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Chemosensor of Gold(I) 4-(3,5-Dimethoxybenzyl)-3,5-dimethyl Pyrazolate Complex for Quantification of Ethanol in Aqueous Solution

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Abstract: By using gold(I) 4-(3,5-dimethoxybenzyl)-3,5-dimethyl pyrazolate complex as a chemosensor, we report a successful quantification of ethanol in aqueous solution based on vapor-induced phosphorescent quenching. Upon monitoring at 278 nm irradiation, the emission intensity at 609 nm of the complex was quenched by the presence of ethanol vapors from the mixture. It was found that the intensity is linearly decreased with increment of ethanol concentration where limit of detection was found to be 11.7% v/v in ethanol/water. When the chemosensor was applied to quantify ethanol content of 4 real samples, the accuracy was achieved up to 96%, which is remarkable.

Keywords: chemosensor, ethanol, Gold(I) complex, quantification

1. Introduction

Ethanol is commonly present in disinfectant, beverage, refrigerant, and it becomes an important reagent in the production of biodiesel¹⁻¹⁴. Declaration of ethanol content in the product's label is really required for the regulation and health risk purposes. Therefore, ethanol content monitoring and adsorption due to environmental issues are necessary for the quality control of the products. Ethanol quantification has been done using spectrofluorometer, Fourier transform infrared (FT-IR) spectroscopy, near-infrared (NIR) spectroscopy, and gas chromatography measurements⁵⁻⁷. Those methods have required large-space and high-technology apparatus which could not be directly used in portable applications. Methods in ethanol content determination have been shifted from desktop instrument to be more portable yet accurate. As an example, Marinho *et al.* reported that ethanol quantification of beverage samples has been evaluated using mobile phone device⁸. In this case, the acid-base reaction of beverage samples with phenolphthalein in their mixture is required for the evaluation of color intensity changes. This reagent is generally reported as a harmful chemical for human health. However, we have not found other reports for the

quantification of ethanol using less harmful of luminescent compounds. Indeed, this chemical sensor (chemosensor) is an indirect interaction of luminescent compounds with vapors of the samples. However, there is no report on the quantification of ethanol using luminescent changes upon interaction with vapor.

Phosphorescence is one of the interesting luminescent properties due to its longer lifetime and bright emission. These phosphorescent properties have been observed in metal azolate complexes such as pyrazolate from its weak metal-metal interaction¹⁵⁻²⁷. Many applications have been reported using metal pyrazolate complexes due to their characteristics in luminescent changes upon interactions with external stimuli. Considering pyrazolate has an electronegative side, it can form interaction and binding with -OH of ethanol vapor upon diffusion to the emission site to give phosphorescent changes. Hence, in this work, we report a novel reagent less procedure to quantify the ethanol content using a metal complex with phosphorescent properties named as gold(I) 4-(3,5-dimethoxybenzyl)-3,5-dimethyl pyrazolate [**1**]. The chemical structure of compound [**1**] was shown in Figure 1. The photoluminescent properties of [**1**] against ethanol vapor exposure as a vapochromic chemosensor have been

studied where its emission changes at 609 nm was used for the detection of ethanol concentration. The limit of detection (LoD) for this approach was found as low as 11.7%. This proposed method was also applied for the quantification of ethanol in the real disinfectant and beverage products with accuracy up to 96%.

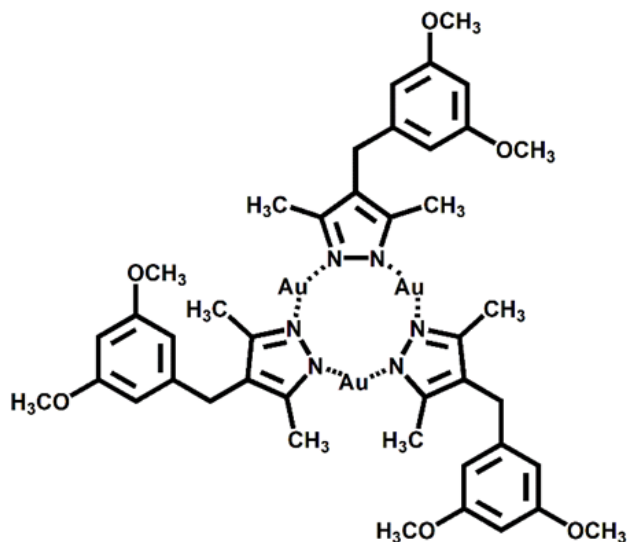


Fig. 1: Molecular structure of gold(I) 4-(3,5-dimethoxybenzyl)-3,5-dimethyl pyrazolate complex [1]

