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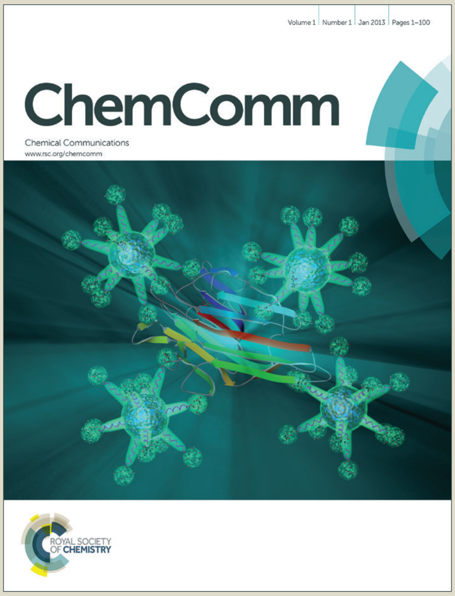

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Ratiometric Oxygen Sensing using Lanthanide Luminescent Emitting Interfaces.

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Herein we decribe the first example of a ratiometric lanthanide luminescent oxygen sensing interface. Immobilisation of terbium and europium cyclen complexes on glass subtrates was achieved by a novel aryl nitrene photografting approach. The resulting interfaces demonstrated a ratiometric oxygen response between 0 0.2 atm partial oxygen pressure.

The detection of molecular oxygen, due to its fundamental importance across a diverse range of biological processes, is essential in many areas of the environmental and life sciences.[1] Traditional methods of detection based on chemical analysis (titration) are time consuming and cumbersome in nature.[2] While electrochemical methods[3] overcome this limitation, electrochemical sensors incorporate multiple components, thus complicating miniaturisation. In addition such systems suffer greatly from interferants inhibiting target diffusion to the active interface through fouling.[1b] As a consequence, there has been significant interest in the development of optical oxygen sensors.[4] Many such sensors are based on molecular oxygen acting as a quencher to the emitters (often a transition metal complex) excited triplet state, thereby inducing a cessation of emission.[5] Utilising this methodology a number transition metal complexes have been employed as luminescent oxygen sensors.[6]

Recently, there has been an increasing interest in lanthanide-based oxygen sensing systems. Lanthanides have a number of attractive photo-physical properties for sensing applications including long lifetimes (which allow for time gating techniques), sharp well defined emission fingerprints, and can be sensitised from proximate chromophores (referred to as "antennae").[7] In the vast majority of cases, such sensitisation is mediated by the triplet state, though energy transfer from the singlet state has also been implicated in some cases and an alternative charge-transfer mediated pathway often dominates for ytterbium complexes.[8] Triplet-mediated energy sensitisation has already been exploited to develop molecular oxygen sensing systems. In cases where there is a close energy match between the donor triplet state and the lanthanide emissive state (i.e. if ΔE in Figure 1a is <800 cm^{-1}), thermal repopulation of the triplet state can allow the two states to equilibrate. This repopulation of the antenna excited state leads to an increase in quenching of this state by the triplet state of molecular oxygen resulting in a decrease in lanthanide emission (Figure 1).[9] It is worth noting that lanthanide oxygen sensitivity has also been achieved by controlling the rate of energy transfer through variation of the chromophore lanthanide separation.[10]

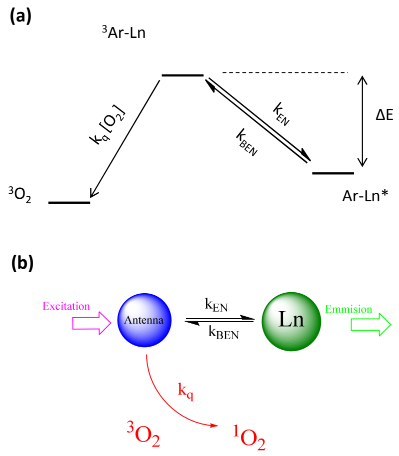

Figure 1. Energy level diagram (a) and schematic representation (b) of the quenching mechanism of triplet oxygen on sensitised lanthanide emission by back energy transfer (BEN). The high lying lanthanide excited state (Ar-Ln*) allows for a high rate of back energy transfer (k$_{BEN}$) to the antenna excited state (^{3}Ar-Ln) leading to significant quenching by triplet oxygen (^{3}O$_2$) which is consequently converted to its singlet form (^{1}O$_2$).

