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High-Performance Quenchometric Oxygen Sensors Based on Fluorinated Xerogels Doped with $[\text{Ru}(\text{dpp})_3]^{2+}$

Rachel M. Bukowski,[†] Rosaria Ciriminna,[‡] Mario Pagliaro,^{*,‡} and Frank V. Bright^{*,†}

Department of Chemistry, 511 Natural Sciences Complex, University at Buffalo, The State University of New York, Buffalo, New York 14260-3000, and Istituto per lo Studio dei Materiali Nanostrutturati, CNR, via Ugo La Malfa 153, 90146 Palermo, Italy

By using hybrid xerogels that are composed of alkyl and perfluoroalkyl ORMOSILs (organically modified silicates) doped with the luminophore tris(4,7'-diphenyl-1,10'-phenanthroline) ruthenium(II), we have produced highly sensitive O_2 sensors (i.e., $I_{\text{N}_2}/I_{\text{O}_2} = 35 \pm 4$) with linear calibration curves that exhibit less than 2% drift over 6 months.

Oxygen is a ubiquitous reactant and an important analyte which must be often quantified in medicine, industry, and in the environment. The search for optically based O_2 sensors to replace older electrochemical methods is a major goal of current chemical research.¹ In this field, doped sol–gel oxides (xerogels) are promising and have long been studied due to their transparency, photostability, and high sensitivity to external reactants.² On the other hand, there is little literature on the utilization of fluorinated ORMOSILs (organically modified silicates) in materials science. Carturan and co-workers studied the preparation of silicon oxyfluoride materials with high fluorine contents through the direct hydrolysis of fluoroalkoxide precursors.³ These researchers also assessed the stability of the Si–F bonds within the silicon network. Atkins and co-workers studied the optical properties of highly fluorinated and photosensitive ORMOSIL-derived films for potential use as waveguides,⁴ and some of us recently described the use of fluorinated xerogels as aerobic catalysts.⁵ To the best of our knowledge, only one sensor based on fluorinated polymers has been reported;⁶ however, no work has been performed on

Table 1. Representative Examples of Reported $I_{\text{N}_2}/I_{\text{O}_2}$ for $[\text{Ru}(\text{dpp})_3]^{2+}$ -Based Quenchometric Sensors

sensor platform	$I_{\text{N}_2}/I_{\text{O}_2}$	ref
methyl-trimethoxysilane xerogel	3.4	7
tetraethylorthosilane (TEOS)-based xerogel PEBBLES	3.9	8
TEOS	5.8	9
silicone-based membranes	5.0	10
Cab-O-Sil M5 fumed silica	7	11
tetramethylorthosilane and <i>n</i> -propyl-trimethoxysilane	4.5	12
TEOS and octyl-triethoxysilane	14	1
RTV-118	25	13

the potential of fluorine-containing ORMOSILs/xerogels as platforms for optical chemical sensors.

In the course of our studies to develop tailored sensor platforms, we have discovered that the O_2 sensitivity from a hybrid xerogel-based quenchometric sensor composed of *n*-propyltrimethoxysilane and 3,3,3-trifluoropropyltrimethoxysilane doped with the luminophore tris(4,7-diphenyl-1,10-phenanthroline) ruthenium(II) ($[\text{Ru}(\text{dpp})_3]^{2+}$) is extremely high. As a benchmark, Table 1 summarizes previous results^{1,7–13} for quenchometric O_2 sensors that have used $[\text{Ru}(\text{dpp})_3]^{2+}$ as the luminophore. Inspection of these data shows that the reported sensitivities (i.e., $I_{\text{N}_2}/I_{\text{O}_2}$) range from 3 to 25.

Luminophore quenching depends on several factors.¹⁴ In the simplest scenario of a luminophore in a homogeneous microenvironment, quenching follows the Stern–Volmer relationship:¹⁴

$$I_0/I = 1 + K_{\text{SV}} [\text{O}_2] = 1 + k_q \tau_0 [\text{O}_2] \quad (1)$$

In this expression, I_0 and I represent the steady-state luminescence

* Address correspondence to either author. E-mails: (F.V.B.) chefbv@buffalo.edu; (M.P.) mario.pagliaro@ismn.cnr.it

[†] The State University of New York.

[‡] Istituto per lo Studio dei Materiali Nanostrutturati.

