Copper(I) complexes as alternatives to iridium(III) complexes for highly efficient oxygen sensing†

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The complex [Cu(xantphos)(dmp)][PF₆] (dmp = 2,9-dimethyl-1,10-phenanthroline) in a nanostructured metal oxyde matrix shows better sensitivity to oxygen (K₅₅ = 9.74 ± 0.87 kPa⁻¹ between 0 and 1 kPa pO₂ and 5.59 ± 0.15 kPa⁻¹ between 0 and 10 kPa pO₂) than cyclometallated iridium complexes in the same conditions.

Photocative complexes based on earth-abundant copper are increasingly studied as alternatives to platinoid metal-based complexes. This is because Cu(I) complexes have attractive photophysical properties (e.g., possibly highly emissive metal-to-ligand-charge-transfer (MLCT) state, long luminescence lifetimes, large Stokes shift) whilst copper is much more abundant to-ligand-charge-transfer (MLCT) state, long luminescence life-times, large Stokes shift) whilst copper is much more abundant than cyclometallated iridium complexes in the same conditions.

Optical oxygen sensing is another key technologic area using phosphorescent noble-metal complexes as champion materials. In this case, the emissive triplet state of the dye is quenched by the oxygen, which has a triplet ground state. In practice, the emission intensity of the dye diminishes as the concentration of oxygen increases. The best reported dyes to date (Table 1) are Pt/PdTFPP (platinum(II)/palladium(II) meso-tetrakis(pentafluorophenyl) porphyrin)5,6 and N969,5 a cationic cyclometallated iridium complex. Although Pt/PdTFPP are much better performing than iridium complexes, an important advantage of the latter is the possibility to vary the emission colour over the entire visible spectrum. In this context, Cu(I) complexes are very attractive for sensing of oxygen. However, only few oxygen sensors based on Cu(I) complexes have been reported to date and all display much lower performance than sensors based on platinoid-group metal complexes.8–14

Smith et al. used crystals of Cu(P^P)(N^N)⁺⁺ complexes (P^P = bis[2(diphenyolphosphino)phenyletheny] (POP) or 4,5-bis(diphenyl phosphino)-9,9-dimethylanthene (xanthonphos) and N^N = 2,9-dimethyl-1,10-phenanthroline (dmp)) or 2,9-diisopropl-1,10-phenanthroline (dipp) that resulted in very low sensitivity (Stern-Volmer constant KSV between 0.002 and 0.058 kPa⁻¹).10,12 Wang et al. developed an optical sensing layer based on [CuPOP(phenecarz)] (BF₄)⁴PS (PS = polystyrene; phenecarz = 2-(9-ethyl-9H-carbaol-2-yl)-1H-imidazo[4,5-f]1,10-phenanthroline) showing KSV = 0.39 kPa⁻¹.11 Shi et al. used MCM-41, a mesoporous material, as solid support for [Cu(POP)(PTZ)] (BF₄)⁴PS (PTZ = 5-(2-pyridyl)tetrazole) and achieved the best copper complex-based oxygen sensing film reported so far in the literature with sensitivity to oxygen KSV = 0.50 kPa⁻¹.19

Herein we investigate three Cu(I) complexes, [Cu(xanthonphos)(dmp)][PF₆] (1), [Cu(xanthonphos)(pzpy)][PF₆] (2), and [Cu(xanthonphos)₂][PF₆] (3) for optical oxygen sensing.
When exposed to oxygen, the luminescence of the films with ten times better sensitivity than previously reported for the first time that these emitters based on earth abundant metals can be used in oxygen-sensitive films, the quantum yields of the analyte concentration. Compared to other organometallic compounds used in the development of oxygen-sensitive films, the quantum yields of these Cu(I)-based films are quite low, $\phi \approx 0.1$ to 0.3 (Table S1, ESI†), and future efforts should aim at increasing the brightness of these dyes. When exposed to oxygen, the luminescence of the films is completely quenched (Fig. 2 for 1; Fig. S2 and S3, ESI† for 2 and 3) but for 3-AP200/19, in which case the intensity decreased only by half (Fig. S3b, ESI†).‡