2. Materials and Method

2.1 Materials and Instrumentation

Material [1] as a chemosensor was used as a chemical sensor material. According to the previous method for the synthesis of this complex material [1]¹⁵⁻²³, we have firstly prepared pyrazole ligand from 3,5-dimethoxy benzyl bromide in three stepwise reactions under an inert condition. The successful synthesis of the ligand based on characterization using FT-IR spectroscopy and mass spectrometry as reported on our previous report²¹) was used for the synthesis of complex [1]. By using the same characterization for the synthesis of pyrazole ligand, the isolation of complex [1] in the powder form was clearly confirmed as shown in our report^{22,23}). Ethanol was purchased from Merck in EMSURE® quality. Spectrofluorometric study was done by using JASCO FP-8500 spectrofluorometer. For real samples, Onemed Alcohol 95%, Onemed Alcohol 70%, Johnny Walker® Black Label®, and Beefeater Gin were used to evaluate the sensing capability.

2.2 Analytical Procedures

Various concentrations of ethanol-distilled water mixtures were used as the standard solution with composition of 0%, 25%, 50%, 75%, and 100% v/v. As much as 5 mg of sensor material [1] was put into a spectrofluorometer sample holder, which was placed inside a crucible. Ethanol-water mixture (150 μ L) was added into the vessel and parafilm was used to cover the

crucible. After 5-minutes exposure to the ethanol vapors, photoluminescent emission spectral changes of the sensor were measured under an irradiation on 278 nm light source. Four ethanol containing commercial products were employed to evaluate the sensor capability. As much as 150 μ L of the sample was fumed to the sensor material at the optimum exposure time and then the emission spectral changes of the sensor material were recorded with the same procedure. The LoD was calculated according to the following equation:

$$LoD = \frac{3 \times \text{standard error of intercept}}{\text{slope}} \quad (1)$$

3. Result and Discussion

Material [1] gave emission intensity with a peak centered at 609 nm under 278 nm light irradiation for excitation wavelength, as shown in Figure 2. Photoluminescent emission of [1] has been previously studied and was classified as phosphorescent compound²³). Excitation at 278 nm could be considered as a transition from ¹LMMCT (ligand to metal-metal charge transfer) ground state to its excited state (¹LMMCT*). The sensor molecule underwent a non-radiative transition from ¹LMMCT* to a spin-forbidden ³MM state. Phosphorescent of this material was resulted from the electronic transition of its triplet state of the metallophilic bonding (³MM) between Au(I)-Au(I) to the singlet ground state of the charge transfer from ligand to metal-metal bonding (¹LMMCT)^{16,18-20,24-27}). Therefore, the emission of the used material was found at 609 nm that is similar to previously reported for the complex with phosphorescent property.

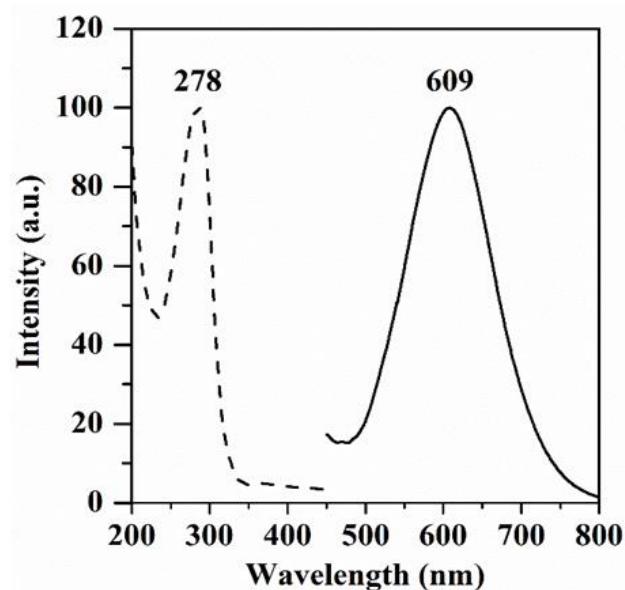


Fig. 2: Excitation (dashed line) and emission (solid line) spectra of material [1]

