

Luminescence-Based Oxygen Sensors: $\text{ReL}(\text{CO})_3\text{Cl}$ and $\text{ReL}(\text{CO})_3\text{CN}$ Complexes on Copolymer Supports

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A new class of luminescent rhenium complexes has been tested as oxygen sensors based on luminescent quenching. $\text{ReL}(\text{CO})_3\text{Cl}$ and $\text{ReL}(\text{CO})_3\text{CN}$ ($L = 2,2'$ -bipyridine or 1,10-phenanthroline and substituted analogues) have several features that seem to indicate suitability as oxygen sensors. These include simple synthesis, long excited-state lifetimes, and high luminescence quantum yields. Intensity and lifetime oxygen quenching measurements were used to study the complexes in various polymer supports including homopolymers of PDMS (polydimethylsiloxane), a methacryloxy containing PDMS (Gp-163), and trimethylsilylmethylmethacrylate (T3642), and copolymers containing Gp-163 and T3642. In contrast to previous studies utilizing $[\text{Ru}(4,7\text{-diphenyl-1,10-phenanthroline})_3]^{2+}$ as an oxygen sensor, quenching of the Re complexes proved much more sensitive to the polymer support. With suitable supports, the rhenium chloro complexes demonstrated significant quenching; but the cyano complexes, in spite of being robust in solution, exhibited severe photochemical instability in polymers. The potential of this class of complexes as oxygen sensors and as molecular probes as well as the ramifications in the design of new and different types of sensors is discussed.

KEY WORDS: Luminescence; oxygen sensors; oxygen quenching; polymer support; $\text{ReL}(\text{CO})_3\text{Cl}$; $\text{ReL}(\text{CO})_3\text{CN}$.

INTRODUCTION

Two of the major challenges for chemists working in the area of probe and sensor technology are (1) systematically to design new luminescent materials with responses to specific analytes and possessing specific emission properties and (2) to understand the interactions between the sensor or sensitizer and the matrix, especially the popular polymeric supports. We describe

here the potential of oxygen sensors based on a new group of transition metal complexes.

Luminescent transition metal complexes, particularly the platinum metals [Ru(II), Os(II), Re(I), Rh(III), and Ir(III)], have shown considerable promise in the area of oxygen sensing. These materials can possess the highly desirable features [1,2] of long lifetimes (100's of ns to $>100 \mu\text{s}$); wavelength-independent high luminescence quantum yields that can exceed 0.5 [3,4]; intense visible absorptions; and high thermal, chemical, and photochemical stability. The long lifetimes make lifetime-based measurements much simpler and less expensive compared to the low nanosecond lifetimes of many organic fluorophores. High luminescence efficiencies and intense visible absorptions increase sensitivity, reduce errors from background, simplify sensor design,

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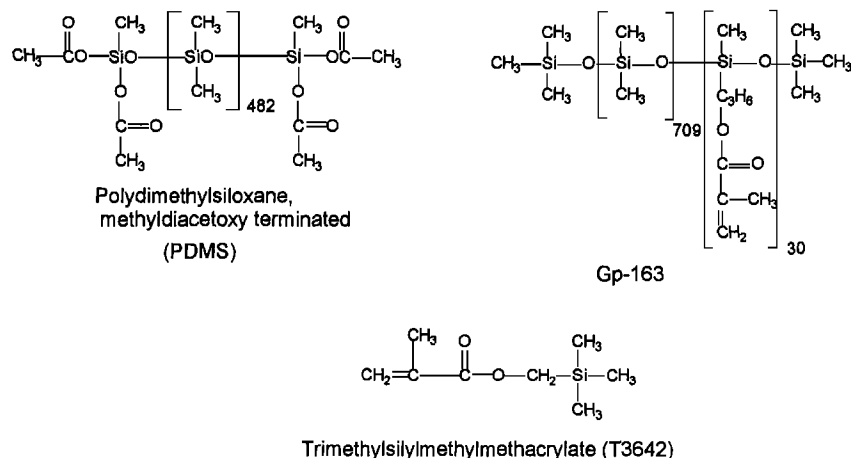


Fig. 1. Structures of prepolymers.

and expand the range of excitation sources. High stability simplifies sterilization and extends sensor lifetime.

