, all of them are only very weak emitters. C_{70}, in contrast, displays a remarkably strong thermally activated E-type delayed fluorescence (DF). An increase in temperature leads to a stronger coupling between excited singlet and triplet states. The triplet states are eventually in thermal equilibrium with the singlet states. A unique DF quantum yield (Φ_{DF}) of about 8% is shown by C_{70} at temperatures of around 150 °C and more, while at 20 °C Φ_{DF} is only about 1%.[9b] C_{70} also displays triplet–triplet absorption in the IR region that is sensitive to oxygen.[10]

The highest O_2 permeabilities are displayed by silica-based polymers. But in all reports of sol–gels doped with unfunctionalized fullerenes, the fullerene was partially aggregated owing to formation of small clusters.[11] These aggregates show largely reduced fluorescence intensities and lifetimes as a result of self-quenching.

We have observed a similar behavior of C_{70} in silica, both in plain and nanoparticle form, but were able to incorporate C_{70} into an organically modified silica without significant aggregation by using a monomer where one alkoxy group is replaced by a phenyl ring.[11] Organosilicas (OS) are less polar and thus more compatible with fullerenes.[12,13] Ethyl cellulose (EC) also is a highly permeable matrix for oxygen sensing.[14] C_{70} is compatible with this matrix. The absence of significant aggregation was demonstrated through various methods[15] and was confirmed by the absence of a shift of the absorbance peaks (Figure 1) and the obtained DF lifetimes (Figure 2).

The sensitivity to oxygen was investigated by time-domain fluorescence lifetime imaging[16] between 650 and 710 nm. A delay time of 1 μs was applied after the end of the excitation pulse, which did not only exclude scattered light, but also prompt fluorescence of C_{70} (which is not quenched by oxygen). To demonstrate the applicability towards spatially resolved detection, we placed a piece of the sensor strip in a custom flow chamber and calculated the DF lifetime for each pixel by using a setup comparable to that in reference [17] (Figure 2).

The DF lifetimes exceed 20 ms in the absence of oxygen at room temperature and below, and result in an extreme sensitivity to oxygen (Figures 2 and 3). The response is instantaneous (< 0.1 s). The best fits for the Stern–Volmer plots were obtained by applying the two-site quenching model.[18] The fluorescence is most pronounced at 120 °C, and C_{70} still shows DF lifetimes greater than 5 ms. The temperature dependence of the sensitivity is therefore the result of the following three effects upon increasing temperature: 1) increasing Φ_{DF}, 2) decreasing DF lifetime, and 3) higher collision rate of O_2. The Stern–Volmer constants depend on temperature in a nonlinear way.

Both systems display Stern–Volmer constants more than one order of magnitude better than state-of-the-art probes (Table 1). The response of the matrices presented here is fully reversible over many hundreds of times and showed no detectable degradation after three months of storage at room temperature in the dark on air.

In conclusion, we introduce an optical oxygen sensor that is especially suited for sensing oxygen down to the ppb range and also at elevated temperatures. The method makes use of E-type delayed fluorescence of the fullerene C_{70} dissolved in appropriate polymers. It enables, for the first time, ppb levels of oxygen at atmospheric pressure to be sensed and imaged by optical means, and thus has a large potential.