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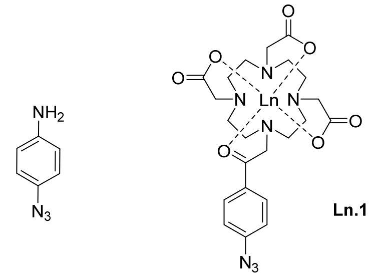
In order to achieve device integration for such oxygen sensing systems it is desirable that the transducing species are effectively immobilised into a solid matrix or onto an interface. While only a limited number of lanthanide monolayers on interfaces have been described,[11] a number of configurations exploiting lanthanide complexes on solid supports have been prepared for oxygen sensing. Amao et al. have reported the immobilisation and oxygen sensing (in water) of thenoyltrifluoroacetonato 1,10-phenanthroline europium (III) complex physisorbed on poly(styrene-co-trifluoroethylmethacrylate) substrates.[12] Other work by the same group describes the employment of a tris(acethylacetonato) 1,10-phenanthroline terbium(III) complex physisorbed on alumina support, used to the same effect.[13] Both systems were responsive from 0 to 100% oxygen concentration. The emission intensity was seen to be sensitive to varying oxygen partial pressure, with 60 % quenching observed in pure oxygen. More recently Qian and coworkers have reported the preparation, and application in oxygen sensing, of terbium incorporating metal organic frameworks on indium tin oxide supports.[14] Atmospheric oxygen sensing was demonstrated by recording emission intensity change with varying partial pressure of oxygen, with 90 % quenching observed in pure oxygen. Parker and co-workers have reported the incorporation of a N-methylphenanthridinium bearing terbium complex into a sol-gel thin film with oxygen sensing in H_2O achieved and an analytical curve up to 0.5 mM obtained by determination of lifetimes.[9a] However, of the surface immobilised optical lanthanide oxygen sensing systems described to date, all are dependent on the concentration of the sensing (or probe) species. It would be desirable to achieve oxygen sensitive responses independent of probe concentration. Ratiometric sensing offers a means of achieving such probe independent response. While a number of lanthanide based ratiometric oxygen sensing systems have been reported,[9d, 15] none of these are at a solid support.

We now report the photografting of lanthanide cyclen incorporating aryl azides on glass interfaces thus yielding the first ratiometric oxygen sensing interface. Photolysis of aryl azides is known to lead to the generation of a highly reactive nitrene species resulting in the formation of a stable film at a range of interfaces.[11d, 16] Co-immobilisation of terbium and europium complexes allows for ratiometric response due the considerably higher sensitivity of terbium to oxygen (as a result of its higher lying excited state).


Ln.1

Azidoaniline

AA

Ln = Tb or Eu

Figure 2. Azides used in this work Azidoaniline, AA (left) and lanthanide complexes of azidophenacyl DO3A, Ln.1 (right).

Initial investigations of the photografting of aryl azides on hydroxyl terminated interfaces was undertaken using azidoaniline (AA, Figure 2) as outlined in the supporting information. Briefly, water contact angles (SI 1) and condensation figures (SI 2) indicate the formation of a stable film on glass and silicon only after generation of the reactive nitrene species by irradiation, demonstrating the formation of stable films and photo-patterning at hydroxyl terminated interfaces. XPS analysis offered tentative evidence for surface tethering by nitrene insertion into the surface OH bond (SI 3 and 4). Ellipsometry indicated the formation of thin films of approximately two aryl units in thickness. These results are largely consistent with previous work[16a, 17] which reports the formation of stable layers on OH terminated interfaces upon aryl azide photolysis, consistent with direct surface tethering. Formation of stable lanthanide incorporating films on glass substrates upon photografting of Ln.1 species (Figure 2) were confirmed by recording excitation (SI 5) and emission (Figure 3) spectra of the modified substrates. The excitation spectra of the Eu.1 (λ_{em} = 616 nm) and Tb.1 (λ_{em} = 546 nm) derived films show strong signals 3 350 nm corresponding to sensitised lanthanide emission via the aryl ketone moiety, as reported previously for the Eu complex.[18] The emission (λ_{ex} = 350 nm) spectra from the europium and terbium cyclen films show the expected characteristic emission spectra for $^5D_0 \rightarrow {}^7F_n$ and $^5D_4 \rightarrow {}^7F_n$ states respectively (Figure 3). Interestingly, in the absence of irradiation to affect photografting during sample preparation, no lanthanide luminescence is observed from the interface, confirming nitrene generation to be implicit in stable film formation.