Another benefit of the transition metal complexes is that molecular engineering permits systematic alteration of spectroscopic and chemical properties [2,5–7]. Such chemical flexibility allows the design of systems that respond to specific environmental variables, permits either ionic or covalent attachment to a support or reagent, and lets absorption and emission properties be tailored to available excitation sources and detectors [2].

To date much of the oxygen sensor work with inorganic systems involved the use of ruthenium complexes as the sensor molecules [8–11]. Though the luminescence of rhenium complexes has been studied and their high sensitivity to oxygen in solution has been noted [12,13], little work has been done to assess their potential as oxygen sensors. Our goal was to explore the possibilities of rhenium-based molecular probes by surveying the luminescence and oxygen quenching properties of several rhenium complexes on different copolymer supports.

The rhenium complexes chosen for study were $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$, $[\text{Re}(\text{t-Bu})_2\text{bpy}(\text{CO})_3\text{Cl}]$, $[\text{Re}(\text{terpy})(\text{CO})_2\text{Cl}]$, $[\text{Re}(\text{Ph}_2\text{phen})(\text{CO})_3\text{Cl}]$, $[\text{Re}(\text{Me}_2\text{Ph}_2\text{phen})(\text{CO})_3\text{Cl}]$, $[\text{Re}(\text{Me}_4\text{phen})(\text{CO})_3\text{Cl}]$, $[\text{Re}(\text{Phphen})(\text{CO})_3\text{CN}]$, and $[\text{Re}(\text{t-Bu})_2\text{bpy}(\text{CO})_3\text{CN}]$. The abbreviations are as follows: bpy, 2,2'-bipyridine; (t-Bu)₂bpy, 4,4'-di(t-butyl)-2,2'-bipyridine; terpy, 2,2',2''-terpyridine; Ph₂phen, 4,7-diphenyl-1,10-phenanthroline; Me₂Ph₂phen, 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline; Me₄phen, 3,4,7,8-tetramethyl-1,10-phenanthroline; and Phphen, 5-phenyl-1,10-phenanthroline. These rhenium complexes have several potential advantages over other metal com-

plexes: they are relatively easy to synthesize, they can have long lifetimes and high luminescence quantum efficiencies [12], and their excited-state properties can be influenced strongly by ligand variation [14–18], which is a useful design feature. The polymer supports all contain siloxane or siloxane-like regions, which are known to have good oxygen transport and quenching properties.

EXPERIMENTAL

Complexes Most of the complexes used were available from previous work [12,16]. The (t-Bu)₂bpy complex was synthesized using similar methods. All complexes were yellow to pale orange commensurate with the strong MLCT absorption in the near uv, which tails into the visible.

Polymers. Preliminary studies were done with various polymer supports. These included a nearly pure poly(dimethylsiloxane) (PDMS) polymer (PS 368.5) from Huls, which is diacetate terminated for water curing; a more polar homopolymer of Gp-163, methacryloxy functional silicone fluid from Genessee Polymers Corp (Gp-163 is a modified PDMS containing (methacryloxy)propyl side chains in place of some methyl groups); and a homopolymer of trimethylsilylmethylmethacrylate (T3642) from Huls. The structures of the polymers are given in Fig. 1. The methacryloxy groups are randomly distributed on the backbone. The manufacturer does not provide information on polydispersity of the Gp-163. The preparation of the polymers was described earlier [8,19]. The copolymers were prepared as described earlier [20]. Film thicknesses were ca. 300 μm.

All Gp-163 films were elastomers at room temperature. The homo T3642 polymer was hard and brittle. All films were clear with no cloudiness. There was no visible evidence for domains under an optical microscope.

