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Optical CO_2 Sensor with the Combination of Colorimetric Change of pH Indicator and Internal Reference Luminescent Dye

Naoki Nakamura and Yutaka Amao*

Department of Applied Chemistry, Oita University, Dannoharu 700, Oita 870-1192

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A new optical CO_2 sensor based on luminescence intensity changes of europium(III) complex, tris(thenoyltrifluoroacetonato)europium(III) dihydrate complex ([Eu(tta)$_3$]) due to the absorption change of pH-indicator dye (thymol blue) with CO_2 was developed and its CO_2 sensing properties were investigated. The observed luminescence intensity (I) from [Eu(tta)$_3$] at 613 nm increased with increasing the CO_2 concentration. The ratio I_0/I_{100}, where I_0 and I_{100} represent the detected luminescence intensities from a layer exposed to 100% nitrogen and 100% CO_2, respectively, that we takes the sensitivity of the sensor is estimated to be 16.0. The response times of the sensing film were 4.0 s for switching from nitrogen to CO_2, and 36 s for switching from CO_2 to nitrogen. The signal changes were fully reversible and no hysterisis was observed during the measurements.

CO_2 measurement techniques are used in various fields, such as chemical, breath monitoring in clinical and environmental monitoring. The gaseous CO_2 has been measured by infrared (IR) absorptiometry[1,2] and by an electrochemical method using a Severinghaus electrode.[3] As CO_2 has a strong infrared absorption band extending from 4200 to 4400 nm, IR absorptiometry has been applied to this optical sensor. On the other hand, the CO_2 sensor using a Severinghaus electrode consists of a glass electrode, which detects the changes in the pH of surrounding bicarbonate ion solution brought about by permeation and subsequent hydration of CO_2 through a thin silicone film. However, the very sensitive IR absorptiometry sensor is subject to strong interference from water vapour and is an expensive system. To overcome these problems, the development of a highly sensitive and convenient CO_2 sensor is necessary. In recent years, the optical CO_2 sensors based on the colorimetric or fluorometric change of pH indicator or CO_2 sensitive dyes have been developed.[4–16] Especially, the optical CO_2 sensors have been used for the measurement of blood CO_2 in clinical fields.[4–6] The optical CO_2 sensors are classified into two types. One is the sensor based on the colorimetric change of pH indicator dye, such as thymolsulfonphthalein (thymol blue), phenolsulfonphthalein (phenol red) and so on;[7–10] The other sensor is basis of the CO_2 induced fluorescence change of luminescent dye[4–6] such as 1-hydroxypyrene trisulfonate and ruthenium(II) complexes.[11–16] The CO_2 sensor based on the fluorescence intensity changes of dye is a simple and convenient method. However, the number of CO_2-quenchable compounds is extremely limited. To solve this problem, the optical CO_2 sensor with the combination of colorimetric change of pH indicator dye and luminescent dye (internal reference dye) will be developed. The luminescence of internal reference dye should be unchangeable by CO_2. In principle, this type of the CO_2 sensor will be developed by the wavelength overlap between the luminescence band of internal reference dye and the absorption band, which is changed by CO_2, of a pH indicator dye. Thymol blue has the absorption band at 600 nm; this band decreases with increasing of CO_2 concentrations. Especially, thymol blue has a large A_0/A_{100} value, where A_0 and A_{100} are absorbance in the 100% nitrogen and 100% CO_2 gaseous, respectively. On the other hand, much attention has been given to the photochemical and photophysical properties of lanthanide complexes.[17] Europium(III) complexes display remarkably strong luminescence with high quantum yields and have long lifetimes ($\tau < 300$ μs).[18] Thus, europium(III) complexes are attractive candidates as internal reference dye materials. Among the europium(III) complexes, tris(thenoyltrifluoroacetonato)europium(III) dihydrate complex ([Eu(tta)$_3$]) has the emission band at 613 nm with excitation of 350 nm and this emission is not affected by CO_2. Moreover, the [Eu(tta)$_3$] has a good stability for an excitation light source. Thus, thymol blue and [Eu(tta)$_3$] are useful for pH-indicator and internal-reference dyes, respectively, and a conventional optical CO_2 sensor using cheap black light will be developed by a device consisting of thymol blue and [Eu(tta)$_3$].

In this work we describe the development of an optical CO_2 sensor with the combination of colorimetric change of thymol blue and [Eu(tta)$_3$] as internal reference dye and we note its CO_2-sensing properties.