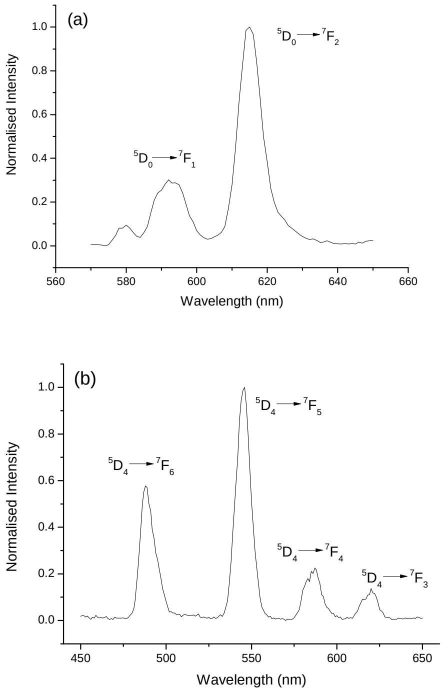


Figure 3. Emission (λ_{ex} = 350 nm) spectra of europium (a) terbium (b) phenacyl DO3A modified glass substrates prepared by deposition and photografting of Eu.1 and Tb.1, respectively.

Luminescence lifetimes of (0.70 ± 0.1) ms were determined for the Eu.1 modified glass substrates; values considerably higher than the corresponding lifetime of 0.3 ms for the solution species (in water).[18] Interestingly, when Eu.1 was physisorbed on glass (no irradiation) and not removed by sonication and washing, the europium emission lifetime was determined to be the same as for the species in solution (0.3 ms). This difference is attributed to reduced non-radiative quenching of the europium centre when grafted to the functionalised surface- possibly as a consequence of reduction of the azide reducing the probability of quenching by ligand to metal charge transfer.[8] Film formation was also verified by XPS. Narrow scans in the Eu 3d region (SI 7) revealed the presence of a europium 3d signal.[19] No Eu 3d signal was observed for the controls (no irradiation to effect photo-grafting) underlining again that the generation of the reactive nitrene species is vital for the formation of a stable film.

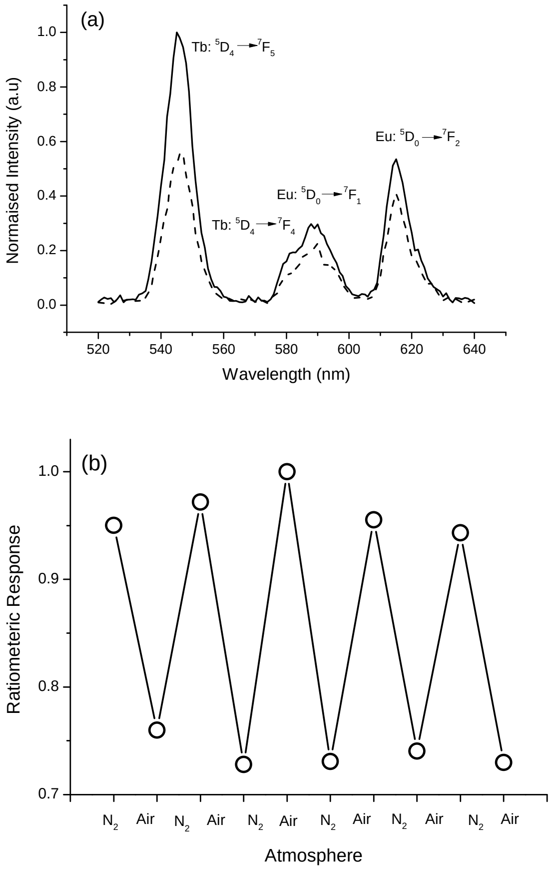


Figure 4. (a) Luminescence spectra of quartz plate with Tb.1 and Eu.1 grafted separately on each of the two faces. Spectra were recorded in nitrogen (—) and air (---) atmospheres and show a considerably higher molecular oxygen quenching response to terbium giving a ratiometric response of ~ 25 %. (b) Ratiometric response calculated from the europium $^5D_0 \rightarrow {}^7F_2$ response and terbium $^5D_4 \rightarrow {}^7F_5$ responses in nitrogen and air.

