Nonlinear phosphorescence quenching mechanism of gadolinium labeled porphyrin by oxygen on filter paper

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ABSTRACT

Nonlinear phosphorescence quenching mechanism of gadolinium labeled hematoporphyrin mono-methyl ether (Gd-HMME) by oxygen on the filter paper was studied. The intensity Stern–Volmer plot was found to be approximately linear for oxygen concentration from 10% to 100%, but showing a negative curvature from 0% to 10%. The lifetime plot has similar changing trend. The intensity plot is slightly higher than the lifetime plot reflecting the existence of static quenching. The nonlinear responses were related to the nonlinear solubility of oxygen, which perfectly satisfy the nonlinear solubility model. Data analysis indicates that the static quenching rate constant is unchanged and the percentage of static quenching is about $35\% \pm 3\%$ in the whole range of oxygen concentration.

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1. Introduction

In the past several decades, room temperature phosphorescence (RTP) of transition metal complexes [1,2] and polycyclic aromatic hydrocarbons [3,4] on sol–gel, polymer, mesoporous silica and the filter paper has been used for oxygen sensing. Intensity and lifetime of RTP can be quenched by oxygen, which is the principle of RTP based oxygen sensors [5,6]. Stern–Volmer plots are widely used for studying RTP quenching by oxygen. In homogeneous conditions, Stern–Volmer plots should always give a linear relationship. Nonlinear Stern–Volmer plots are often obtained when quenching takes place in solid matrix [7–9]. Stern–Volmer plots based on Pt(II)-porphyrin complexes assembled in mesoporous silica were nonlinear within a wide range of oxygen concentration [10]. Nonlinear quenching was also obtained based on phosphorescence of polypyridyl ruthenium(II) complexes covalently attached on glass surfaces [11]. Several models have been proposed to explain such nonlinearity, among which the two-site model [12] and the nonlinear solubility model [13] are commonly used to explain the downward Stern–Volmer plot. In the nonlinear solubility model, the decay curves can be fitted using a single exponential function [11].

In our previous work, the intensity Stern–Volmer plots for Gd-HMME on filter paper can be linearly fitted within the oxygen concentration from 10% to 100% [14]. However, vertical intercepts of the fitted lines were greater than 1. This indicates that there is a nonlinear increase for oxygen concentration from 0% to 10%. This phenomenon that Stern–Volmer plot is nonlinear at low concentration and linear at higher concentration needs to be explained. In addition, the corresponding Stern–Volmer plot for lifetime also needs to be studied.

In this work, detailed changing properties of I_0/I versus oxygen concentration from 0% to 10% for Gd-HMME on the filter paper were studied. Phosphorescence spectra of Gd-HMME were recorded and analyzed for oxygen concentrations from 0% to 10%. The phosphorescence lifetimes at different oxygen concentrations were measured and the lifetime Stern–Volmer plot was obtained. The nonlinear phenomenon was theoretically investigated based on rate equations as well as the adsorption model of oxygen on solid matrix.

2. Experimental

2.1. Materials

Methanol was purchased from Tianjin Fuyu Fine Chemical Co., Ltd. Anhydrous gadolinium chloride was bought from J&K Scientific Ltd. Hematoporphyrin monomethyl ether was obtained from Shanghai Xianhui Pharmacuetical Co., Ltd. Imidazole was purchased from Tianjin Guangfu Fine Chemical Research Inst. High pure oxygen and nitrogen were from Harbin Liming Co., Ltd. Slow speed quantitative filter paper with 1–3 μm pores was bought from Fushun filter paper factory.

2.2. Preparation of oxygen sensor

Oxygen sensors containing Gd-HMME on equal-sized circular filter paper were prepared. Gd-HMME was synthesized in imidazole at high temperature with gentle argon flow protection by Srivastava's method [15]. The synthesis process of Gd-HMME was provided in the Supporting Information. The synthesized mixture was dissolved with methanol to get 10 ml 1.2 mg/ml Gd-HMME methanol solution. Gd-HMME methanol solution was diluted to 0.1 mg/ml, 0.2 mg/ml, 0.4 mg/ml and 0.6 mg/ml. Oxygen sensing samples were prepared by 10 μl methanol solution of Gd-HMME spotted on the circular filter paper with 10 mm diameter with 2-20 μl pipettor (Dragon Laboratory). After air drying for 1 h, the samples were moved into a gas chamber.

2.3. Measurements

A diode laser centered at 405 nm was used to excite Gd-HMME. Photoluminescence spectra were recorded by a fiber optic spectrometer (Ocean Optics USB2000). Intensity Stern–Volmer plot of the sensor was studied by measuring photoluminescence spectra of the sensor under different oxygen concentrations. To get different oxygen concentrations, high pure nitrogen and oxygen were mixed into the gas chamber to get 0–100% oxygen with 2% interval via gas flow displayers and mass flow controllers (Seven star electronics). To determine the lifetime of Gd-HMME photoluminescence on the filter paper, decay profile was measured. The determination of the lifetimes of Gd-HMME phosphorescence was provided in the Supporting information.

