Molecular Self-Assembly of Group 11 Pyrazolate Complexes as Phosphorescent Chemosensors for Detection of Benzene

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Abstract. We highlight the systematic study on vapochromic sensing of aromatic vapors such as benzene using phosphorescent trinuclear pyrazolate complexes (2) with supramolecular assembly of a weak intermolecular metal-metal interaction consisting of 4-(3,5-dimethoxybenzyl)-3,5-dimethyl pyrazole ligand (1) and group 11 metal ions (Cu(I), Ag(I), Au(I)). The resulting chemosensor 2(Cu) revealed positive response to benzene vapors in 5 mins by blue-shifting its emission band in 44 nm (from 616 to 572 nm) and emitted bright orange to green, where this change cannot be recovered even with external stimuli. Comparing to 2(Ag) with longer metal-metal distance (473 nm) with same sensing time and quenching in 37%, 2(Au) gave quenching in 81% from its original intensity at 612 nm with reusability in 82% without external stimuli and emitted less emissive of red-orange from its original color. The shifting phenomenon in 2(Cu) suggests diffusion of benzene vapors to inside molecules for formation of intermolecular interaction with Cu(I)-Cu(I) interaction while quenching phenomenon in 2(Au) suggests diffusion of benzene vapors to between the Au(I)-Au(I) interaction. These results indicate that suitable molecular structure of ligand and metal ion in pyrazolate complex is important for designing chemosensor in the detection of benzene vapors.

1. Introduction
Vapor sensor materials have been developed using phosphorescent metal complexes with characteristics of luminescent properties. These materials have received more attention as one of chemical sensors (chemosensors) that display selective, reversible and naked-eye luminescent changes upon exposure to specific volatile organic compounds (VOCs). Moreover, it has been proved to be one of the most effective, cheap and convenient methods and materials in the 21\textsuperscript{st} century for the detection of harmful vapors [1-2]. In particular, phosphorescent d\textsuperscript{6}, d\textsuperscript{8} and d\textsuperscript{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 [3-5]. Considering luminescent changes such as shifting, quenching, positive response and photoinduced energy transfer, phosphorescent metal complexes from those metal ions have showed great attention as vapochromic chemosensors with high
tunability and rigidity of supramolecular metal-solvent, metal-metal, π–π, hydrogen bonding and host-guest interactions [3, 6–8].

Development of chemosensors with high sensitivity and selectivity has received much attention for sensing benzene vapors and its homologues [9] such as benzene, ethylbenzene, trimethylbenzene, toluene and xylenes. These vapors in our environment such as workplaces and home [10–11] can cause many diseases from their high volatility and harmful properties to human inhalation or dermal absorption such as leukemia, myeloma and lymphoma [1]. However, they are less attention to develop chemosensors based on their optical properties with high sensitivity and selectively. On the other hands, many researchers have focused on the use of expensive and complicated instrumentations for development of sensing methods using gas chromatography [12], fiber optic [13–14], diode laser IR spectroscopy [15], electronic nose sensor array [16] and metal oxide semiconductor films [17].

Recently, many reports have showed the study of chemosensors for the detection of benzene vapors using metal complexes such as Ru(II) [18], Zn(II) [19], Au(I) [20], Ag(I) [21], Pt(II) [22] and Cu(I) [23]. Since the sensing sites have been reported based on the formation of crystal voids without any effective interaction with the chromophore as functional groups, low sensing capabilities were found so far. Hence, rational design of chromophores of chemosensor molecules is really important to provide stronger interactions between sensing sites and vapors (analytes). For example, Che et al. have used diimine platinum(II) bis(s-acetylide) complexes [25] to trigger luminescent color and emission changes upon interaction with VOCs due to hydrogen bonding and Pt–Pt interactions, leading to different crystals packing [26–27]. Considering the phosphorescent properties of pyrazolate complexes from the weak metal-metal interactions as supramolecular columnar assembly in nanostructures [28–30] and nanocomposites [31–35], we have reported the utilization of trinuclear copper(1) pyrazolate complexes for chemosensors of ethanol [36–37] using different kinds of pyrazole ligands bearing short alkyl side-chains. We found that chemosensors from 4-(3,5-dimethoxybenzyl)-3,5-dimethyl pyrazole ligand provided the best sensing capability. On the other hand, Kishimura have reported that this chemosensor gave positive response upon exposure to benzene vapors with irreversible changes [38]. Since group 11 metal ions have been synthesized as pyrazolate complexes with different metal-metal distances [30], it is interesting challenge to synthesize different pyrazolate complexes (2) from group 11 metal ions and 4-(3,5-dimethoxybenzyl)-3,5-dimethyl pyrazole ligand (1) as chemosensors for the detection of benzene vapors. Indeed, we observed that chemosensor 2(Au) was the best sensing material for the detection of benzene vapors by quenching of its emission intensity up to 81% (reversible changes) compared to chemosensor 2(Cu) with shifting phenomenon after prolong the exposure time. These results suggest that benzene vapors will probably diffuse to inside molecules to cut-off the metal-metal interaction for light-emitting capability and to benzyl ring for the formation of π–π interaction.