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Table 2. Composition of the Primary Sol Solution

xerogel	TFP-TriMOS (mL)	<i>n</i> -propyl-TriMOS (mL)	H ₂ O (mL)	EtOH (mL)	0.1 M HCl (mL)
TFP/propyl	1.50	0.689	0.633	1.50	0.08

intensities in the absence and presence of O₂, respectively; τ_0 is the excited-state luminescence lifetime in the absence of quencher; [O₂] is the O₂ concentration; K_{SV} is the Stern–Volmer quenching constant; and k_q is the bimolecular rate constant describing the efficiency of the collisional encounters between the luminophore and the quencher. For this ideal case, a plot of I_0/I vs [O₂] will be linear with a slope equal to K_{SV} and an intercept of unity, allowing a simple single-point sensor calibration.

The following reagents were used: tris(4,7'-diphenyl-1,10'-phenanthroline) ruthenium(II) chloride pentahydrate ([Ru(dpp)₃]·Cl₂·5H₂O) (GFS Chemicals), *n*-propyltrimethoxysilane (>95% purity) (*n*-propyl-TriMOS) and 3,3,3-trifluoropropyltrimethoxysilane (>95% purity) (TFP-TriMOS) (Gelest, Inc.), ethyl alcohol (200 proof) (Pharmco), and HCl (Fisher Scientific). [Ru(dpp)₃]²⁺ was purified as described in the literature.¹⁵ All other reagents were used as received, and all aqueous solutions were prepared with deionized water that had been treated with a Barnstead NANOpure II system. Standard glass microscope slides from Fisher Scientific Co. were used as the substrates, and the steady-state fluorescence measurements were carried out by using a SLM-Aminco model 48000 MHF spectrofluorometer as described elsewhere.¹ Sensors' response times were <5 s.

Table 2 presents the composition of the sol stock solution. All of the precursors were physically mixed at room temperature and then sonicated for 1 h. An 80- μ L portion of this sol stock solution was then physically mixed with 20 μ L of 4 mM [Ru(dpp)₃]²⁺ dissolved in EtOH ([Ru(dpp)₃]²⁺ in the final sol was 0.8 mM). This luminophore-doped sol solution was used to form thin (1.0 \pm 0.2 μ m thick), spin-coated films on clean glass microscope slides (3000 rpm, 30 s). All of the films were stored under ambient conditions in the dark.

Figure 1 presents the Stern–Volmer plot for a [Ru(dpp)₃]²⁺-doped TFP-TriMOS/*n*-propyl-TriMOS-based sensor film. The Stern–Volmer plot is linear ($r^2 = 0.994$) over the full oxygen concentration range studied (0–100% O₂).

This linearity suggests that all the [Ru(dpp)₃]²⁺ molecules are reporting from very similar microenvironments within the xerogel. Nonlinear Stern–Volmer plots arise when luminophores report simultaneously from more than one microenvironment that exhibits different k_q or τ_0 values.^{1,13} Figure 2 presents a typical time-resolved intensity decay trace for the [Ru(dpp)₃]²⁺-doped xerogel in the absence of quencher (N₂). The time-resolved intensity decay profiles were fit to a number of models (exponential series and continuous distributions). A single exponential decay law best described the observed intensity decay. This result is also consistent with the luminophore molecules all reporting

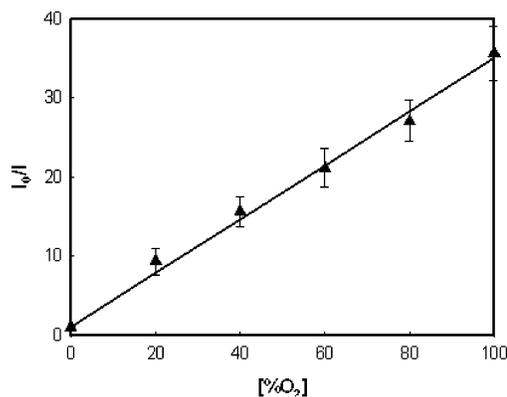


Figure 1. Stern–Volmer plot for a [Ru(dpp)₃]²⁺-doped TFP-TriMOS/*n*-propyl-TriMOS-based sensor film.