Experimental

Ethyl cellulose (ethoxyl 48%), tributyl phosphate, and thymol blue were obtained from Wako Pure Chemical Co. Ltd. Tetraoctylammonium hydroxide was obtained from Tokyo Chemical Industry Co. Ltd. [Eu(tta)$_3$] was obtained from Acros Organics. Polystyrene (PS, average MW 280000, GPC grade) was purchased from Aldrich. Non-luminescence glass slides were obtained from Mitsubishi Chemical Co., Ltd. The other reagents were of the highest grade available.

The CO_2 sensing film was composed of CO_2 indicator dye / phase-transfer agent / polymer / plasticizer / solid support / reference luminescence dye / polymer, i.e., thymol blue / tetraoctyl

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ammonium hydroxide / ethyl cellulose / tributyl phosphate / non-luminescent glass slide / [Eu(tta)$_3$] / polystyrene. At first, thymol blue immobilized in ethyl cellulose film was prepared onto the one side of non-luminescent glass slides (1.4 × 5.0 cm) according to the previously reported method.[9] Component solution (1) was prepared by adding 1.1 µmol of thymol blue to 2 mL of a 0.7 mol dm^{-3} tetraoctylammonium hydroxide in methanol solution. Component solution (2) was 0.25 g of ethyl cellulose in 2.5 mL toluene. The solution for thymol blue film consisted of 1.5 mL of solution (1), 2.5 mL of solution (2), 0.5 mL of tributyl phosphate and 7.0 mL of toluene. Tributyl phosphate was used to form the plasticzed film. The thymol blue film was formed by casting 0.2 mL of the above solution onto one side of a non-luminescent glass slide (1.4 × 5.0 cm). The film was dried at room temperature and then [Eu(tta)$_3$] immobilized in polystyrene film was formed by casting 0.2 mL of a mixture of 1.0 µmol of [Eu(tta)$_3$] in toluene solution onto the opposite side of the glass slides. The prepared film was defined as CO_2 sensor film.

The optical and sensing properties of CO_2 sensor film was studied using UV-vis absorption and fluorescence spectra changes. The UV-vis absorption spectra of the CO_2 sensor film were recorded using a spectrophotometer (Multispec-1500, Shimadzu). Fluorescence spectra of the CO_2 sensor film were measured using a Shimadzu RF5300-PC fluorescence spectrometer with a 150 W xenon lamp as an excitation light source. Excitation and emission bandpasses were 3.0 nm. The sample substrate was mounted at a 45° angle in the quartz cell to minimize light scatter from the sample and substrate. The excitation light is irradiated from the thymol blue layer side and the reflectance light is also detected from the thymol blue layer side. Different CO_2 standards (in the range 0–100%) in a gas stream were produced by controlling the flow rates of CO_2 and nitrogen gases entering a mixing chamber. The total pressure was maintained at 760 Torr (1 Torr = 133.322 Pa). All the experiments were carried out at room temperature.

Results and Discussion

The CO_2 induced absorption spectrum change of thymol blue immobilized in ethyl cellulose film is shown in Fig. 1. The absorption spectrum under nitrogen saturated condition ([CO_2] = 0%) was used as reference spectrum. The absorbance at 613 nm decreased with increasing the CO_2 concentration, as shown in the inset of Fig. 1. Abs$_0$ indicated the absorbance under 100% nitrogen condition. The colorimetric changes of this film were fully reversible and hysterisis was not observed during the measurements. Thus, the thymol blue immobilized in ethyl cellulose film can be used for optical CO_2 indicator based on the colorimetric changes.

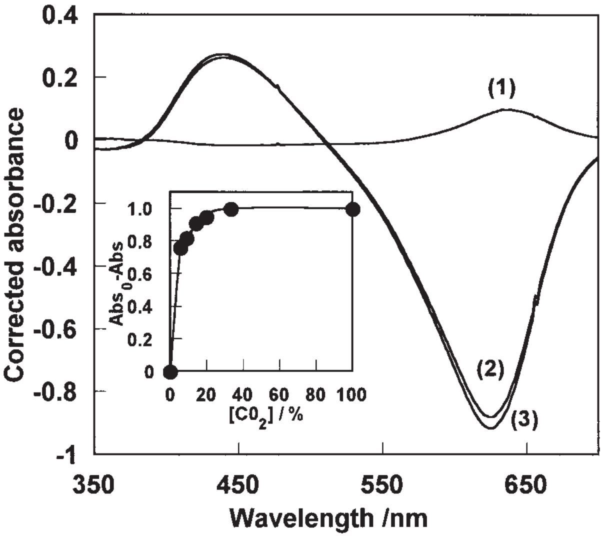


Fig. 1. UV-vis absorption spectrum change of thymol blue immobilized in ethyl cellulose film under various CO_2 concentrations. [CO_2] = 0 (1), 20 (2) and 100% (3). The inset shows the relationship between differential absorbance at 613 nm and CO_2 concentrations. Abs$_0$ indicated the absorbance under 100% nitrogen condition.

