Journal of Metals, Materials and Minerals, Vol.23 No.1 pp.61-65, 2013

Dissolved Oxygen Sensor Film Using Ruthenium Polypyridine Complex As Luminophore

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Abstract

Ruthenium polypyridine complex was synthesized by using RAFT process. The Ruthenium was immobilized in 2 silicone matrices, polydimethylsiloxane(PDMS) and KE 200 (silicone elastomer base)/CX200 (curing agent). KE 200/CX200 is the alcohols curing type silicone. Both sensor films showed absorption peak at 460 nm and luminescence peak at 610 nm. The KE200/CX200 film gave linear response to dissolved oxygen up to 80% O_2 (18 ppm) follow Stern-Volmer equation with R^2 of 0.990. The measured luminescence intensity decreased with increasing dissolved oxygen water temperature from 25 to 70°c. After being irradiated with 460 nm light source for 3 hrs, the sensor film still showed good stability.

Key words: Ruthenium polypyridine complex, RAFT, Dissolved oxygen, Luminophore

Introduction

Dissolved oxygen in water plays an important role in biological, clinical, environmental and industrial applications. Therefore, sensing of dissolved oxygen has attracted a lot of scientific efforts and still remains an important research topic. Various techniques have been used to measure dissolved oxygen. Optical oxygen sensor offers higher sensitive measurement and less maintenance cost compared to that of a clark-type established electrochemical sensor. Most optical oxygen sensors are based on the luminescence quenching of an oxygen sensitive dye, where a variety of luminescence dyes have been incorporated into silicone rubber, polymer membranes(1) and in the sol-gel matrix.(2) The most common dyes used are metalloporphyrins and transition metal complexes. Pt(II) and Pd(II) octaethylporphyrins show high quantum yield and good sensitivity towards oxygen molecules. Different Ru complexes have also been used as oxygen sensitive dyes because of their highly emissive metal-to-ligand charge transfer (MLCT). Silicone or polysiloxanes materials consist of a silicon-oxygen backbone (-Si-O-Si-O-Si-O-…) and it has good gas permeability. Silicone polymer also has high thermal stability, chemical inertness and optical transparency.(3)

To determine dissolved oxygen concentration, the measurement of luminescence intensity is usually performed. The emitted intensities are varied as a function of the oxygen concentrations and is expressed as Stern-Volmer equation:

$$\frac{I_0}{I} = 1 + K_{sv}[O_2]\,. \qquad (1)$$

where I_0 and I represent the steady-state luminescence intensities, in the absence and presence of O_2, respectively. K_{sv} is the Stern-Volmer quenching constant which can be obtained from Stern-Volmer plot[4]. Luminescence sensing based on intensity measurement is most popular because of its simple and low cost compared with those based on the luminescence life time or phase fluorometric measurements. However, the measured intensity may be affected by changes in the light source intensity or by photoleaching of the dye. To achieve the problem of dye leaching, modification of oxygen sensitive dyes or matrix and newly synthesized luminophores are needed. In this study, we investigate oxygen response of newly synthesized luminophore $[(bpy)_2Ru(bpy\text{-}RAFT_2)](ClO_4)_2$ encapsulated in 2 different silicone matrices as a function of oxygen concentration.

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Materials and Experimental Procedure

Synthesis of $[(bpy)_2Ru(bpy\text{-}RAFT_2)](ClO_4)_2$.

The synthesis of $[(bpy)_2Ru(bpy\text{-}RAFT_2)](ClO_4)_2$ was done at CSIRO laboratory Australia, as reported by Chen *et al.*[5] The following reagents were used: $[(bpy)_2Ru\{bpy\ (CH_2OH)_2\}\ ](ClO_4)_2$ (0.41 g, 0.5 mmol), 4-cyano-4(thiobenzoyl) sulfanyl-pentanoic acid (RAFT acid, 0.31 g, 1.1 mmol), dicyclohexylcarbo diimide, DCC (0.24 g, 1.2 mmol), 4-(N,N-dimethylamino) pyridine, DMAP (10 mg) and dichloromethane-acetonitrile (10 mL:10 mL). Yield was 0.34 g, 50%.

Preparation of Sensor Membrane.

