

Supramolecular assembly of group 11 phosphorescent metal complexes for chemosensors of alcohol derivatives

H O Lintang^{1*,2,3}, N F Ghazalli^{4,5} and L Yuliaty^{1,2,3}

¹Ma Chung Research Center for Photosynthetic Pigments, Universitas Ma Chung, Malang 65151, East Java, Indonesia

²Department of Chemistry, Faculty of Science and Technology, Universitas Ma Chung, Malang 65151, East Java, Indonesia

³Centre for Sustainable Nanomaterials, Ibnu Sina Institute for Scientific and Industrial Research, Universiti Teknologi Malaysia, 81310 UTM, Johor Bahru, Johor, Malaysia

⁴Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM, Johor Bahru, Johor, Malaysia

⁵School of Fundamental Science, Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia

E-mail: hendrik.lintang@machung.ac.id

Abstract. We report on systematic study on vapochromic sensing of ethanol by using phosphorescent trinuclear metal pyrazolate complexes with supramolecular assembly of weak intermolecular metal-metal interactions using 4-(3,5-dimethoxybenzyl)-3,5-dimethyl pyrazole ligand (**1**) and group 11 metal ions (Cu(I), Ag(I), Au(I)). Upon excitation at 284, the resulting complexes showed emission bands with a peak centered at 616, 473 and 612 nm for **2**(Cu), **2**(Ag) and **2**(Au), respectively. Chemosensor **2**(Cu) showed positive response to ethanol vapors in 5 mins by blue-shifting its emission band from 616 to 555 nm and emitting bright orange to green. Otherwise, **2**(Au) gave shifting from its emission band centered at 612 to 587 nm with $\Delta\lambda$ of 25 nm (41%) and color changes from red-orange to light green-orange while **2**(Ag) showed quenching in its original emission intensity at 473 nm in 40% with color changes from dark green to less emissive. These results demonstrate that sensing capability of chemosensor **2**(Cu) with suitable molecular design of ligand and metal ion in the complex is due to the formation of a weak intermolecular hydrogen bonding interaction of O atom at the methoxy of the benzyl ring with the OH of the vapors at the outside of the molecules.

1. Introduction

Over the last few years, many research groups have been focused on the development of vapochromic sensor materials with high sensing capability to detect the presence of volatile organic compounds (VOCs), which are considered to be important issues due to their significant contribution to pollution [1-3]. In particular, phosphorescent d^6 , d^8 and d^{10} metal compounds with extended π or coordination donor systems have been widely developed as vapochromic chemosensors with several advantages from their photophysical properties such as sensitivity of emission, Stokes shifts, excitation of single photon and longer lifetime [4-6]. Considering luminescent changes such as shifting, quenching, positive response and photoinduced energy transfer, phosphorescent metal complexes have shown great attention as vapochromic chemosensors with high tunability and rigidity of supramolecular metal-solvent, metal-



metal, π - π , hydrogen bonding and host-guest interactions [4, 7-9]. For example, Nagel and co-workers in 1988 [10] synthesized palladium (Pd) and platinum (Pt) double-complex or mixed salt for the detection of vapors. This type of complex was fabricated into fiber optics for the detection of VOCs by Lancaster 1995 [11]. In 1998, Maan and co-workers had also successfully synthesized Pt-Pt double-complex salt for vapochromic sensors of organic vapors with color, absorption and emission changes [12].

Group 11 complexes from d^{10} metal ions and various types of ligands have been investigated as phosphorescent chemosensors such as monometallic gold and bimetallic gold-silver complexes [13]. Although copper complexes can be synthesized using less expensive precursors and showed a strong luminescent intensity and longer lifetime compared other group 11 metal complexes [14,15], they have received less attention as chemosensors so far. Previously, we have reported that phosphorescent trinuclear copper(I) pyrazolate complexes from 3,5-dimethyl and 4-(3,5-dimethoxybenzyl)-3,5-dimethyl pyrazole ligands were successfully synthesized and then used for chemosensors of ethanol vapors [16]. Interestingly, compared to other non-side chain, 3,5-dimethyl, 3,5-bis(trifluoromethyl) and 3,5-diphenyl pyrazole ligands, the resulting trinuclear copper(I) 4-(3,5-dimethoxybenzyl)-3,5-dimethyl pyrazolate complex (**2(Cu)**) only showed a positive response to ethanol by shifting the emission band from 604 to 554 nm where the original intensity can be recovered without external stimuli at room temperature [17]. Considering the different metal ions from group 11 have produced metal complexes with different metal-metal distance as a sensing site [18], we report the sensing capability of trinuclear group 11 metal trinuclear pyrazolate complexes from the same ligands for detection of ethanol vapors. Indeed, we found that sensing capability of **2(Cu)** was the best chemosensors for detection of ethanol vapors compared to another group 11 metal complexes. This finding suggests that there is no significant effect of metal-metal distance on accessibility of vapors to sensing site where the vapors are more likely to interact with O atom at the methoxy of the benzyl ring with at the outside of the molecules through a weak intermolecular hydrogen interaction.