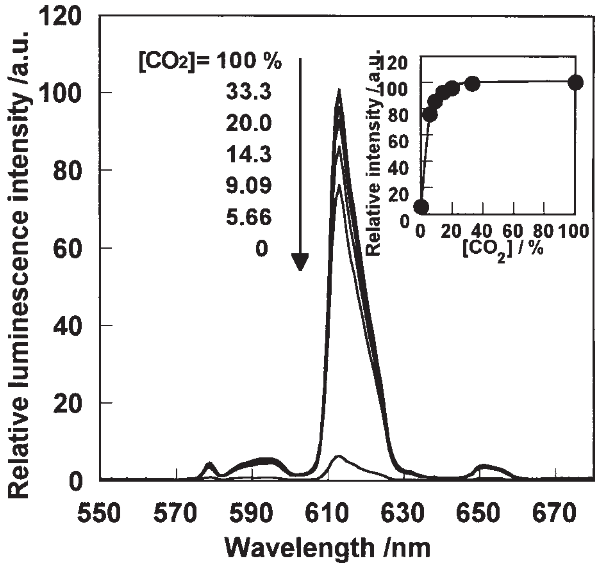
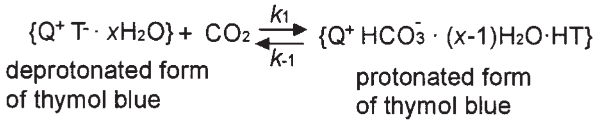


Fig. 2. Luminescence spectrum change of CO_2 sensor film under various CO_2 concentrations. The inset shows the relationship between observed luminescence intensity at 613 nm and CO_2 concentrations. The excitation wavelength was 350 nm.

The CO_2 induced luminescence spectrum change of CO_2 sensor film when excited at 350 nm under various CO_2 concentrations is shown in Fig. 2. As the absorption band at 613 nm of thymol blue decreased with increasing the CO_2 concentration, the observed luminescence intensity from [Eu(tta)$_3$] at 613 nm increased as shown in the inset of Fig. 2. On the other hand, no change of luminescence of [Eu(tta)$_3$] immobilized in polystyrene film was observed by CO_2 gas, indicating that the luminescence of [Eu(tta)$_3$] was not affected by the CO_2. Thus, an optical CO_2 sensor based on the luminescence intensity change of [Eu(tta)$_3$] by the absorption change of thymol blue with CO_2 was developed. The ratio I_0/I_{100} is used to represent the sensitivity of the sensing layer, where I_0 and I_{100} represent the detected fluorescence intensities from a sensor film exposed to 100% nitrogen and 100% CO_2, respectively. In general, the sensor having the ratio I_0/I_{100} more than 3.0 is a suitable sensing device.[18] The I_0/I_{100} value of CO_2 sensor film is estimated to be 16.0.

The sensing properties of CO_2 sensor film were studied. The reaction process between thymol blue and CO_2 can be described as shown in Scheme 1; where $\{Q^+T^- \cdot xH_2O\}$ is the ion pair formed between the tetraoctylammonium cation



Scheme 1. The reaction process between thymol blue and CO_2.

Q^+ and the deprotonated form of thymol blue T^-. The ratio of the concentrations of the thymol blue in its protonated and deprotonated forms is proportional to the concentration of CO_2. In Scheme 1, K is the equilibrium constant. On the other hand, the observed luminescence intensity at 613 nm increased in proportion to the transmittance (T) of the deprotonated form of thymol blue (T^-). The T of the deprotonated form of thymol blue is expressed as follows:

$$T = 10^{-\mathcal{E}d[\{Q^+T^-\cdot xH_2O\}]} \tag{1}$$

where $\mathcal{E}$ and d are molar extinction coefficient and thickness of sensor film, respectively. Thus, $-\mathcal{E}d$ is constant and can be replaced by A. The relationship between I and T is expressed as follows:

$$I = BT = B10^{A[\{Q^+T^-\cdot xH_2O\}]} \tag{2}$$

where B is a constant. The concentration of $\{Q^+T^-\cdot xH_2O\}$ was expressed as Eq. 3:

$$[\{Q^+T^-\cdot xH_2O\}] = -KA[\{Q^+T^-\cdot xH_2O\}]_0/(K + [CO_2]) \tag{3}$$

Here, $-KA[\{Q^+T^-\cdot xH_2O\}]_0$ is replaced by a constant C. Then Eq. 2 is re-written to Eq. 4.