The correlation graph between the volume fraction of ethanol concentration and the relative changes in its

emission intensity (I_0/I) at various exposure times (up to 5 minutes) is shown in Figure 3. The higher volume fraction in the mixture solution gave a higher amount of the ethanol vapor exposure to the sensor materials [1]. The quenching of its emission intensity at 609 nm was significantly reduced when the concentration of ethanol was increased up to 50%. It was then constantly reduced with increment of ethanol vapors with concentration of 75% and 100%. The final quenching of its emission intensity with 100% ethanol was achieved up to around 60%.

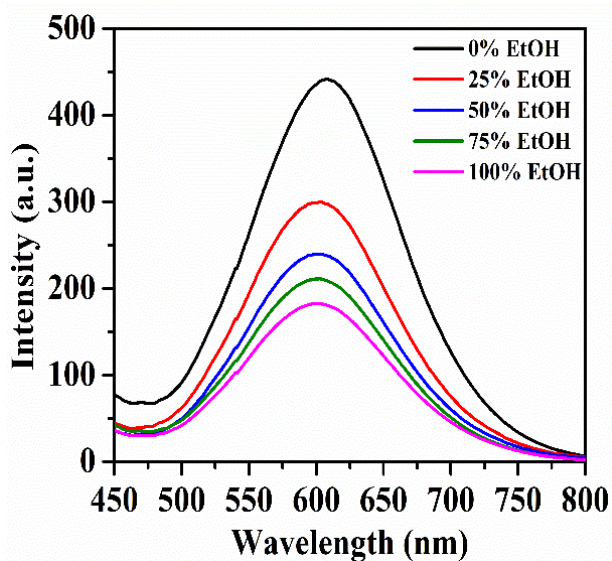


Fig. 3: Emission spectral changes of material [1] with variation of ethanol concentration

By using the emission spectral changes as shown in Figure 3, it is possible to evaluate the relationship between emission changes and the increment of ethanol concentration. This quenching phenomenon was figured from the undistinguishable plot between various concentrations in 5 minutes of the exposure. Figure 4 shows the relationship that is proportional to the volume fraction of ethanol on the sample.

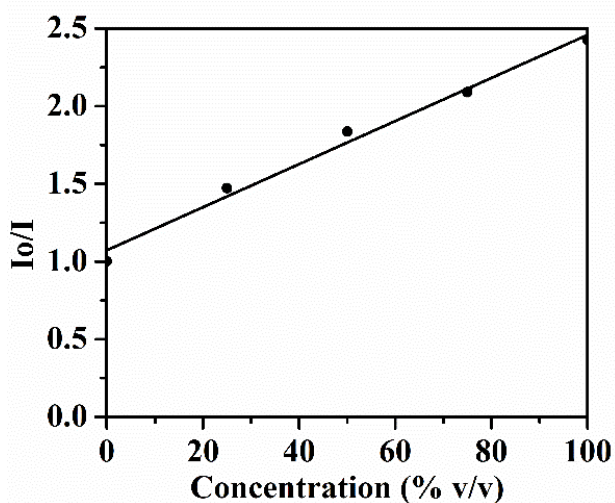


Fig. 4: Relative intensity I_0/I of material [1]

Furthermore, the sensor material [1] was tested to real disinfectant and beverage products for evaluating the validity of ethanol quantification as proposed in this work. Two representatives of each disinfectant and beverage samples were Onemed Alkohol 95%, Onemed Alkohol 70%, Johny Walker® Black Label®, and Beefeater Gin, respectively. By the label, the ethanol contents of those products shall be found with concentration of 95%, 70%, 40%, dan 47%. Using this vapochromic sensor, it was found that the detected ethanol contents for Onemed Alkohol 95%, Onemed Alkohol 70%, Johny Walker® Black Label®, and Beefeater Gin were 93%, 69%, 44%, and 47%, respectively. From these results, the accuracy was achieved up to 96%. Such sensing performance of material [1] is remarkable as shown in Table 1.