2. Experimental

2.1 Instrumentations

Fourier Transform Infrared Spectroscopy (FT-IR) was used on Thermo Scientific model a Nicolet iS50 using potassium bromide (KBr). Mass spectra were recorded by electrospray ionization (ESI) source for ionization using JEOL model a JMS-T100LP (AccuTOF LC-plus) with dichloromethane (DCM) and addition of methanol (MeOH) or acetone for direct injection in 10 μ L/min at needle voltage of 2000 V. Absorption spectra were measured using Shimadzu Diffuse Reflectance (DR) Ultraviolet-Visible (UV-Vis) spectrophotometer (UV-2600). Luminescent properties were monitored on a JASCO model of FP-8500 spectrofluorophotometer. The photography images were taken using Panasonic Lumix digital camera (DMC-FZ38) under a UV lamp (Vilber Lourmat, 8 watts) in daylight or in the dark room. Photon Technology International (PTI) with a model of QuantaMaster 400 containing of near infrared (NIR) PMT detector model 914 under liquid N_2 cooling system and a Xenon lamp (75 W) was used as steady state photoluminescent spectrophotometer for the determination of emission and excitation maxima in the lifetime measurement.

2.2 Synthesis of Group 11 Trinuclear Metal Pyrazolate Complexes

Trinuclear copper(I) pyrazolate complex **2(Cu)** was prepared according to our previous reports [14-17]. As shown in Figure 1, at room temperature, the mixture of 4-(3,5-dimethoxybenzyl)-3,5-dimethyl pyrazole ligand (**1**) and tetrakis (acetonitrile) copper (I) hexafluorophosphate ($[Cu(MeCN)_4]PF_6$) in dry tetrahydrofuran (THF) was reacted for 5 mins using a Schlenk technique and followed by adding the distilled dry Et_3N under an inert condition. After overnight reaction, THF was removed from the reaction mixture under reduced pressure, and the remaining residues were dried-off to isolate the desired complexes. In-situ recrystallization was carried out using dry DCM and MeOH at room temperature to give solid powder of **2(Cu)** after dried under reducing of vacuum pressure in 85% yields. The same

procedure was repeated for synthesis other metal complexes using silver(I)hexafluorophosphate (AgPF_6 ; 1.02 g, 4.06 mmol) and chloro(dimethyl sulfide) gold(I) ($[\text{Au}(\text{SMe}_2)]\text{Cl}$; 1.19 g, 4.06 mmol) to give **2(Ag)** and **2(Au)** as white powder in 75% and 95% yields [19-25].

2.3 Evaluation of Sensing Capability

Chemosensors complexes **2(Cu, Ag, Au)** in 22 mg were used for evaluation of sensing capability by directly expose of ethanol vapors (200 μL) from 0 to 5 mins. The study was carried out by arranging cell holder for spectrofluorophotometer containing chemosensors into the sealed beaker for desired exposure time and followed by evaluation of sensing capability using spectrofluorophotometer and photographs.