$$I = B10^{\{-C/(K+[CO_2])\}} \tag{4}$$

The observed luminescence intensity change by CO_2 was expressed to be I/I_0. I_0 is the luminescence intensity at 613 nm of CO_2 sensor film in 100% nitrogen gas. Thus, the relationship between observed luminescence intensity at 613 nm and CO_2 concentration was following the Eq. 5.

$$I/I_0 = 10^{\{-C(1/(K+[CO_2])+1/K)\}} \tag{5}$$

Figure 3 shows the plot of I/I_0 versus the CO_2 concentration. In Fig. 3, the solid line is the best-fit using Eq. 5. The correlation factor of the plots, r^2, is estimated to be 0.997 by the least squares method. This result indicates that CO_2 sensor film can be calibrated by Eq. 5.

An operational stability test was conducted by reading the luminescence intensity signal of CO_2 sensor film while CO_2-saturated and nitrogen-saturated states were alternated for 400 s as shown in Fig. 4. The response times for optical CO_2 sensor are defined the 95% response and recovery times exhibited by the sensors when they are exposed to an alternating atmosphere of CO_2 and nitrogen, respectively. The response times of the sensing film were 4.0 s for switching from nitrogen to CO_2, and 36 s for switching from CO_2 to nitrogen. The signal changes were fully reversible and hysterisis was not observed during the measurements. The previously reported values for the response and recovery times of optical CO_2 sensors using pH indicator in polymer film were over 1 min.[7,8,14] Thus, this CO_2 sensor film has the fast response and recovery times compared with previously reported optical CO_2 sensor.

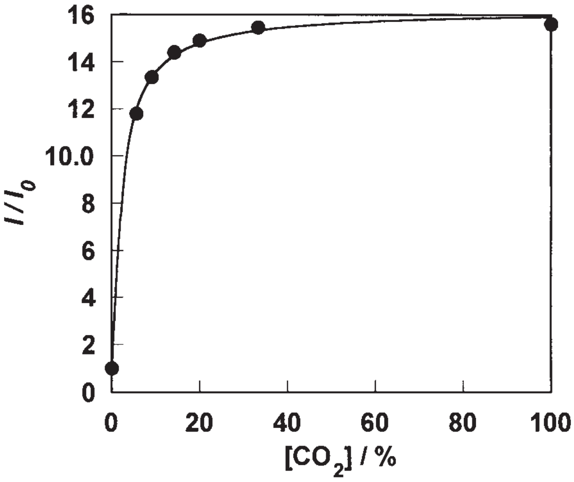


Fig. 3. The I/I_0 value of CO_2 sensor film under various CO_2 concentrations. The excitation and emission wavelengths were 350 and 613 nm, respectively. The solid line is the best-fit using Eq. 5.

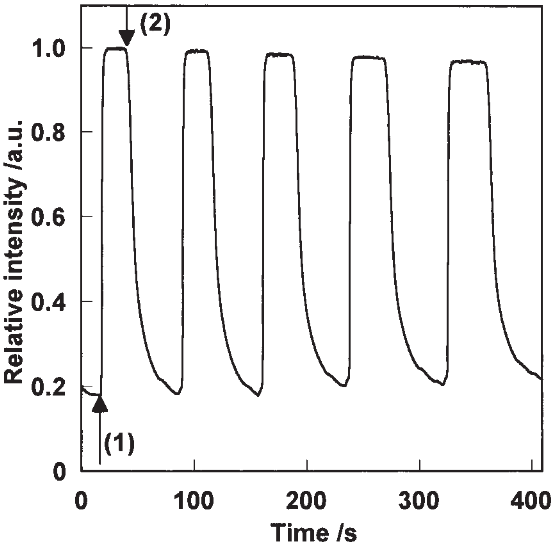


Fig. 4. Response time and relative intensity change for CO_2 sensor film on switching between 100% nitrogen (1) and 100% CO_2 (2). The excitation and emission wavelengths were 350 and 613 nm, respectively.

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