



Oxygen sensing properties of gadolinium labeled hematoporphyrin monomethyl ether based on filter paper



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ABSTRACT

Oxygen sensing properties of a luminescent material gadolinium labeled hematoporphyrin monomethyl ether (Gd-HMME) based on filter paper were studied. Photoluminescence of Gd-HMME at 712 nm was confirmed to be phosphorescence by a time-resolved spectroscopic analysis and its dependence on oxygen. Quantum yield of the phosphorescence was determined to be 0.014 in air saturated methanol solution ($\lambda_{exc} = 532$ nm). A linear range was found from 10% to 100% oxygen concentration in Stern–Volmer plots for Gd-HMME based on filter paper. Fast response time, recovery time (t_r , 0.4 ± 0.2 s; t_r , 1.4 ± 0.2 s) and high photostability were achieved. Our results indicate that Gd-HMME is a promising indicator for optical oxygen sensing.

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1. Introduction

In the past few decades, optical sensors for molecular oxygen (O_2) have attracted wide interests [1,2] because the detection of O_2 in gas, aqueous, and organic phase is very important in many fields, such as industrial process control, environmental monitoring [3], biological detection [4], medicine [3], aerodynamics [5,6], plant science [7], pharmaceutical [8], chemistry analysis [9], and food packaging [10]. They usually consist of an indicator dye encapsulated within an O_2 permeable matrix [11]. The development of luminescence-based oxygen sensors focuses on novel dyes with high brightness and photostability as well as efficient substrates for fast, stable, sensitive and selective oxygen sensing [12].

Various complexes, such as polypyridyl transition metal complexes [13] and metalloporphyrins [14,15] have been developed as optical oxygen sensing dyes because of their relatively large Stokes shifts and long luminescent lifetimes [16–18]. Oxygen sensors based on such compounds have seen a huge development in

different detection modalities in recent years [19–25]. Pt(II) and Pd(II) complexes of porphyrin dyes exhibit strong phosphorescence at room temperature, which is readily quenched by O_2 [26]. Benzoporphyrins complexes [27], iridium porphyrins with axial ligands [28] and PtTFPL [29] show good oxygen sensing properties in the red and very-near infrared spectral region (600–900 nm) with the potential for oxygen measurements in animal tissue and complex specimens. Gadolinium porphyrins have relatively high QY of triplet states because of the heavy-atom effect [30] and special energy levels of Gd^{3+} ($[Xe]4f^7$), i.e., the lowest excited energy level is above the first excited singlet and triplet states of porphyrin. The phosphorescence of gadolinium with tetraphenylporphyrin in ethanol solutions and in thin films has been reported to be used in optical oxygen sensing [31]. In our recent study, Gd-HMME was found to display relatively strong room temperature phosphorescence emission on liquid phase with long excited state lifetime and large Stokes shift [32].

The study on efficient substrates for optical oxygen sensing materials has also attracted considerable attention. Sol–gel [33,34] and polymer films [35,36] are generally used as host materials to encapsulate the luminescent complexes [37,38]. Filter paper used in solid substrate room temperature phosphorimetry [39] has the advantages of easy design, simple structure and low cost compared with other substrates.

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In this study, optical oxygen sensing properties of Gd-HMME based on filter paper were investigated. Gd-HMME was synthesized and characterized with UV–vis absorption spectra. Absorption coefficients of Gd-HMME were determined by absorption spectroscopic analysis. Photoluminescence spectra of Gd-HMME were measured. Luminescence quantum yield of Gd-HMME was obtained by using Rhodamine 6G (R6G) as the reference. Stern–Volmer plots of Gd-HMME based on filter paper versus oxygen concentration were studied. Response time and photostability of Gd-HMME based on filter paper were measured. The effect of humidity on the Stern–Volmer plots was also studied.

2. Experimental

2.1. Materials

Anhydrous gadolinium chloride (GdCl_3) was bought from J&K Scientific Ltd. Hematoporphyrin monomethyl ether (HMME) was obtained from Shanghai Xianhui Pharmaceutical Co., Ltd. R6G was purchased from Sigma–Aldrich Company. Methanol was purchased from Tianjin Fuyi Fine Chemical Co., Ltd. as solvent. High purity nitrogen and oxygen were from Harbin Liming Co., Ltd. Chronic quantitative filter paper with 1–3 μm pores was bought from Fushun filter paper factory.

2.2. Preparation of oxygen sensor

Gd-HMME was synthesized by a method published by Srivastava [40]. Detailed synthesis process of Gd-HMME was as follows: mixture of 6 g imidazole, 9.6 mg HMME and excess anhydrous GdCl_3 (25 mg) was added into a 250 ml three-necked bottle with argon flow protection for 30 min before synthesis. Then, the mixture was heated and kept at 200 °C and stirred magnetically for 2 h protected with argon flow. The mixture was dissolved with methanol to get 10 ml 1.2 mg/ml Gd-HMME methanol solution after cooling down to room temperature.