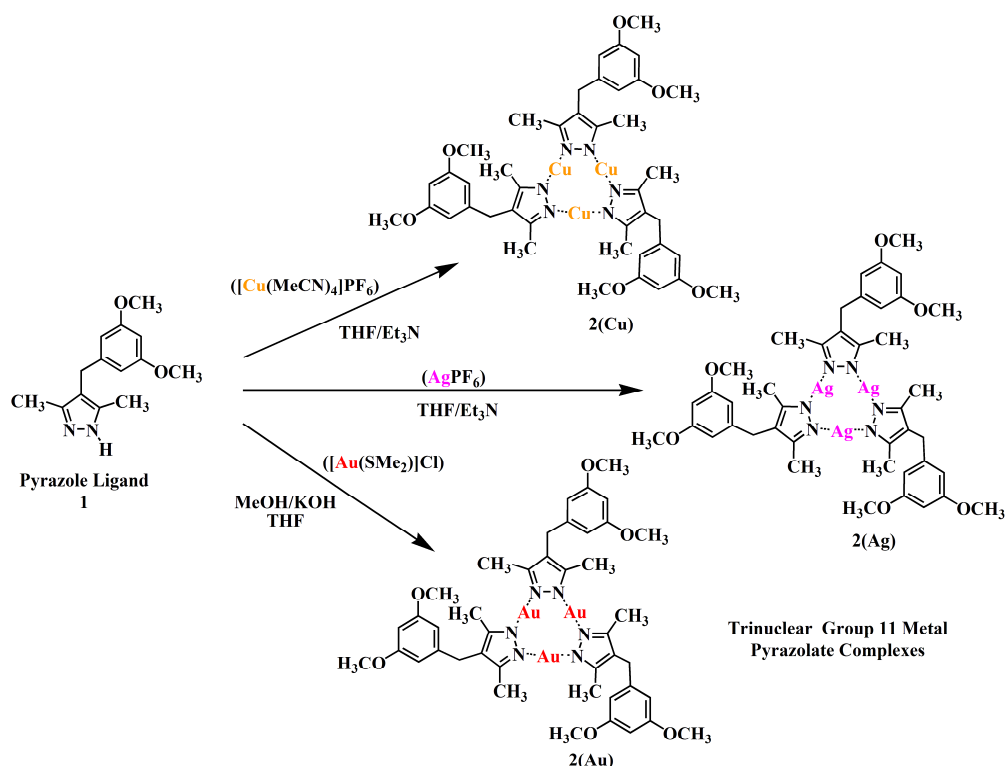


Figure 1. Schematic and molecular structures of trinuclear pyrazolate complexes **2(Cu, Ag, Au)** from pyrazole ligand **1** with different metal ions.

3. Results and Discussion

3.1 Structure elucidation of Group 11 Trinuclear Metal Pyrazolate Complexes

To confirm the synthesis of complexes **2(Cu, Ag, Au)**, FT-IR and mass spectroscopy measurements were carried out to observe characteristic vibration bands of functional groups and molecular weight compared to ligands **1**. Figure 2(i) shows FT-IR spectra of ligand **1** with characteristic vibration bands at 3201-3058 and 1750-1595 cm^{-1} for N-H stretching and bending from 1° or 2° amine groups. These vibration bands of **1** did not observe in that of **2(Cu, Ag, Au)** (Figure 2(ii-iv)) due to the formation of N-Cu-N with vibration bands at 560-832 cm^{-1} . As the results, **2(Cu, Ag, Au)** still preserved C-H, C-N and N-N stretchings of **1** with vibration bands at 2835, 1371-1289 and 1289-1151 cm^{-1} for **2(Cu)**, 2834, 1339-1291 and 1205-1156 cm^{-1} for **2(Ag)** and 2991, 1376-1289 and 1207-1155 cm^{-1} for **2(Au)**. The mass spectra showed that the observed molecular weights were 927.60, 1057.12 and 1326.29 Da for $[\text{M}+\text{H}]^+$ with molecular formula of $\text{C}_{42}\text{H}_{51}\text{M}_3\text{N}_6\text{O}_6$ (M is group 11 metal ions). Moreover, monoisotopic

patterns and observed molecular weights for all complexes were almost similar to the predicted ones. Hence, all complexes were successfully synthesized.

3.2 Optical Properties of Group 11 Trinuclear Metal Pyrazolate Complexes

The luminescent properties of d^{10} complexes have been found to show phosphorescent properties with unique molecular geometries. The absorption spectra were measured to find the maximum energy for excitation of electrons from ground to excited state in the emission measurement. By using the peak top of the absorption spectra at 270, 273 and 280 nm for **2(Cu, Ag, Au)**, respectively as excitation wavelength (λ_{ext}), emission spectra were observed with a peak centered at 616, 473 and 612 nm for **2(Cu, Ag, Au)** as shown in Figure 2. Monitoring at maxima emission wavelength (λ_{em}), it provided the excitation spectra for maximum absorption of light with a peak centered at 274, 280 and 280 nm for **2(Cu, Ag, Au)**, which were closed to the peak top of absorption of luminophores. These results were in good agreement with their colors as green, orange and red under exposure to a UV hand lamp at 254 nm in the dark room (Figure 3d), respectively. The calculated Stokes shift ($\Delta\lambda$) was 338, 193 and 332 nm with phosphorescent lifetime (τ) of 8.16 ± 1.8 , 7.84 ± 0.7 and 8.91 ± 0.7 μs and at room temperature, indicating the characteristics of phosphorescent compounds from metal-metal interaction [14-18].

