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Optical oxygen sensors based on platinum porphyrin dyes encapsulated in ORMOSILS

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ABSTRACT

A strategic approach to develop an "ideal" sensor platform is addressed. Novel quenchometric O_2 sensing materials with 100-fold adjustable sensitivity (I_{N_2}/I_{O_2} from 3 to over 300), reverse and fast response (1 s), linear calibration, and long-term stability are developed. These materials are spin-casted composite ORMOSILs (organically modified silicates) xerogel films sequestered with luminophore Pt(II) octaethylporphine (PtOEP) and Pt(II) meso-tetra(N-methyl-4-pyridyl)porphyrin tetrachloride (PtTMP). The composite xerogels studied are pentafluorophenylpropyltrimethoxysilane (PFTMOS)/*n*-octyltrimethoxysilane (C_8TMOS)/tetramethoxysilane (TMOS) and 3,3,3-trifluoropropyltrimethoxysilane (TFTMOS)/*n*-propyltrimethoxysilane (C3TMOS). Luminescence spectroscopy (steady state and time resolved) have been used to investigate their analytical figures of merit for gaseous O_2 sensing and to determine the underlying reasons for the observed performance. Results show that, except for PtTMP-doped PFTMOS/C8TMOS/TMOS, all other xerogel composites show linear Stern–Volmer relationship and the single exponential time-resolved intensity decay, which indicate the homogeneous environment of the luminophore. For PtTMP-doped PFTMOS/C8TMOS/TMOS xerogels, the Stern–Volmer plots are non-linear and the time-resolved intensity decay profiles are best fitted by double exponential decay model, which are resulted from the heterogeneous environment of the luminophore. The sensitivity of the sensing materials can be tuned by adjusting the xerogel composition and luminophore. For PtOEP-doped PFTMOS/C8TMOS/TMOS, while keeping C8TMOS and TMOS at the same mol ratio, sensitivity (I_{N_2}/I_{O_2}) decreases from 333 to 246 with increased PFTMOS% from 0 to 30%, which is due to the decreased bimolecular quenching constant (k_q). However, $I_{N_2}/I_{O_2} = 3$ was observed from PtTMP-doped PFTMOS/C8TMOS/TMOS. For PtTMP-doped TFTMOS/C3TMOS, sensitivity increases with increased TFTMOS% from 0 to 50% and decreases with further increased TFTMOS% from 50 to 100%, which is mainly due to corresponding increase and decrease of k_q. An optimized composition with high sensitivity is observed at 10 PFTMOS/45C8TMOS/45 C8TMOS with $I_{N_2}/I_{O_2} = 330$.

1. Introduction

Analytical figures of merit for an "ideal" sensor platform include high sensitivity, long-term stability, wide dynamic detection range, high precision and accuracy, easy to operate, robust, and low cost. It is essential to develop an O_2 sensor as "ideal" as we can because O_2 is an important common target analyte in biological, clinical, environmental, and industrial applications. Historically, O_2 was quantified first by Clark electrode (CE) [1] based on the electrochemical analysis, in which O_2 is consumed and the electrode can be easily poised by the sample. Given these limitations, researchers have expended substantial effort to develop optically based O_2 sensors [2]. The most common of these sensors exploit the well-known effects of O_2 quenching on the luminescence of an immobilized luminophore.

Sol–gel processing methods [2,3] have been widely used to immobilize various functional molecules. There is a significant body of literature on the use of luminophore-doped sol–gel-derived xerogels as a platform for O_2-responsive sensor development [4–7]. Common features of these sol–gel-derived O_2 sensing materials include: non-linear calibration curves and/or sensor response that are not stable over the long term. Some research group recently reported on class II ORMOSILS composed of tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS) and mono-alkylsiloxanes of the form (C_nH_{2n+1})-Si-$(OR)_3$ ($n = 1$–12, R = Me or Et) doped with luminescent Ru(II) diimines as a vehicle for producing O_2-responsive chemical sensors with linear calibration curves, good sensitivity, and excellent long-term stability (more than 2 years). In related research they showed [8–11] that Ru(II) diimine-

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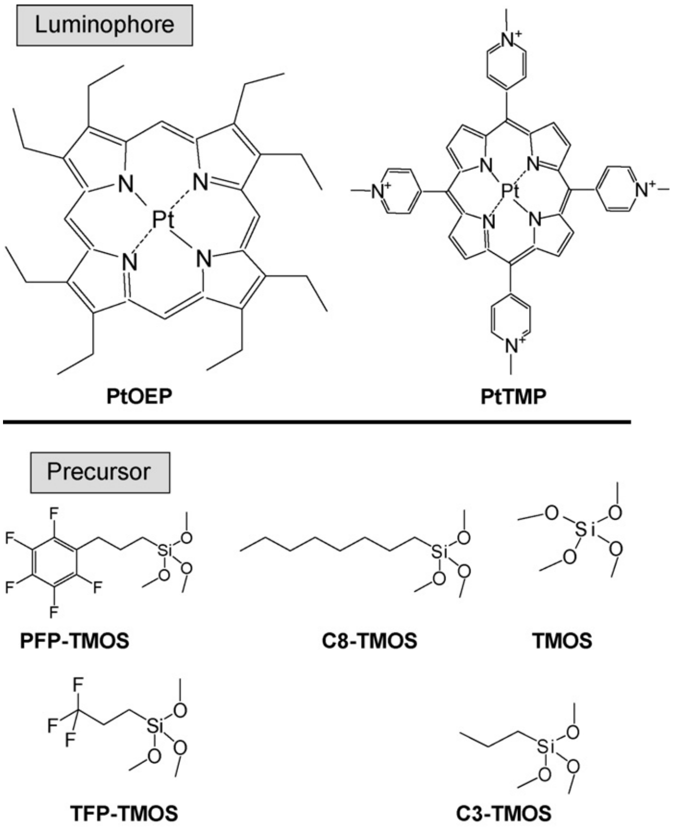