We assume that the copolymers are cross-linked rather than a blend, because of the clarity. There were no visible microscopic boundaries, and smaller domains would have led to scattering centers and cloudiness. This is consistent with the expected similar reactivity of the components; both are substituted acrylates. In addition, there can be no regions of pure poly-T3642 since the linear T3642 polymer is soluble in the solvent used during the wash cycle.

Sensor Preparation. Copolymer sensor films were prepared as described earlier [8,19]. The rhenium complexes were dissolved in CH_2Cl_2 ($\approx 5 \times 10^{-4} M$). The polymer films were immersed in the solution for 15–30 min during which the film swelled by a factor of about 2–4. The films were then dried slowly in a CH_2Cl_2 atmosphere to give high-quality transparent yellow films with no evidence of crystals. Since polymerized T3642 is a CH_2Cl_2 soluble linear polymer, the complex and polymer were dissolved together in CH_2Cl_2 (2.5×10^{-3} mol complex/mol polymer repeating unit) and cast on glass slides. The sensor films were stored in a dark, dry place until used.

There was difficulty in uniformly dispersing the more polar $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ and $[\text{Re}(\text{t-Bu}_2\text{bpy})(\text{CO})_3\text{Cl}]$ in the very hydrophobic PS 368.5 polymer and the pure T3642 homopolymer. With very slow evaporation, we could avoid forming detectable microcrystals under the optical microscope. All measurements are reported for films with no crystals detectable on microscopic examination.

Emission Spectra. Fluorescence spectra were measured on a Spex Fluorolog 2 + 2 spectrofluorimeter using an excitation wavelength of 388 nm or near the peak of the MLCT absorption. A pulsed N_2 laser (337-nm) decay system was used to measure room temperature τ values, and a Tektronix TDS-540 digital oscilloscope was used for recording transients. The emissions were monitored at 540 nm.

Luminescence Characteristics. Luminescence quenching methods utilize decreases in emission intensities or luminescence lifetimes in the presence of quencher as a quantitative measure of the amount of quencher present. Provided that quenching is entirely diffusional, the excited state lifetimes and luminescence intensities are related to the quencher concentration by the Stern–Volmer equations

$$\frac{\tau_0}{\tau} = 1 + K_{sv} [Q] \quad (1)$$

$$\frac{I_0}{I} = 1 + K_{sv} [Q] \quad (2)$$

$$K_{sv} = k_2 \tau_0 \quad (3)$$

where τ 's and I 's are luminescence lifetimes and intensities, respectively. The subscript "0" denotes the measurement in the absence of quencher. K_{sv} represents the Stern–Volmer quenching constant, and k_2 is the bimolecular quenching constant. Ideally, plots of τ_0/τ or I_0/I versus $[Q]$ will be linear, with identical slopes of K_{sv} . In practice, however, when working with polymers as support systems, nonlinear Stern–Volmer quenching is often observed as a result of heterogeneity in the polymers [21].

While complete Stern–Volmer curves were not obtained, two measures of quenching ability were utilized. These are the sensitivity of the sensor to oxygen quenching, S , and the linearity of the response, L . S is given by

$$S = (I_0/I_{\text{oxygen}}) - 1 \quad (4)$$

where I_0 is the intensity in the absence of oxygen and I_{oxygen} the intensity at 1 atm of pure oxygen. The linearity index L is given by

$$L = \frac{\left[(I_0/I_{\text{oxygen}}) - 1 \right]}{\left(\frac{[\text{O}_2]_{\text{oxygen}}}{[\text{O}_2]_{\text{air}}} \right) \left[(I_0/I_{\text{air}}) - 1 \right]} \quad (5)$$

where I_0 , I_{oxygen} , and I_{air} are the intensity measurements in vacuum, oxygen, and air, respectively, and $[\text{O}_2]_{\text{oxygen}}$ and $[\text{O}_2]_{\text{air}}$ represent the concentrations of oxygen in 1 atm of pure oxygen and air, respectively. A linearity index equal to 1 indicates a perfectly linear Stern–Volmer plot, while 0.2 indicates a plot for which there is no further quenching on going from air to 1 atm of oxygen.