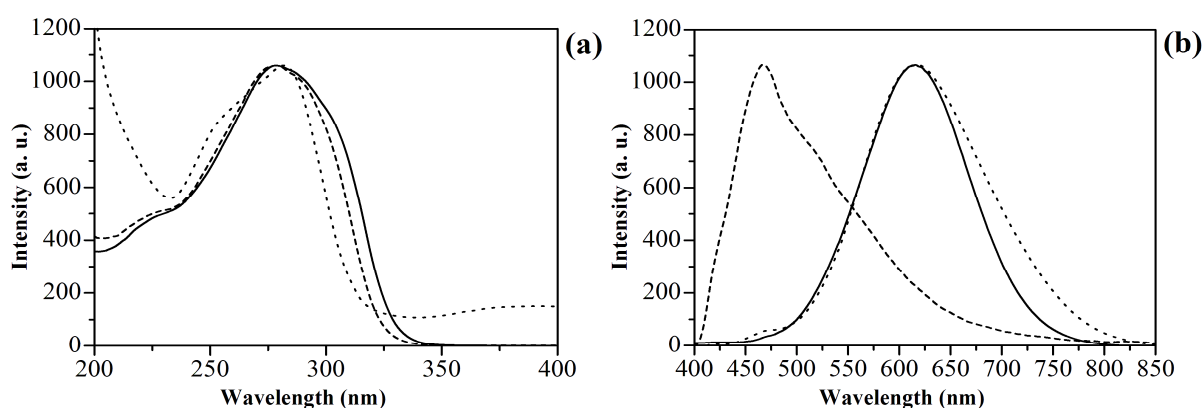


Figure 2. (a) Normalized excitation and (b) emission spectra of **2(Cu)** (solid line), **2(Ag)** (dash line) and **2(Au)** (dot line).

3.3 Evaluation of Sensing Capability

Sensing capability of group 11 pyrazolate complexes was studied using ethanol vapors in the closed system for vapochromic chemosensors of alcohol derivatives. As reported in our paper [17], upon exposure to ethanol vapors in 5 mins until no significant shifting in emission wavelength and color, chemosensor **2(Cu)** was found to show shifting phenomenon of the emission band centered at 616 to 554 nm with $\Delta\lambda$ of 62 nm with excitation at 270 nm (Figure 3a) which was in good agreement with its changes in color from bright orange to green (Figure 3e). Interestingly, when chemosensor **2(Ag)** was utilized for the same VOC, the emission band centered at 473 nm was significantly quenched in 40% upon excitation at 273 nm (Figure 3b) of its original intensity. This phenomenon was well supported with its color changes from dark green to less emissive (Figure 3f). On the other hand, an emission band centered at 612 nm for chemosensor **2(Au)** was shifted to 587 nm upon excitation at 280 (Figure 3c) with $\Delta\lambda$ of 25 nm. The color of chemosensor **2(Au)** was changed from red-orange to light green-orange (Figure 3g). Hence, chemosensor **2(Cu)** provides the best sensing capability for detection of ethanol vapors compared to others. The proposed mechanism for the shifting phenomenon was discussed in the previous report [17], in which the vapors is more likely to use a weak intermolecular hydrogen bonding for interaction with electronegative O atom at the methoxy of the benzyl ring at the outside of the molecules. This shifting phenomenon was also observed for **2(Au)** with small $\Delta\lambda$ due to a little bit shorter metal-metal distance compared to **2(Cu)**. On the other hand, **2(Ag)** with longer metal-metal distance

tends to provide accessibility of vapors to its sensing site for quenching of emission intensity until certain level. Such sensing capability of chemosensor **2(Ag)** might possible to occur from the competition of vapors to Ag(I)–Ag(I) interaction and π – π interactions.