Two types of sensor membranes were prepared, one was from dye and KE200/CX200 silicone solution, another was from dye and polydimethyl siloxane (PDMS) silicone solution. A 2.4 mg of $[(bpy)(Ru(bpy\text{-}RAFT_2)](ClO_4)_2$ dye was slowly dissolved in 1.5 mL ethanol (EtOH) giving concentration of 1.6 mg/L. The KE200/CX200 silicone solution was prepared by mixing silicone elastomer base KE200 with a curing agent CX200 (Shin-Etzu, Japan) by a weight ratio of 10:1.While, the polydimethyl siloxane (PDMS) silicone solution was prepared by mixing silicone base and a curing agents (Sylgard, Dow chemical) with a weight ratio of 1:1. Polyester sheets substrate were pre-cleaned by sonicating in a mixture of 1:1 ethanol-deionized water for 20 mins and dried at room temperature. The sensor membranes were prepared by mixing a 200µL ethanol pre-dissolved dye with 0.3 g of each previously prepared silicone solution. The dye-silicone mixture was stirred until homogeneous solution was obtained, the resulting solution was then casted onto polyester substrate of 1×1 cm, yielding yellowish sensor membrane which was cured at room temperature for 12 hrs before used. Later, in Figs 2, 5, 6 and 8, the membrane prepared from Ru- complex dye and KE / CX will be refered to as "Bis-Ru/KE-CX" while those from the dye and PDMS will be refered to as "Bis-Ru/PDMS".

Membrane Characterization.

Absorbance of the sensor membrane was measured by UV-vis spectrophotometer (Shimadzu, UV1601) using reflective reflectance mode. Thermogravimetric analyser (TGA7-PERKIN-ELMER) was used to study the thermal property of the sensor membrane.

Luminescence Measurements.

The luminescence intensity measurements were performed by using LS 55 Perkin Elmer luminescence spectrometer. Excitation and emission wavelengths were 460 and 615 nm, respectively. All measurements were carried out while a sensor membrane was placed in a 4.5 cm^3 cuvette. Oxygen (99.7%) and nitrogen (99.99%) were supplied by Praix air Thailand, they were used to prepared water samples of different oxygen concentrations (0, 20, 40, 60, 80 and 100% oxygen). Two mass flow controllers (KOFLOC) were used to control the oxygen and nitrogen flow rates before mixing in a chamber containing deionized water. For stability measurement, the membrane was exposed to a visible light source of 460 nm for 180 mins, in dissolved oxygen-saturated water, the luminescence intensities of the irradiated membrane were measured every 10 mins.

Results and Discussion

Figure 1. shows the dicationic-RAFT agent structure which exhibits high energy transfer, Ru(II) polypyridine chromophore functions as an energy transfer trapping core.[5] RAFT is a reversible addition-fragmentation chain transfer process, used in organic synthesis.

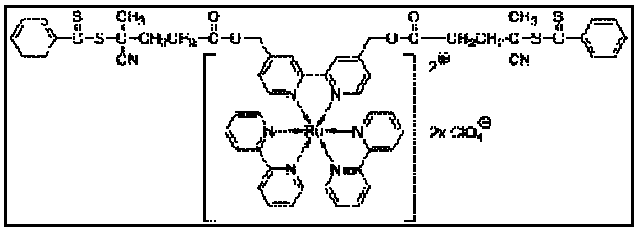

Figure 1. The structure of $[(bpy)_2Ru(bpy\text{-}RAFT_2)\ ](ClO_4)_2$ Bis(2,2'-bipyridyl)-[4,4'-(bis(4-cyano-4 (phenylcarbonothioylthio) pentanoyl) methyl) -2,2'-bipyridyl]ruthenium(II)di(perchlorate).

The synthesis of this Ru(II) containing RAFT agent involves reactions in the presence of certain thiocarbonylthio compound (RAFT acid). This luminophore is used for the first time here, as an oxygen sensor dye and successfully immobilized in silicone matrix, resulting yellowish membrane. Both KE/CX and PDMS silicone can be cross-linked into networks which allow the dye molecules to be immobilized within the network. After polymerization and cross-linking, solid KE/CX and PDMS membranes presented an external hydrophobic surfaces.[6] , making difficult for water to pass

through. However, oxygen gas can permeate the membrane and interact with dye molecules.

Thermogravimetric analysis shown in Figure 2. indicates that PDMS has higher stability than KE/CX, with onset temperature of 454.18°C and lower % weight loss (68.17%wt loss) compared with those of KE/CX silicone membrane (396.88°C and 90.615 %wt loss, respectively).