2. Experimental

2.1 Instrumentations

Fourier Transform Infrared Spectroscopy (FT–IR) spectra was measured using Thermo Scientific on a model of Nicolet iS50 using potassium bromide (KBr) for preparation of a pellet with sample. Mass spectra were recorded using JEOL on a model of JMS–T100LP (AccuTOF LC–plus). Sample in dichloromethane (DCM) and methanol (MeOH) or acetone for direct injection (10 µL/min, 2000 V) was ionized using electrospray ionization (ESI) method. 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 on a Panasonic Lumix of DMC–FZ38 digital camera under exposure to a UV lamp with a model of Vilber Lourmat (8 watt) at 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 N₂ 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 [28,29]. 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)]PF$_6$) in dry tetrahydrofuran (THF) was reacted for 5 mins using a Schlenk technique and followed by adding the distilled dry triethyl amine (Et$_3$N) under an inert condition. After overnight reaction, THF was removed from the reaction mixture under reduce pressure and the remaining residues were dried-off to isolate the desired complexes. In–situ recrystallization was carried out using dy DCM and MeOH at room temperature to give solid powder of 2(Cu) after dried under reduce 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(dimethylsulfide) gold(I) ([Au(SMe$_2$)]Cl; 1.19 g, 4.06 mmol) to give 2(Ag) and 2(Au) as white powder in 75% and 95% yields.

2.3 Evaluation of Sensing Capability

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

![Figure 1](image_url)

**Figure 1.** Schematic and molecular structures of trinuclear pyrazolate complexes 2(M) from pyrazole ligand 1 with their metal ions (M salts; [Cu(MeCN)]$_4$PF$_6$ salt for Cu(I), AgPF$_6$ salt for Ag(I) and [Au(SMe$_2$)]Cl salt for Au(I)).

3. Results and Discussion

3.1 Structure Elucidation of Group 11 Trinuclear Metal Pyrazolate Complexes

In order 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 the functional groups and molecular weight compared to the ligand 1. Figure 2(i) shows FT-IR spectrum 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 2834, 1339-1291 and 1205-1156 cm⁻¹ for 2(Ag) and 2991, 1376-1289 and 1207-1155 cm⁻¹ for 2(Au), respectively. The mass spectra showed that the observed molecular weights were 927.60, 1057.12 and 1326.29 Da for [M+H]+ with molecular formula of C₄₂H₅₁M₃N₆O₆ (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.

![Figure 2. FT-IR spectra of (i) pyrazole ligands 1 and (ii) trinuclear pyrazolate complexes 2(Cu), (iii) 2(Ag) and (iv) 2(Au).](image)

3.2 Optical Properties of Group 11 Trinuclear Metal Pyrazolate Complexes

The luminescent properties of d¹⁰ complexes have been found to show phosphorescent properties with unique molecular geometry. 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 for 2(Cu, Ag, Au), respectively as excitation wavelength (λext) as shown in Figure 3a, emission spectra were monitored to give a peak centered at 616, 473 and 612 nm for 2(Cu, Ag, Au) as shown in Figure 3b. Monitoring at maxima emission wavelength (λem) it provided the excitation spectra for the maximum absorption of light with a peak centered at 274 (2(Cu)), 280 (2(Ag)), and 280 nm (2(Au)), which were closed to the peak top of absorption of the luminophores (Figure 3a). By exposure to a UV lamp (λext = 254 nm) in the dark room, the complexes 2(Cu, Ag, Au) as greenish, gray and white powders at daylight (Figure 3c(i-iii)) emitted green, orange and red color emissions (Figure 3c(iv-vi)). These photograph images and emission spectra were in good agreement with visualized color emissions. Moreover, the calculated Stokes shifts (Δλ) from the difference between wavelength of emission and excitation maxima was 338, 193 and 332 nm with lifetime (τ) of 8.16±1.8, 7.84±0.7 and 8.91±0.7 μs at room temperature, indicating the characteristics of phosphorescent compounds from the weak Cu(I)-(Cu(I) interaction [28-38].
Figure 3. (a) Normalized excitation and emission spectra of 2(Cu) (solid line), 2(Ag) (dash line) and 2(Au) (dot line) as well as (b) their photography images of chemosensors 2(Cu) (i), 2(Ag) (ii) and 2(Au) (iii) at daylight and 2(Cu) (iv), 2(Ag) (v) and 2(Au) (vi) in the dark room upon exposure to a UV lamp (λ_{ext} = 254 nm).