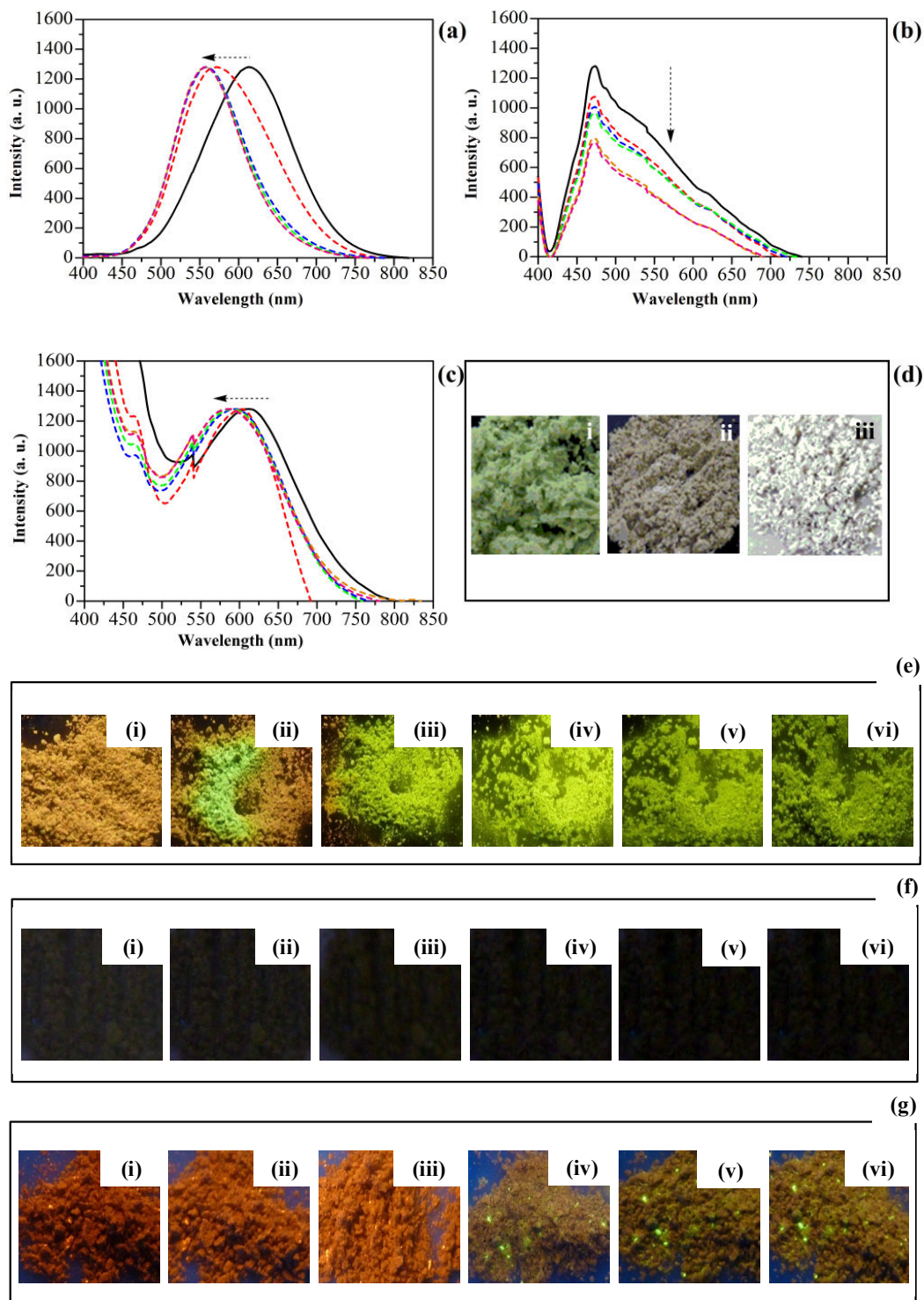


Figure 3. Emission spectral changes of (a) chemosensors **2(Cu)**, (b) **2(Ag)** and (c) **2(Au)** upon exposure to ethanol from 0 (black solid line) to 5 mins (red, blue, green, orange and pink dash line, respectively) and (d) their photography images of chemosensors **2(Cu)** (i), **2(Ag)** (ii) and **2(Au)** (iii) before exposure to ethanol. The photography images of (e) chemosensors **2(Cu)**, (f) **2(Ag)** and (g) **2(Au)** upon exposure

to ethanol for (i) 0, (ii) 1, (iii) 2, (iv) 3, (v) 4 and (vi) 5 mins. The photographs were taken at room temperature on exposure to a UV hand lamp at 254 nm in the dark room.

4. Conclusion

In conclusion, we have successfully synthesized trinuclear metal pyrazolate complexes **2**(Cu, Ag, Au) from 4-(3,5-dimethoxybenzyl)-3,5-dimethyl pyrazole ligand **1** in 85%, 75%, and 95% yields. All complexes showed characteristic phosphorescent properties with emission bands centered at 616, 473 and 612 nm, large Stokes shifts and luminescent lifetime decay in the range of microseconds, which were in good agreement with their colors from green, orange and red, respectively. Upon exposure to ethanol vapors, chemosensors **2**(Cu) showed the best sensing capability with shifting of its emission center compared to others due to the formation of a weak intermolecular hydrogen bonding interaction with vapors at the O atom of the methoxy at the benzyl ring. By using molecular design of ligand and metal ion in the synthesis of complexes, the phosphorescent chemosensors with high sensing capability can be prepared for the detection of VOCs in next future.

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