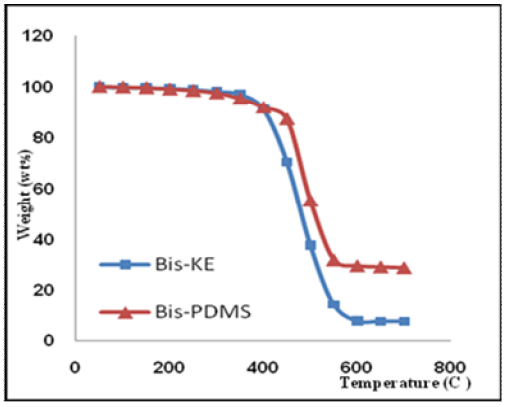

Figure 2. Thermograms of $[(bpy)_2Ru(bpy\text{-}RAFT_2)]$ $(ClO_4)_2$ embedded in silicone using heating rate of 10°C /min (50 to 700°C).

Figure 3. shows the absorption bands of Ru(II) polypyridine at 300 and 460 nm. The absorption band at 300 nm is due to a combination of the π-π* transitions of bipyridine ligands and dithiobenzoyl group. The one at 460 nm can be assigned to the MLCT of the Ru(II) complex.[5]

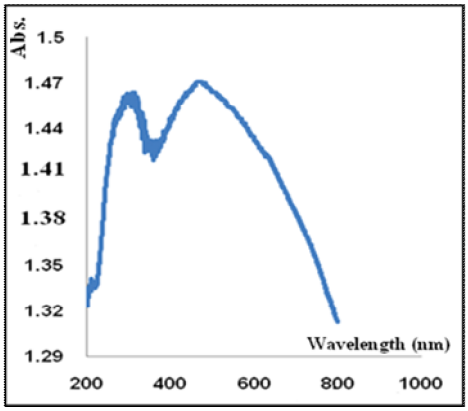

Figure 3. Absorption spectrum of $[(bpy)_2Ru(bpy\text{-}RAFT_2)]$ $(ClO_4)_2$ sensor

When the sensor membrane was excited at 460 nm, the luminescence spectrum of $[(bpy)_2 Ru(bpy\text{-}RAFT_2)](ClO_4)_2$ appeared at 610 nm, as shown in Figure 4. Both silicone matrices have the same absorption and emission wavelengths. The luminescence intensity decreased when the sensors were measured in dissolved oxygen water and also varied with different oxygen concentrations.

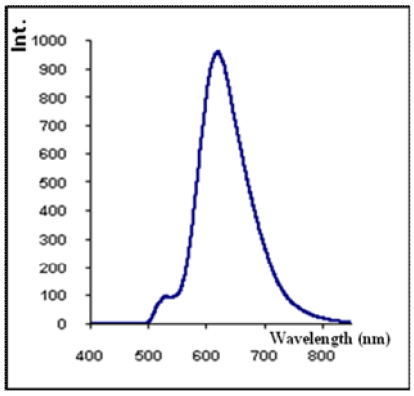

Figure 4. Luminescence spectrum of $[(bpy)_2Ru(bpy\text{-}RAFT_2)](ClO_4)_2$ sensor.

The Stern-Volmer plots of both membranes are shown in Figure 5. and a calibration curve is shown in Figure 6.

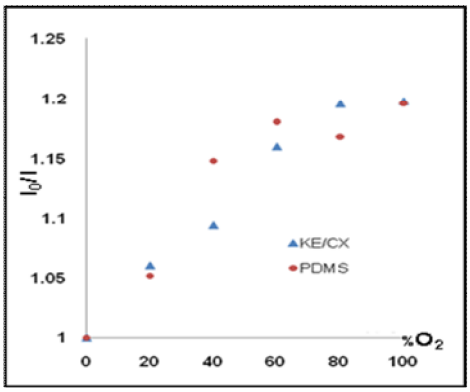

Figure 5. Stern-Volmer plots of the Bis-Ru/KE-CX and Bis-Ru/PDMS sensors.