The films were characterized first by intensity measurements following the procedure described in ESI†. The variations of the luminescence intensity with the oxygen concentration as well as the Stern–Volmer plots are shown in Fig. 3 and Fig. S4 (ESI†) for 1-AP200/19 and 1-PS, in Fig. S5 (ESI†) for 2-AP200/19 and 2-PS and in Fig. S6 (ESI†) for 3-PS. The fitting parameters for films containing 1 are reported in Table 2 (see Table S2 for other films, ESI†). As anticipated, the use of the nanostructured support AP200/19 increased the oxygen sensitivity, as shown by the increase of the Stern–Volmer constant values. In particular 1-AP200/19 sensitivity is more than 5 times the sensitivity of 1-PS. Such sensitivity improvement has previously been observed for Pt(n), Ru(n), and Ir(n) oxygen sensitive dyes and is now demonstrated for the first time with Cu(i) dyes, which confirms that the improvement is qualitatively due to the nanostructured film.

The most sensitive sensing films are based on 1 and 2-AP200/19 ($K_{SV1} = 5.45$ and 5.13 kPa $^{-1}$, respectively). Comparing these results with classical Pt(n), Ru(n), and Ir(n) sensing films using the same nanostructured matrix (see Table 1), it is clear that Cu(i) sensing films are very promising for O$_2$-sensing applications. Indeed, Ir(n) sensing films show lower sensitivity. Only PtTFPP shows higher sensitivity in the same condition ($K_{SV} = 25.68$ kPa $^{-1}$).§

Intensity measurements are not sensitive enough to characterize the sensing films in the range 0–1 kPa pO$_2$. Therefore we used a multifrequency phase-modulation method for luminescence spectroscopy using a rectangular-wave modulated excitation source with a short duty cycle for measuring lifetime for this range of oxygen concentrations. It provides: (1) a more complete characterization of the luminescence system (multiple frequencies measured at once), and (2) an improvement in the accuracy for determining the analyte concentration.

After finding the appropriate modulation frequency for each sensing film for best signal-to-noise ratio, 10% duty cycle...
Oxygen-sensitive properties of 1-PS and 1-AP200/19 were determined following the procedure described in ESI†. The calibration curves for 1-PS and 1-AP200/19 when exposed to different oxygen concentrations are shown in Fig. 4 and the results are summarized in Table 2. As for intensity measurements, the incorporation of the dye into AP200/19 increased the sensitivity of the film to oxygen. Gratifyingly, intensity and lifetime measurements provided similar results for high oxygen concentrations ($K_{SV1}$ of 1-AP200/19 by intensity is 5.45 kPa$^{-1}$ and by lifetime is 5.59 kPa$^{-1}$ for the range 0–10 kPa O$_2$). At low oxygen concentrations (range 0–1 kPa O$_2$) $K_{SV1}$ of 1-AP200/19 is 9.74 kPa$^{-1}$, demonstrating the high sensitivity of the film in these conditions.

To demonstrate that these new sensing films can also be used for ultra-low oxygen detection, we used synthetic air (mixture of oxygen and nitrogen) to achieve a minimum oxygen concentration of 0.05 kPa. The quenching reaction does not consume oxygen and therefore the process is reversible as demonstrated by results shown in Fig. S4–S6 (ESI†). As the most relevant application for these sensing films is trace oxygen analysis, the response and recovery times have been calculated between 1 and 5 kPa pO$_2$, which provide more relevant information than response times to 100 kPa pO$_2$ and recovery to anoxic condition. The $t_{0.05}$ response times for all of the sensing films are given in Table S4 (ESI†). All of them are shorter than 11 s when changing from 1 to 5 kPa pO$_2$ and shorter than 16 s when changing from 5 to 1 kPa pO$_2$. The registered response times are in fact the response times of the full system that is the time needed to change O$_2$ concentration from 1 to 5 kPa pO$_2$ and vice versa.