In lifetime measurements, the decay curves were fit to a sum of exponentials.

$$D(t) = \sum \alpha_i \tau_i \quad (6)$$

where the α 's and the τ 's are the preexponential contributions and lifetimes, respectively. In all cases, it was necessary to use three exponentials to get good fits to the decay curves. With three exponentials, the fits were quantitative with uniformly distributed residuals and no evidence for systematic deviations. Since our lifetime

Table I. Survey of Copolymer Supports for Re(bpy)(CO)₃Cl Complexes

| Polymer support | $S = [(I_0/I_{\text{oxygen}}) - 1]$ | | |
|-----------------------------|-------------------------------------|---|--|
| | Re(bpy)(CO) ₃ Cl | Re(t-Bu) ₂ bpy(CO) ₃ Cl | Re(Ph ₂ phen)(CO) ₃ Cl |
| PS368.5 homopolymer | Negligible | Negligible | Negligible |
| Gp-163 homopolymer | | | 1.5 |
| T3642 homopolymer | 0.1 | 0.8 | 0.6 |
| Gp-163/0.7% T3642 copolymer | | | 2.8 |
| Gp-163/9% T3642 copolymer | | | 3.9 |

apparatus is not a time-correlated single-photon instrument, the absolute χ^2 's are meaningless.

The preexponential weighted mean lifetime was computed from

$$\tau_M = \sum \alpha_j \tau_j / \sum \alpha_j \quad (7)$$

This quantity reduces the complex decays to a single unique and meaningful parameter.

The fractional contribution to the preexponential factor was given by

$$f_{j,\text{preexp}} = \alpha_j / \sum \alpha_j \quad (8)$$

and the fractional contribution to the static luminescence intensity of each component was given by

$$f_{j,\text{area}} = \alpha_j \tau_j / \sum \alpha_j \tau_j \quad (9)$$

where the summations are over all the terms used in the decay time fit. It should be noted that because of the lack of uniqueness in fits to decays of sums of exponentials [21], one should not put too much faith in the individual lifetime contributions. In cases where there are three decay times, what is seen is probably a distribution of decay times rather than a few discrete values. However, the need for three decays allows us to exclude a single Gaussian distribution as the underlying lifetime distribution. Without considerably more data, we believe that an attempt to fit the data to distributions is a form of numerology devoid of significant information content.

RESULTS AND DISCUSSION

All the complexes gave single-exponential decays in solution as expected for single species in a homogeneous environment. This is in marked contrast to the polymer data where the complex decay kinetics and non-linear Stern–Volmer curves showed pronounced heterogeneity. The polymer emissions were blue shifted (ca.

40 nm) compared to CH₂Cl₂ solutions. However, in all cases these emissions were sufficiently red to be consistent with metal-to-ligand charge transfer (MLCT) transitions. All complexes exhibit MLCT absorption bands in the near-UV.

Measurements of [Re(Phphen)(CO)₃CN] and [Re(t-Bu)₂bpy(CO)₃CN] complexes loaded onto a 9 wt% T3642 copolymer showed that the copolymer/complex combination was photochemically unstable. There was a visible yellow-to-brown color change where the polymer film was irradiated, and the luminescence intensity decreased markedly. This is in contrast to the behavior of the cyano complexes in either CH₂Cl₂ or acetonitrile, where irradiation for days produced no discernible photochemistry. Further work must be done to explain the observed photochemistry and to determine whether or not other copolymer supports can be utilized with the rhenium cyano complexes. The remainder of our discussion focuses on the chloro complexes.