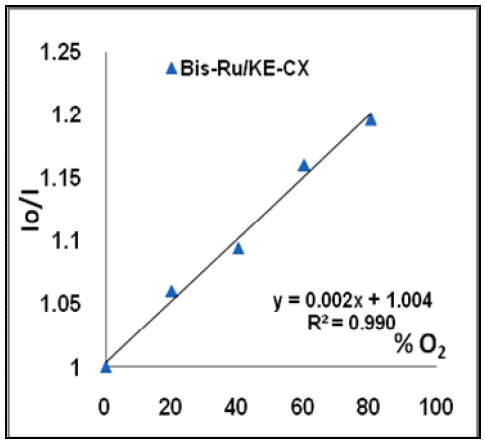

Figure 6. Calibration curve of a Bis-Ru/KE-CX sensor (in 0-80% O_2).

It can be said that, different matrices yield different oxygen diffusion rates and hence have a direct influence on the quenching efficiency of oxygen to the luminophore. Although the intensity ratio and slope of the two silicone membranes are of small values, as shown by the Stern-Volmer plots in Figure 5, the KE/CX membrane has better profile, giving linear range from 0 to 80 % DO (0 to 20 ppm) as shown in Fig. 6, which is good enough for the measurement of dissolved oxygen quantitatively. The rather low quenching by oxygen is possibly partly due to the thickness of the membrane. Since, oxygen diffusion rate depends on the ambient temperature, luminescence intensity of the Ru(II) polypyridine luminophore at different water temperatures was also studied, as shown in Figure 7.

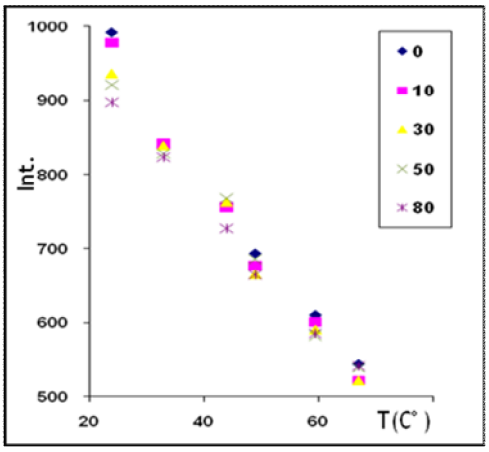

Figure 7. The variation of the fluorescence intensity as a function of water temperature (in 0-80% O_2).

In Figure7. at different oxygen concentrations of 0, 10, 30, 50 and 80%, the luminescence intensity decreases as the temperature increases from 25 to 35, 45, 60 and 65°C reflecting the effect of temperature on the Ru(II) polypyridine luminescence. The results may be explained by the dynamic quenching mechanism of oxygen molecules on the investigated luminophore.[7]

When Ru(II) polypyridine luminophore embedded in KE/CX membrane was exposed to light source of 460 nm for 180 mins, the intensity tended to be stable as shown in Figure 8. This indicated that photoleaching of the luminophore did not occur within 3 hours of continuous irradiation.

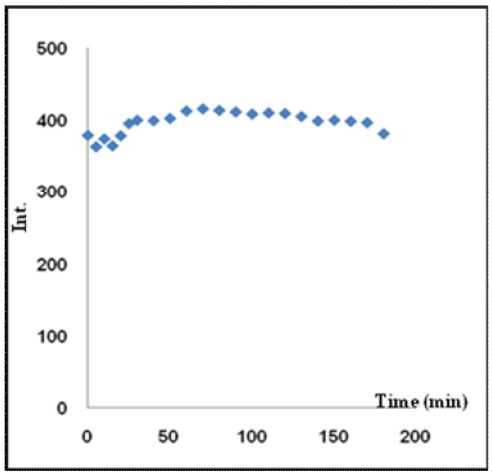

Figure 8. Stability of the sensor encapsulated in KE-CX subjected to 460 nm light source.

Conclusions

New luminophore $[(bpy)_2Ru\ (bpy\text{-}RAFT_2)](ClO_4)_2$, encapsulated in KE/CX silicone is a promising sensor membrane to be used as optical dissolved oxygen sensor. It gave linear Stern-Volmer plot up to about 80 % oxygen (20 ppm DO). Higher water temperature which affects the fluorescence of the dye by decreasing intensity can be explained by dynamic quenching mechanism of oxygen molecules. Further study is needed to improve sensitivity of the sensor.

Acknowledgments

Project funding from the National Electronics and Computer Technology Center (NECTEC) of Thailand is greatly acknowledged. The authors thank Center for Advanced Studies in Tropical Natural Resources, National Research University-Kasetsart University (CASTNAR, NRU-KU) and the Department of Chemistry, Faculty of Science, Kasetsart University for facilities support.

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