Table 1. Ethanol content of four tested products

Tested Product	Ethanol Content	
	(% measured)	(% by label)
Onemed Alkohol 95%	93	95
Onemed Alkohol 70%	69	70
Johny Walker® Black Label®	44	40
Beefeater Gin	47	47

Linear fitting of the plotted graphic in Figure 4 shows that the R-squared value is 0.988. The intercept and slope values of the plot are 1.07 ± 0.05 and $(1.39 \pm 0.09) \times 10^{-2}$, respectively. Moreover, by using equation (1), the sensing capability of [1] was found to have sensitivity with LoD as low as 11.7%. These findings are useful for the chemosensor field as well as the analytical field due to a simple and valid process which rarely reported before. Furthermore, a prototype for a handheld device could be built to perform portable ethanol quantification so that it can be used in the field.

In this work, the prepared material [1] has been used as a vapochromic chemosensor for the ethanol quantification. Because of that, the sensor material [1] was placed on the crucible while the ethanol-water mixture was added near the sensor materials without any direct physical contact. As it is known that the vapor pressure of ethanol is higher than that of water, hence ethanol is easier to evaporate and reach the surface of the sensor material. In this case, ethanol vapor will interact with the methoxy moieties of 4-(3,5-dimethoxybenzyl)-3,5-dimethyl pyrazolate ligand through a weak interaction using hydrogen bonding²³. On that hydrogen bonding, the hydroxyl group of ethanol acts as a proton donor while the methoxy substituent becomes

the proton acceptor. This interaction caused interruption of a weak Au(I)-Au(I) metallophilic bonding. As the Au(I)-Au(I) bonds became less frequent, the material lost its light-emitting capability, indicating from the quenching of its photoluminescent spectrum²⁸⁾. The schematic image for the representation of the plausible interaction between ethanol vapors and sensor materials [1] was displayed in Figure 5.

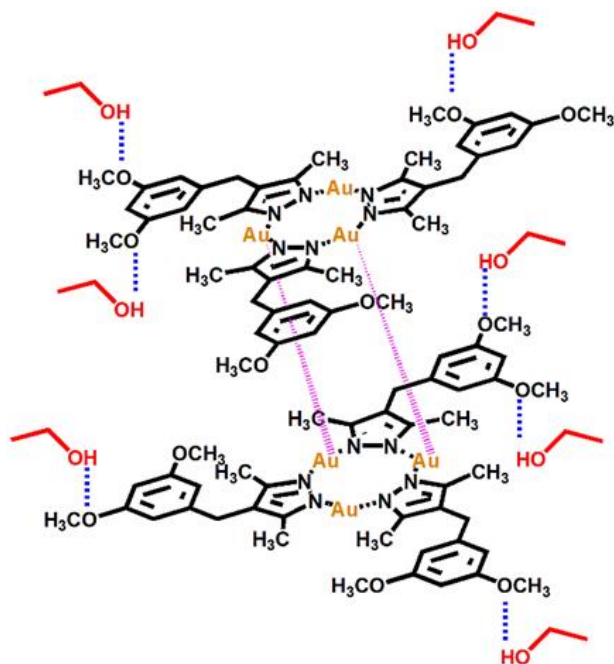


Fig. 5: Dimer of trimer of gold(I) 4-(3,5-dimethoxybenzyl)-3,5-dimethyl pyrazolate complex with purple and blue dash line indicating metallophilic and hydrogen bonding, respectively.

4. Conclusion

Analytical importance of material [1] complex for the quantifying ethanol has been studied by using vapochromic detection. Based on the photoluminescent properties of this sensor material at 609 nm with an excitation at 278 nm, a novel method has been achieved for the ethanol quantification. In this case, exposure of ethanol vapors to the sensor material [1] was observed to cause quenching in its photoluminescent spectrum. The optimum exposure time was 5 minutes to give the highest emission changes up to 60%. Furthermore, the volume fraction of ethanol in aqueous solution was linearly quenched by the emission of the sensor material with LoD of 11.7%. Indeed, this phenomenon is promising to be used analytically for the quantification of ethanol content in the real sample with accuracy of 96%. The reliability of this method was satisfied enough through a test on four ethanol containing disinfectant and beverage products with high accuracy.

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