Preparation process of oxygen sensor was as follows: oxygen sensing samples were prepared by 10 μl methanol solutions of Gd-HMME at 0.1, 0.2, 0.4, 0.6 and 1.2 mg/ml spotted on filter paper circles of 10 mm diameter with 2–20 μl pipettor (Dragon Laboratory). After dried for 1 h, the samples were moved into a gas chamber which provides an airtight environment.

2.3. Measurements

UV–vis absorption spectra were measured using a miniature fiber optic spectrometer (Ocean Optics QE65000) equipped with a deuterium lamp. The determination of the molar absorption coefficients was carried out by absorption spectroscopic analysis. Absorbance of Gd-HMME was determined based on Beer–Lambert law, $A = -\lg(I(\lambda)/I_0(\lambda)) = \varepsilon(\lambda)CL$, where A is the absorbance of Gd-HMME, $I(\lambda)$ is the transmission spectrum of Gd-HMME, $I_0(\lambda)$ is the transmission spectrum of the blank (methanol), $\varepsilon(\lambda)$ is the absorption coefficient of Gd-HMME, C is the concentration and L is the optical path length. In the measurement, 2.5 μM Gd-HMME was put into a silica cuvette with the length of 1 cm.

A diode laser centered at 405 nm was used to excite Gd-HMME. Photoluminescence spectra were recorded by a miniature fiber optic spectrometer (Ocean Optics USB2000). To determine the luminescence quantum yield of Gd-HMME in air saturated solution, R6G was used as the reference excited by a 532 nm solid state laser (CLO Laser DPGL-500L).

To determine the lifetime of Gd-HMME photoluminescence in methanol solution, decay profile was measured. A square wave was given to a diode laser controller (Thorlabs ITC510) to control

a diode laser centered at 405 nm (Thorlabs TCLDM9). Photoluminescence signals were recorded by a grating spectrometer (Zolix Omni- λ 300) and amplified by a photomultiplier tube (Zolix PMTH-S1-R212) with a high voltage power supply (Zolix HVC1800). The time-resolved signal was averaged with a digital phosphor oscilloscope (Tektronix DPO5054) and the decay curve was sent to a personal computer for lifetime determination. The lifetime evaluation was performed by fitting the decay curve to an exponential function using adjustable parameters.

Stern–Volmer plots of the sensor were studied by measuring photoluminescence spectra of the sensor under different oxygen concentrations. To get different oxygen concentrations, high purity nitrogen and oxygen were mixed into the gas chamber via gas flow displays and mass flow controllers (Seven star electronics). Five times recorded signals were averaged to get photoluminescence spectra for each oxygen concentration.

The response time, relative intensity change and reversibility for phosphorescence intensity of Gd-HMME were measured upon switching between deoxygenation and air. To vacuumize the gas chamber, one end of the gas chamber was connected to a vacuum pump (Songjiu electric 2XZ-2B) while the other end was closed. Real-time photoluminescence spectra were recorded to get the response time and recovery time. Photostability of the sensor was measured under the illumination of a 405 nm laser with the power density of 1 mW cm^{-2} for 120 min under high purity nitrogen.

The Stern–Volmer plots of two humid conditions (dry and humid gas) were studied by phosphorescence spectroscopic analysis. To obtain dry and humid conditions, mixed gas flow were controlled to pass allochroic silicagel or water, respectively, before the gas was put into the gas chamber.

3. Results and discussion

3.1. UV–vis absorption spectra and absorption coefficients

Gd-HMME was characterized using UV–vis absorption spectra. Fig. 1 presents the chemical structures of HMME and Gd(III)-HMME as well as the synthesis procedure. Gadolinium ion has a relatively large ionic radius of 93.8 ppm and its corresponding metalloporphyrins have an out-of-plane structure [41] as shown in Fig. 1. Fig. 2(a) shows the typical UV–vis absorption spectrum of HMME. The absorption spectrum of HMME comprises the following bands (nomenclature given by Platt [18]): four Q bands, which can be seen at 499 nm, 530 nm, 568 nm and 614 nm, B bands (Soret band) is the origin of the second excited state and appears between 380 and 420 nm. Fig. 2(b) shows the UV–vis absorption spectrum of 2.5 μM Gd-HMME. The measured Soret band of Gd-HMME is at 406 nm and two Q band peaks are at 538 nm and 571 nm. The Soret band of Gd-HMME showed a very good compatibility with the laser diode centered at 405 nm as the excitation source. Reduction of the number of Q bands is due to the symmetry change from D_{2h} (HMME) to C_{4v} (Gd-HMME) [31]. Red shift of the Q band resulted from the out-of-plane structure.

Absorption coefficients of Gd-HMME were calculated according to Beer–Lambert law. Absorption coefficients of the three absorption peaks in methanol were determined to be: 406 nm ($2.53 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$), 538 nm ($2.45 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and 571 nm ($2.35 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) by absorption spectroscopic analysis.

3.2. Photoluminescence properties of Gd-HMME

Normalized photoluminescence spectra of HMME (black solid line) and Gd-HMME (red solid line) in methanol solutions are shown in Fig. 3. HMME has two emission peaks at 623 nm and 687 nm from the black solid line in Fig. 3. It is well known that two

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