3. Theoretical basis

Fig. 1 shows the energy level schematic diagram of Gd-HMME and O$_2$ as well as probable energy transfer process between Gd-HMME and molecular o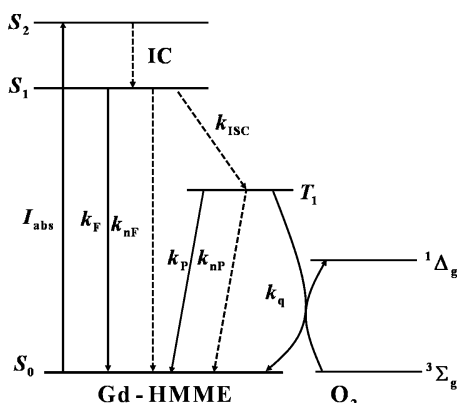xygen. When Gd-HMME is excited from its singlet ground state S_0 to an excited singlet state, it rapidly decays to its lowest excited singlet state S_1 by internal conversion (IC). Gd-HMME relaxes to S_0 either by a non-fluorescent transition or by a fluorescence emission. Gd-HMME in state S_1 may also transfer to the first excited triplet state T_1 by intersystem crossing. Then Gd-HMME in state T_1 may relax to state S_0 by a non-phosphorescent transition, a phosphorescence emission or by energy transfer to the oxygen. Definitions of variables describing the energy transfer process are listed in Table 1.

The time-dependent concentrations of Gd-HMME at each state are described by the following rate equations:

$$\frac{d[S_1]}{dt} = \alpha v \rho \sigma [S_0] - (k_F + k_{nF} + k_{ISC})[S_1], \qquad (1)$$

$$\frac{d[T_1]}{dt} = k_{ISC}[S_1] - (k_P + k_{nP} + k_q[O_2])[T_1], \qquad (2)$$

where v is the light speed in methanol; ρ is the photon number density of the pump; σ is the absorption cross section of Gd-HMME; α is a constant; $[S_0]$, $[S_1]$ and $[T_1]$ are the concentrations of Gd-HMME in S_0, S_1 and T_1, respectively; $[O_2]$ is the oxygen concentration.

From Eqs. (1) and (2), in the steady state, the phosphorescence intensity (I) is related to $k_P [T_1]$ as follows,

$$I = k_P \frac{k_{ISC} \alpha v \rho \sigma [S_0]}{(k_P + k_{nP} + k_q[O_2]) \cdot (k_F + k_{nF} + k_{ISC})}. \qquad (3)$$

Here the reciprocal of the sum $(k_P + k_{nP} + k_q[O_2])$ is identical to the lifetime(τ). From Eq. (3), the classic Stern–Volmer equation, $\frac{I_0}{I} = 1 + k_q \tau_0 [O_2]$, can be obtained in the ideal case, where τ_0 is the lifetime in the absence of oxygen.

4. Results and discussion

Typical photoluminescence spectra of Gd-HMME (0.6 mg/ml) supported on the filter paper in high pure nitrogen (black solid line) and oxygen (red solid line) are shown in Fig. 2(a) together with the filter paper itself (green solid line). The photoluminescence spectra of Gd-HMME supported on the filter paper contain four peaks of Gd-HMME and background emission of the filter paper. After subtracting the background emission of the filter paper, photoluminescence spectra of Gd-HMME can be extracted and are shown in the inset of Fig. 2(a). Among the four emission peaks, peaks at 585 nm and 626 nm are weak fluorescence with the lifetime of 10 ns [16]. Two strong red shift photoluminescence peaks in the very near-infrared region (712, 790 nm) are room temperature phosphorescence emissions [14]. It is clear that the phosphorescence of Gd-HMME is significantly quenched by oxygen. Stern–Volmer plots for different concentrations of Gd-HMME are obtained and shown in Fig. 2(b). There is an obvious nonlinear increase from 0% to 10% oxygen concentration (p_{O_2}) as shown in the amplified inset figure of Fig. 2(b).

Fig. 1. Energy level schematic diagram of Gd-HMME and O$_2$ as well as the energy transfer process.

Table 1
Definitions of variables describing interactions between Gd-HMME and oxygen.

Symbol	Definition
I_{abs}	Light absorption to excite Gd-HMME to S_2
k_F	Rate constant of fluorescent transition from S_1 to S_0
k_{nF}	Rate constant of non-fluorescent transition from S_1 to S_0
k_{ISC}	Rate constant of inter-system crossing
k_P	Rate constant of phosphorescent transition from T_1 to S_0
k_{nP}	Rate constant of non-phosphorescent transition from T_1 to S_0
k_q	Quenching rate of T_1 by O$_2$