A preliminary survey (Table I) was performed in order to determine the most suitable polymer support for the various Re complexes. We chose as representative complexes the relatively polar [Re(bpy)(CO)₃Cl]; the structurally similar [Re(t-Bu)₂bpy(CO)₃Cl], which is much more hydrophobic than the bpy complex due to the t-Bu groups; and [Re(Ph₂phen)(CO)₃Cl], since our earlier work with Ru(II) complexes demonstrated that the 4,7-Ph₂phen ligand was particularly conducive to promoting luminescence and provided good hydrophobicity for compatibility with siloxane polymers [8].

Surprisingly, PS 368.5 homopolymer showed negligible quenching for all three complexes. Even though we could see no crystals, we suspect the problem was insolubility of the complex in the support. The absence of visual crystallization is no guarantee of the absence of microcrystallization [22]. No further studies were made with this polymer.

In T3642 homopolymer, the quenching was more reasonable and we were able to examine the sensitivity as a function of complex. The bpy complex was the poorest, while the (t-Bu)₂bpy and Ph₂phen complexes were comparable. Based on this result and the fact that the Ph₂phen complex had the longest excited state lifetime, we examined the Ph₂phen complex with other polymers. As shown in Table 1, the best response was obtained with 9 wt% T3642 in Gp-163; thus, it was decided to utilize this copolymer for detailed studies with the other Re complexes.

Noteworthy is that a very small addition of T3642 to Gp-163 dramatically improves quenching response. In most cases the addition of copolymers had a deleterious effect on the sensor response. Abrupt changes in behav-

Table II. Oxygen Quenching for ReL(CO)₃Cl Complexes in 9% T3642/Gp-163 Support

| Metal complex | S [$(I_0/I_{\text{ox,quen}}) - 1$] | L | τ_{MO} (ns) |
|--|---|------|-------------------------|
| Re(bpy)(CO) ₃ Cl | 0.5 | 0.47 | 211 |
| Re(<i>t</i> -Bu) ₂ bpy(CO) ₃ Cl | 0.7 | 0.74 | 484 |
| Re(terpy)(CO) ₂ Cl | 0.2 | 0.66 | 149 |
| Re(Ph ₂ phen)(CO) ₃ Cl | 2.9 | 0.50 | 3450 |
| Re(Me ₂ Ph ₂ phen)(CO) ₃ Cl | 2.4 | 0.49 | 2030 |
| Re(Me ₄ phen)(CO) ₃ Cl | 2.7 | 0.45 | 4090 |

ior with small changes in polymer composition are not uncommon. With pyrene, we observed very dramatic effects on response and luminescence properties when adding even 0.5 wt% of some copolymers [20]. While it appears that the sensitivity increases with the weight percentage of T3642 copolymer, a limited supply due to the burning down of the manufacturer's plant prevented further testing of T3642 copolymers.

Table II summarizes the responsivity and linearity for each complex in the 9% T3642/Gp-163 support. The decay parameters for each complex in the absence of oxygen are given in Table III.

All of the systems show substantial nonlinearity. This is a common feature in many polymer-supported systems and appears to be a result of heterogeneity of the sensor environment. The heterogeneity also manifests itself as multiple exponential decays. Research in progress seeks to probe this heterogeneity more directly in the hopes of improving sensor technology, since an understanding of the microstructure of such systems should allow more rational sensor design.

The sensitivities for the rhenium complexes having bpy or terpy ligands are significantly lower and the lifetimes are noticeably shorter than those for the complexes with phenanthroline ligands. The addition of a phenanthroline ligand increases sensitivities from 0–1 to 2–3 and lengthens lifetime from 100–500 to 2000–5000 ns. The addition of *t*-butyl groups to bpy results in greater sensitivity and a longer lifetime. The addition of two methyl groups to (Ph₂phen), on the other hand, decreases the sensitivity and shortens the lifetime. The terpy has the shortest lifetime and the lowest sensitivity. Terpy is a poor ligand for luminescence in Ru(II) complexes, with the Ru(terpy)₂²⁺ being essentially nonluminescent at room temperature. Apparently, although reasonable luminescences are obtained with Os–terpy complexes [23], terpy is not the optimal ligand in the case of Re complexes either.