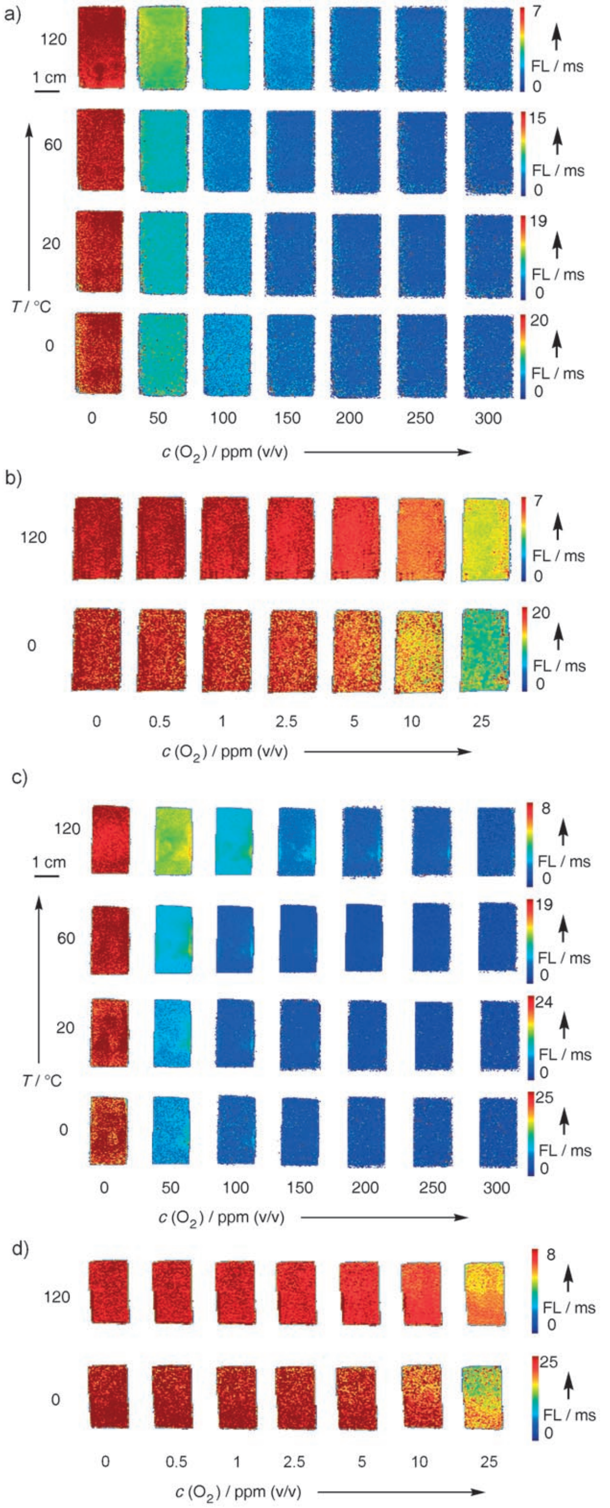

Figure 2. Pseudocolored fluorescence lifetime (FL) images of C_{70} in organosilica (a,b) and C_{70} in ethyl cellulose (c,d) between 0 and 120 °C and O_2 concentrations from 0 to 300 ppm in nitrogen at atmospheric pressure (dark red: maximum FL; dark blue: zero). Parts (b) and (d) are exemplary measurements at oxygen concentrations in the low-ppm range.

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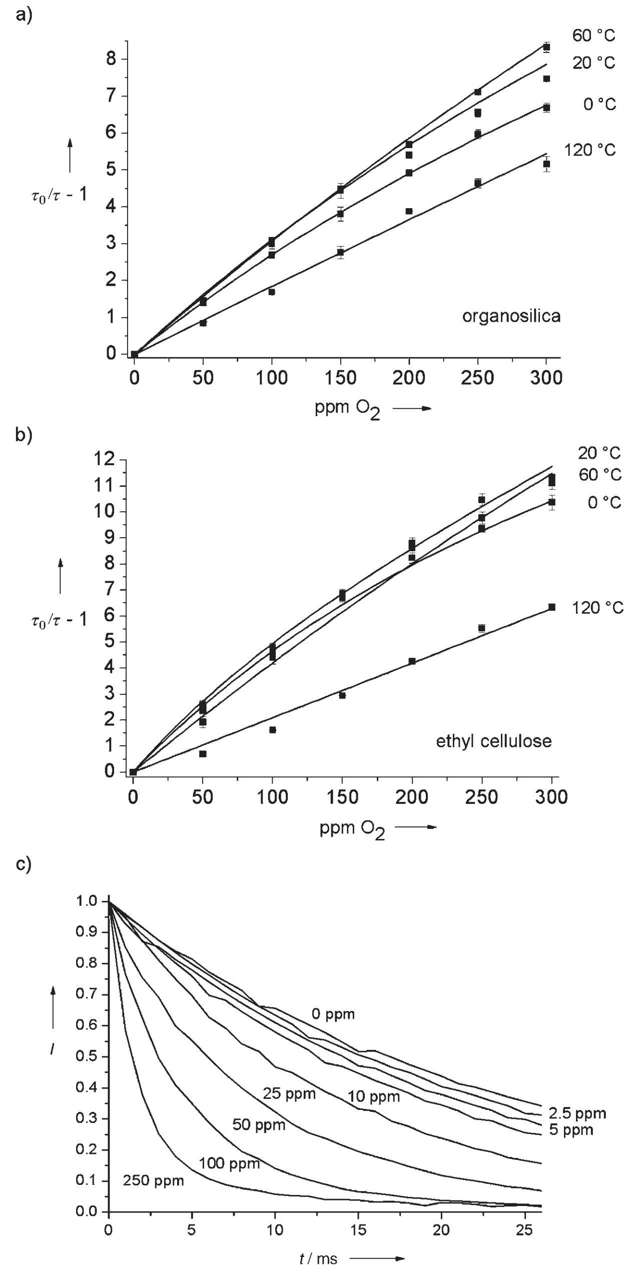

Figure 3. Lifetime-based Stern–Volmer plots at various temperatures for both types of fullerene-doped membranes; a) OS; b) EC; c) exemplary time profile for EC at 20 °C (integrated values over the whole area).

Experimental Section

C_{70} (> 98 %) was obtained from Term USA, toluene (99.7 %) and EC (49 % ethylation) from Sigma-Aldrich, and N_2/O_2 mixtures from Linde. OS was prepared according to reference [11].

C_{70}-OS was prepared by dissolving C_{70} (0.5 mg) and OS (50 mg) in toluene (1 g). The solution was ultrasonicated and heated at 40 °C for 15 min. C_{70}-EC was obtained by dissolving C_{70} (0.5 mg) and EC (50 mg) in toluene (1 g) and stirring at room temperature for 15 min. The viscous solutions were spread as 120-µm-thick films (using a coater from RK Print Coat Instruments) onto a 100-µm polyester foil. The solvents were allowed to evaporate overnight to yield layers of around 6 µm thickness.

Luminescence was excited by four blue LEDs (Luxeon V Star) with an interference filter centered at 470 nm. FL images were obtained with the Imagex TGi CCD camera (Photonic Research Systems). Three images were acquired and averaged for each oxygen concentration and temperature.

Table 1: Stern–Volmer constants and detection limits for O_2 sensing based on DF quenching of C_{70} in OS and EC at various temperatures.[a]

Probe	T [°C]	K_{SV1} [mg(O_2) L^{-1}]$^{-1}$	Detection limit [µg(O_2) L^{-1}][b,c]
C_{70}-OS	0	25.1	0.42
	20	28.4	0.37
	60	26.0	0.40
	120	15.1	0.67
C_{70}-EC	0	47.0	0.22
	20	52.9	0.20
	60	36.1	0.28
	120	16.9	0.60

[a] See the Supporting Information for details and a comparison with other common probes. [b] At 1 % quenching ($\tau/\tau_0 = 0.99$). [c] 1 µg of O_2 per liter corresponds to a concentration of 62.5 nmol L^{-1} or 807 ppb (v/v) at atmospheric pressure.

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