Having confirmed the formation of, and sensitised phosphorescence emission from, the lanthanide modified interfaces, application of the interfaces to ratiometric oxygen sensing was investigated. Initially mixed films were prepared by photografting a 20 mM mixture of Tb.1 and Eu.1 onto a quartz interface. However, the resulting emission spectra (λ_{ex} = 350 nm) of the interfaces exhibited only the characteristic europium emission fingerprint with no terbium emission observed (see SI 8). This is attributed to energy transfer from the terbium complex to the europium excited state, leading to quenching of terbium emission and is indicative of a dense film with europium and terbium in close spatial proximity. This might occur in one of two ways - either via through space energy transfer from the chromophore triplet state on Tb.1 following back energy transfer, or as a consequence of direct energy transfer from terbium to europium.[20] In order to preclude such interactions, spatial separation of the components at the interface was achieved by photo-grafting the components onto opposite sides of a single quartz plate. Upon excitation at 350 nm both the characteristic terbium and europium emission signals were observed (Figure 4a). The ability of the system to function as a ratiometric oxygen sensor was probed by recording luminescence spectra in both nitrogen atmosphere (—) and air (---) as described in the experimental section. A considerably larger intensity decrease was observed for the terbium $^5D_4 \rightarrow {}^7F_5$ response upon switching from a pure nitrogen atmosphere to air than for the europium $^5D_0 \rightarrow {}^7F_2$ signal giving a ratiometric response of ~ 25 %. The ratiometric response was calculated to be both highly predictable and reversible (Figure 4 b).‡ The enhanced oxygen sensitivity of the terbium component, relative to its europium counterpart is consistent with expectations as discussed above. The lifetimes further confirm the expected mechanism with the lifetime of the Tb.1 derived films reflecting this, giving a value of (0.60 ± 0.05) ms in nitrogen and (0.51 ± 0.03) ms in air. Similar results were found for Eu.1 derived films with lifetimes of (0.68 ± 0.01) and (0 ± 0.08) ms found in nitrogen and air, respectively.

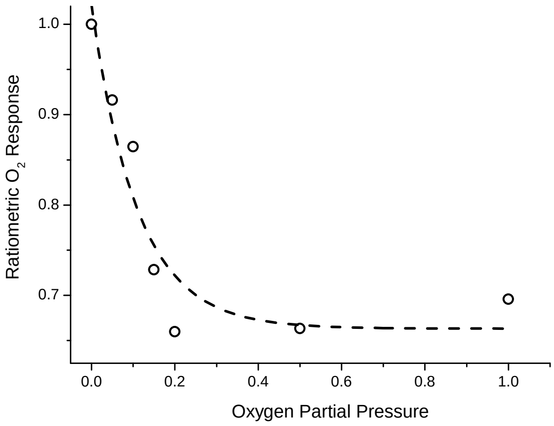


Figure 5. Effect of oxygen partial pressure on ratiometric oxygen response from a quartz substrate modified with Eu.1 and Tb.1.

Figure 5 shows the ratiometric response of a Tb.1 and Eu.1 modified quartz plate to changing atmospheric oxygen percentage. As expected the ratiometric response changes with oxygen concentration. The system is seen to be oxygen sensitive at partial pressures between 0 and 0.2 atm, the region of oxygen concentration most relevant in biological systems.

In summary we have described the preparation of the first ratiometric lanthanide luminescent oxygen sensing interface. A dual immobilisation of terbium and europium components on quartz was specifically achieved by a novel nitrene based surface grafting approach and used to underpin effective sensing. Oxygen sensitivity between 0 and 0.2 atm was achieved with a high degree of reversibility.

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Notes and references

‡ We have selected the terbium $^5D_4 \rightarrow {}^7F_5$ and europium $^5D_0 \rightarrow {}^7F_2$ responses due to their strong intensity and convenient position within the visible region (unlike the $^5D_0 \rightarrow {}^7F_4$ signal), compatible with rhodamine filter sets and convenient for future microscopy investigations.

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