Generally, with the exception of the (Ph₂phen) and (Me₄phen) substituted complexes, sensitivity corresponds directly to lifetimes—the longer the lifetime, the greater the sensitivity. This is reasonable if the quenching constants are similar for all the complexes. The trend indicates that the changes in quenching are most likely caused by different lifetimes and that the rate constants are fairly constant.

Even though the lifetimes of some of the Re complexes are comparable to some of the longer lived Ru(II) sensors, the Re(I) sensitivities to oxygen quenching are substantially lower. These quenching results track the solution results where oxygen quenching of Re(I) complexes exhibits bimolecular rate constants roughly an order of magnitude lower than Ru(II) and Os(II)α-diimine complexes in solution.

Table III. Lifetime Measurements for ReL(CO)₃Cl Complexes on Gp-163/9% T3642 Support

| Metal complex | τ_1 (ns) | Frac. area (preexp) | τ_2 (ns) | Frac. area (preexp) | τ_3 (ns) | Frac. area (preexp) |
|--|------------------|------------------------|------------------|------------------------|------------------|------------------------|
| Re(bpy)(CO) ₃ Cl | 106 | 0.071 (0.232) | 309 | 0.541 (0.603) | 807 | 0.388 (0.165) |
| Re(<i>t</i> -Bu) ₂ bpy(CO) ₃ Cl | 163 | 0.080 (0.237) | 458 | 0.576 (0.607) | 1,060 | 0.345 (0.157) |
| Re(terpy)(CO) ₂ Cl | 57 | 0.187 (0.489) | 176 | 0.504 (0.427) | 550 | 0.309 (0.084) |
| Re(Ph ₂ phen)(CO) ₃ Cl | 960 | 0.072 (0.255) | 2,990 | 0.504 (0.568) | 8,060 | 0.424 (0.187) |
| Re(Me ₂ Ph ₂ phen)(CO) ₃ Cl | 620 | 0.130 (0.427) | 2,050 | 0.456 (0.452) | 6,900 | 0.489 (0.122) |
| Re(Me ₄ phen)(CO) ₃ Cl | 690 | 0.069 (0.433) | 4,070 | 0.267 (0.285) | 10,200 | 0.664 (0.282) |

CONCLUSIONS

The rhenium complexes studied here proved to be only marginally useful sensor molecules for ambient quenchometric oxygen sensors. However, the lower sensitivity is an asset for use at higher oxygen pressures such as in hyperbaric oxygen chambers and underwater equipment. The reduced sensitivity allows the complex still to emit significantly at higher oxygen pressures. Since the sensitivity and lifetime of the sensor rely heavily on the complex structure, it may be possible to enhance sensor performance by varying the structures of the complexes. Additionally, other polymer supports may permit tuning the response of the complexes studied. Although a useful copolymer/complex combination was not found for the rhenium cyano complexes as ambient quenchometric oxygen sensors, they should not be excluded as possible sensor molecules. They have extremely high quantum yields, long lifetimes, and high photochemical stability in solution, as opposed to the polymer supports examined here. Further work is in progress.

There are other areas where the low oxygen sensitivity is a virtue. These complexes have high emission anisotropies [24,25], which, coupled with their long lifetimes and relative insensitivity to oxygen quenching, makes them attractive, dynamic emission polarization probes of slow rotational motions in polymeric and biopolymeric systems. Here the reduced oxygen quenching sensitivity is a virtue since it minimizes the need for careful removal of oxygen to achieve the longest lifetimes. Re complexes may also find use as luminescence-based pH sensors, which is another area where low oxygen quenching is desired. In this context our results provide useful insight into developing polymer-supported pH sensor systems.

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