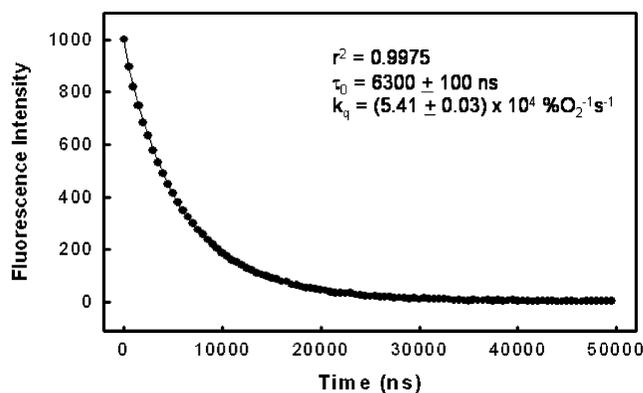


Figure 2. Time-resolved intensity decay trace ($\lambda_{ex} = 440$ nm; $\lambda_{em} > 550$ nm) for a [Ru(dpp)₃]²⁺-doped TFP-TriMOS/*n*-propyl-TriMOS-based sensor film. Fit to a single-exponential decay model is shown (solid line).

from largely equivalent microenvironments within the xerogel. The results in Figures 1 and 2 are to be contrasted with many other quenchometric sensor platforms that exhibit downward-curving Stern–Volmer plots and multiexponential time-resolved intensity decay profiles (see refs 1 and 13 and references therein).

Interestingly, early studies of luminophore-doped xerogels used time-resolved luminescence as a tool to investigate the distribution of dopants within sol–gel doped oxides.¹⁶ The unique structural diversity that these studies revealed led the way to the impressive variety of optical applications of sol–gel-derived materials.^{2,17}

The [Ru(dpp)₃]²⁺-doped TFP-TriMOS/*n*-propyl TriMOS-based sensor films exhibit a I_{N_2}/I_{O_2} of 35 ± 4 ; a sensitivity significantly greater than observed with any previous [Ru(dpp)₃]²⁺-based quenchometric sensor (Table 1). The origin of the large I_{N_2}/I_{O_2} (i.e., increase in K_{SV}) arises from an increase in k_q and not from a significant change in τ_0 . That is, the oxygen diffusivity within these hybrid xerogels is considerably higher in comparison to

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(17) Sol–gel optics have applications in a number of areas, including micro-diffraction elements, macroscopic optical elements, miniature lasers, optical coatings, packaging applications, display technology, and active optical components such as modulators and switches. For a thorough report on these and other applications up to reach the market, see: Sheppard, L. *Sol Gel Processing of Ceramics and Glass*; Electronics.ca Publications: Kirkland, Quebec, Canada, 2002; available at the URL: <http://www.electronics.ca/reports/materials/GB114U.html>

other xerogel platforms, in analogy to what happens in aerobic oxidations catalyzed by similar ruthenium-doped fluorinated xerogels.⁵

The smoothness and the homogeneity of the composite ORMOSIL films is very high, and their crack-free formation proceeds without any added surfactant, due to enhanced hydrophobicity and consequent lower surface tension at the solid/liquid interface during drying of the intermediate alcogel. Under ambient storage conditions, the stability of these hybrid xerogel sensors was constant to within 2% over a 6-month period, which should be compared to the 5-fold decrease in sensitivity in pure TEOS-based xerogels.¹ Such a stable sensor response over time is consistent with the increased hydrophobicity of the sol–gel ORMOSILS cages that overcomes the xerogel shrinkage and pore collapse with time and is a crucial factor in the development of a

reliable sensor platform which contrasts with the poor stability of most sensing species immobilized at the surface of organic and inorganic polymers.¹⁸ The reduced degree of cross-linking of the ORMOSILS cages, in turn, releases the constraints imposed by the cages upon the entrapped dopant molecules, providing the needed flexibility which is instrumental in many photochemical applications of doped sol–gel derived materials.²

In conclusion, fluorinated ORMOSILs doped with the [Ru(dpp)₃]²⁺ luminophore yield O₂ responsive sensors that are sensitive and stable, offering fast detection and simplified calibration thanks to the uniform luminophore distribution within the xerogel matrix. A most promising result considering also the enhanced physical stability of fluorinated ORMOSILs¹⁹ and the versatility and ease of miniaturization and fabrication of sol–gel derived sensors^{2a}

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