Fig. 1. Chemical structures of luminophores and sol–gel precursors in the study.

doped hybrid xerogels that are composed of two of the following methoxysilanes: TMOS, *n*-propyltrimethoxysilane (C3-TMOS), 3,3,3-trifluoropropyltrimethoxysilane (TFP-TMOS), phenethyltrimethoxysilane (PE-TMOS), and pentafluorophenylpropyltrimethoxysilane (PFP-TMOS) could yield sensing materials with twofold improvements in sensitivity in comparison to aforementioned class II ORMOSILS.

In comparison to Ru(II) diimines, certain metalloporphyrin complexes [12,13] exhibit longer luminescent lifetimes (τ) [12,14] and high quantum yields [15]. Given that quenching-based luminescent sensing material sensitivity depends on the unquenched τ, it is not surprising to learn that there have been several reports [14,16–18] on the development of materials doped with Pt-containing porphyrin complexes as O_2 sensors. Most of these previous reports have used organic polymers as the host matrix. In several instances, researchers have used fluoropolymers as the host materials [19]. Fluorinated materials are attractive because they are less prone to fouling and they exhibit higher O_2 solubilities in comparison to hydrocarbons [20]. However, when compared to xerogels most of these organic polymer platforms possess lower porosities.

In this paper we report on the analytical figures of merit for a series of fluorinated hybrid xerogel materials that are derived from TMOS, C3-TMOS, TFP-TMOS, PFP-TMOS, and *n*-octyltrimethoxysilane (C8-TMOS) that have been doped with Pt(II) octaethylporphine (PtOEP) or Pt(II) meso-tetra(*N*-methyl-4-pyridyl)porphyrin tetrachloride (PtTMP) (Fig. 1). Specifically, we report the effects of xerogel composition on the Stern–Volmer quenching constant (K_{SV}), the unquenched luminophore lifetime (τ_0), and bimolecular quenching constant (k_q) that describes the interaction between the quencher molecules (O_2) and the xerogel-sequestered luminophore.

2. Theory

The model that best describes the bimolecular quenching of a luminophore by O_2 depends on the luminophore distribution within the host matrix and the total fraction of all luminophore molecules that occupy individual microdomains or ensembles of sites [2,3].

2.1. Stern–Volmer limit

In the simplest scenario where identical luminescent molecules are distributed within an analyte-permeable host matrix, the luminescent molecules are distributed within the host such that they are each equally accessible to the quencher species, and the microenvironment surrounding each luminophore molecule is largely similar, one can write:

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + K_{SV}[Q] \tag{1}$$

This expression relates the ratio of the steady-state luminescence intensities or excited-state luminescence lifetimes in the absence of quencher (I_0 or τ_0, respectively) to the intensity or lifetime in the presence of quencher (I or τ, respectively) through the dynamic Stern–Volmer quenching constant, K_{SV}, and the quencher concentration [Q]. For this ideal case, a plot of I_0/I or τ_0/τ vs. [Q] (called the Stern–Volmer plot) will be linear with a slope equal to K_{SV} and an intercept of unity. K_{SV} depends on τ_0 and the bimolecular quenching constant (k_q) between the luminophore and the quencher molecule ($K_{SV} = \tau_0 k_q$); k_q depends on the quencher solubility coefficient in the host matrix (S) and the quencher diffusion coefficient (D) within the host matrix. Eq. (1) is also mathematically equivalent to a single exponential decay of $I(t)$.

2.2. Multiple domain limit

If we consider a more complex scenario, where identical luminophore molecules are simultaneously distributed within a number of different microdomains, the luminophores may exhibit characteristic quenching constants that are associated with *each* distinct microdomain. This situation is appropriate when a few discrete luminophore microdomains or multiple interaction types are expected *a priori* as in cases involving ground-state heterogeneity (e.g., solid-state matrices, interfacial adsorption). Under these circumstances one can write the overall Stern–Volmer expression as the superposition of Stern–Volmer expressions resulting in a summation over all species/domains:

$$\frac{I_0}{I} = \left[\sum_{i=1}^{m}\left(\frac{f_i}{1 + K_{SV,i}[Q]}\right)\right]^{-1} \tag{2}$$

For a system comprised of m microdomains where f_i denotes that fraction of the total emission (in the absence of quencher) that arises from the ith microdomain, $K_{SV,i}$ is the Stern–Volmer quenching constant associated with the ith component, and all other terms are as described above ($\sum f_i = 1$).

If we consider the case of two microdomains (i.e., $m = 2$), often referred to as the Demas two-site model, one can write:

$$\frac{I_0}{I} = \left[\frac{f_1}{1 + K_{SV,1}[Q]} + \frac{f_2}{1 + K_{SV,2}[Q]}\right]^{-1} \tag{3}$$

Eq. (3) is mathematically equivalent to a double exponential decay of $I(t)$ where each component independently fulfills a classic Stern–Volmer relationship.