An important concern common to all optical sensors is the degradation of their quantum efficiency following prolonged sampling and continuous illumination. To evaluate the photostability of the sensing films, they were illuminated with a UV lamp ($\lambda = 315$ nm and 6 Watt power) during 6 h. The photostability study (Fig. 5 for 1-PS and 1-AP200/19 and Fig. S10, ESI† for other films) was carried out at 21 °C for three oxygen concentrations (0.2, and 8 kPa). Data were collected every hour, using intensity measurements. The most stable sensing film was 2-PS, which suffered the least degradation (12% of the signal after 6 hours).

Finally, the effect of humidity on the sensing response was assessed to further evaluate the applicability of the films. Five sensing films based on 1-PS and 1-AP200/19 were used to determine the concentration of oxygen between 0 and 20 kPa.
at different levels of relative humidity (0, 10, 20, 40 and 80% RH) [Fig. S11, ESf]. 1-PS was not affected by RH because of the hydrophobicity of PS. On the other hand, the sensitivity of 1-AP200/19 decreased as the RH increased. It is due to the high hydrophilicity of this matrix, which had been previously pointed out.20 Thus, 1-AP200/19 is more useful for gaseous analysis and the relative humidity of the environment has to be taken into account during the calibration of the sensing film.

Three luminescent Cu(i)-complexes were investigated for the optical sensing of low and ultra-low oxygen concentrations using intensity and phase-based apparent lifetime measurements. The organometallic complexes were incorporated into a classical PS membrane and a nanostructured, metal oxide matrix AP200/19.

This is the first time that Cu(i) complexes have been incorporated into AP200/19. The spectral properties of these dyes are not affected by the solid support. The most sensitive sensing films are 1-AP200/19 and 2-AP200/19 (K_{SV1} = 5.45 and 5.13 kPa^{-1}, respectively, in the range 0–10 kPa P_{O2}). Interestingly they show higher sensitivity than reported sensing films based on photoresistant cyclometallated Ir(III) complexes (e.g. K_{SV}(N960-AP200/19) = 4.79 kPa^{-1}) but still lower than PtTFPP complex (K_{SV}(PtTFPP-AP200/19) = 25.68 kPa^{-1}). As expected from the definition of K_{SV}, sensitivity is primarily better correlated to the lifetime of excited state of the emitting species than to the photoluminescent quantum yield of the film, which provides a direction of research to further increase the sensitivity of these promisingly low cost copper-based emitters.

Furthermore these sensing films are suitable for ultra-low oxygen detection down to 0.05 kPa P_{O2}. In particular the parameter Δt_{0.05} (33.55 ± 0.37%) shows that 1-AP200/19 is again more sensitive at ultra-low O_{2} concentrations than films based on Ir(n) complexes and as much as the half of the most sensitive AP200/19-based sensing films at ultra-low O_{2} concentration reported in the literature (Δt_{0.05} for PtTFPP-AP200/19 is 62.53 ± 3.66%).

The reasons for the excellent performance of 1 are primarily attributed to the pertinent choice of matrix and measurement method. As other complexes are not as performing as 1, specific properties of 1 are also important for high performance. However definitive conclusions about this aspect cannot be drawn because only 1 could be fully studied.

Overall, we have clearly demonstrated that copper-based luminescent complexes are a credible alternative to more expensive emitters for oxygen sensing and deserve particular attention for the development of low cost O_{2} sensing films.

The authors gratefully acknowledge the financial support of the Spanish Ministry of Economy and Competitiveness (CTQ2011-25316 and Medina-Rodriguez’s grant reference BES-2009-026919), the Regional Government of Andalusia [Excellence projects P07-FQM-2625 and P07-FQM-2738], and the European Union (MulTHIC, IEF-326107, and Hetriridium, CIG-322280). Also, the authors are grateful to Ifford Imaging Switzerland GmbH (Switzerland) for supplying the metal oxide membranes.

Notes and references

‡ 3-AP200/19 gave irreproducible O_{2}-sensing results and is not discussed further. This is attributed to its more hydrophobic nature compared to other dyes, resulting in significant aggregation in the highly polar AP200/19.

§ Only films using 1 were characterized using lifetime measurements in the frequency domain (phase-resolved method) because of the impossibility to excite other films with the 375 nm UV LED used in our set-up.

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