3.3 Evaluation of Sensing Capability

Sensing capability of chemosensor group 11 pyrazolate complexes was evaluated using spectrofluorophotometer and photography images for the vapochromic chemosensors of benzene vapor in the closed system. Upon exposure to benzene vapors from 0 to 5 mins, chemosensor 2(Cu) showed blue-shifting of its emission band centered at 616 nm to 572 nm (Figure 4a) with a Stokes shift (Δλ) in 44 nm (Figure 4b). This phenomenon was in good agreement with their color changes from orange to orange-green (Figure 5a). This shifting was less than the sensing of ethanol with the same chemosensor due to the number of stacking for benzene vapors to benzyl of the pyrazole ring (3 arms) is lesser than that of hydrogen bonding interaction of ethanol to the methoxy of the benzyl (6 methoxy groups) [37]. Moreover, the same phenomenon was also observed for the reusability testing as reported by Kishimura [38]. Interestingly, when chemosensor 2(Ag) was utilized for the same VOC, the emission band centered at 473 nm was quenched (Figure 4c) in 37% (Figure 4d) with color changes from dark green to almost less emissive with increasing sensing time to 5 mins as shown in Figure 5b(i-vi). The metal-metal distance of Ag(I)-Ag(I) is longer that Cu(I)-Cu(I) interaction so that certain number of benzene vapors will only allow to be diffused into the metal-metal.
Figure 4. Emission spectral changes of (a) chemosensors 2(Cu), (c) 2(Ag) and (e) 2(Au) upon exposure to benzene vapors from 0 (black solid line) to 5 mins (red, blue, green, orange and pink dash line, respectively) and their sensing capabilities for (b) chemosensors 2(Cu), (d) 2(Ag) and (f) 2(Au).

Figure 4e shows quenching phenomenon in an emission intensity of chemosensor 2(Au) upon exposure to benzene vapors within 5 mins. In sharp contrast to chemosensors 2(Cu) and 2(Ag), this chemosensor showed about 81% quenching from its original peak top (Figure 4f). Moreover, this positive response emitted less emissive of red-orange from its original color as shown in Figure 5c(i-vi) to support the emission spectral changes. Such quenching using this chemosensor has not yet been
reported so far. The shorter Au(I)-Au(I) interaction with more broader near-infrared emission peak compared to chemosensor 2(Cu) will tend to highly encourage benzene vapors to be diffused and stacked to between two complex molecules so that the metal-metal interaction will be cut-off. Such diffusion will also possible to stack benzene molecule with benzyl ring of the pyrazole ring with appearance of small emission peak at 460 nm from aggregation induce emission. Considering the reusability up to 82% without using external stimuli in 10 mins as shown in Figure 5(d), chemosensor 2(Au) provided the best sensing capability for the detection of benzene vapors compared to the others.

Figure 5. The photography images of (a) chemosensors 2(Cu), (b) 2(Ag) and (c) 2(Au) upon exposure to benzene vapors for (i) 0, (ii) 1, (iii) 2, (iv) 3, (v) 4 and (vi) 5 mins and (d) emission spectral and color changes from (i) 1 to (vi) 5 mins and (i’) after standing for reusability testing in 10 mins. The photographs were taken at room temperature on exposure to a UV lamp with wavelength excitation of 254 nm in the dark room.

4. Conclusion
In conclusion, we have successfully synthesized trinuclear group 11 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 characteristics of phosphorescent properties with emission bands centered at 616, 473 and 612 nm, large Stokes shifts and luminescent lifetime decays in the range of microseconds, which were in good agreement with their colors emissions from green, orange and red, respectively. Upon exposure to benzene vapors, chemosensors $2(Au)$ showed the best sensing capability with quenching in intensity of its emission center up to 81% and the reusability in 82% without external stimuli compared to chemosensors $2(Ag)$ and $2(Cu)$. These results demonstrated that benzene vapors will be able to be diffused and then inserted between the Au(I)-Au(I) interaction to cut-off the interaction for light-emitting capability. 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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