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Cation Sensing Capabilities of A Nitrophenyl Cinnamaldehyde Derivative

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ABSTRACT. The cationic chemosensor based on organic compound bearing an aminophenol moiety as a receptor for metal analyte and a cinnamaldehyde moiety as chromophoric fragment has been developed. In this work, we report the colorimetric sensing of nitrophenyl cinnamaldehyde derivative, namely methyl-3-(2-hidroxy-5-nitrophenyl amino)-3-phenylpropanoate, towards a variety of metal cations, such as Cu^{2+}, Fe^{3+}, Ni^{2+} and Zn^{2+}. The cation sensing abilities of the sensor were observed for $Cu^{2+}$and Fe^{3+} with a color change from colorless to pink and faint yellow, respectively, The characteristic UV-Vis spectra changes were observed upon addition of $Cu^{2+}$and Fe^{3+} cations. The hypsochromic absorption spectra shifts were obtained, indicating the cations and sensor complexations had formed. A metal-to-ligand-charge-transfer (MLCT) had occurred and the charge density of the sensor changed resulting in appearance of new absorption peaks in the UV-Vis spectra and color changes of the sensor solution upon addition of the $Cu^{2+}$and Fe^{3+}.

Keywords: cation sensor; chemosensor, chromophoric fragment; cinnamaldehyde derivative

INTRODUCTION

Cations play many important roles in biological and chemical processes in human life. However, excessive cation concentration level has a negative impact on environment and human health. The amount of cation on the environment need to be control to minimize their negative impacts (Ali, Khan, & Ilahi 2019; Tchounwou et al., 2012; Jaishankar et al., 2014). Various analytical methods have been used for cation detections such as titrimetry, potentiometry, flame atomic emission spectrometry, atomic absorption spectroscopy and ion selective electrodes. However, these methods are expensive and in-efficient because they require a lot of samples and special treatment during preparation (Bansod et al., 2017; Dalmieda & Kruse, 2019; Hyalij, Bhagure & Chavan, 2017; Kumar et al., 2017; March, Nguyen, & Piro, 2015; Topcu et al., 2018). A low-cost and efficient ion monitoring and measuring can be carried out using colorimetric cation chemosensors (Aderinto & Imhanria, 2018; Chen et al., 2020; Kaur & Kumar, 2011; Normaya et al., 2019; Pham et al., 2019; Upadhyay et al., 2019; Wang, Fang & Cao, 2015).

A cation chemosensor requires receptor unit and/or ligand which is able to donate electron pairs for forming coordination covalent bond with cations (Aderinto & Imhanria, 2018; Chen et al., 2020; Kaur & Kumar, 2011; Normaya et al., 2019; Pham et al., 2019; Upadhyay et al., 2019; Wang, Fang, & Cao, 2015). A chemosensor also has need to have an electron withdrawal group as a chromogenic signaling unit. Interactions between sensor and ion produce color changes that can be detected visually. The color change affects the shift of the absorbance peak in the UV-Vis region (Suryanti et al., 2014; Suryanti et al., 2017).

The cation chemosensors synthesized from natural compounds as a starting materials are still limited. Cinnamaldehyde is a potential starting material for synthesizing of cation chemosensors. Compound 4-chloro-2-[(3-(4-(dimethylamino) phenyl)allyl-dene)amino]phenol, a cinnamaldehyde derivative, has been recognized as a colorimetric Ni^{2+} sensor in aqueous solution (Peralta-Domínguez et al., 2015). Another cynnamaldehyde derivative, 3-methyl-(2-hydroxy-5-nitrophenylamino)-3-phenylpropanoate (1)

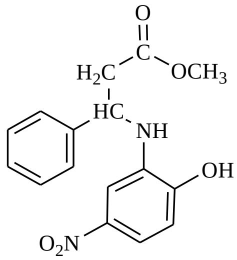

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Figure 1. Structure of 3-methyl-(2-hydroxy-5-nitrophenylamino)-3-phenylpropanoate (**1**).

(**Figure 1**), was synthesized from cinnamaldehyde through 4 step reactions (Suryanti, Wibowo, Pranoto, Isnaeni, Sari & Handayani, 2016).

Compound **1** has been recognized as a chemosensor for oxyanions, such as $H_2PO_4^-$ and AcO^-. In compound **1**, the hydrogens of NH and OH groups form hydrogen bonds with anions, whereas the nitrophenyl group acts as chromogenic signaling unit (Suryanti, Wibowo, & Handayani, 2020). Besides, compound **1** possesses lone pair electrons on N and O atoms of the NH and OH groups, respectively, which have possibility in forming coordinate covalent bonds with cations. Therefore, compound **1** was expected to act as a chromogenic cation sensor. In this work, we report the colorimetric sensing of compound **1** towards a variety of cations, such as Fe^{3+}, Cu^2, Ni^{2+} and Zn^{2+}.

EXPERIMENTAL SECTION

Materials

All cations in the form of nitrate salts were purchased from Merck (Darmstadt, Germany) and used without further purification. All solvents employed were of analytical grade and also used without further purification.

Synthesis of Compound 1

Compound **1** was synthesized from cinnamaldehyde following a previously reported procedures (Suryanti et al., 2016). The steps included oxidation reaction of cinnamaldehyde, which was followed by esterification of the acid. The final step was the reaction between the ester and 2-amino-4-nitrophenol to yield the final products, namely methyl-3-(2-hidroxy-5-nitrophenyl amino)-3-phenylpropanoate (compound **1**).

Cation Binding Studies

Solution **1** (1×10^{-5} M) was dissolved in acetone. Stock solutions of metal cation with concentration of 1×10^{-3} M were prepared by dissolving $Fe(NO_3)_3.9H_2O$, $Cu(NO_3)_2.4H_2O$, $Ni(NO_3)_2.6H_2O$ or $Zn(NO_3)_2$ in distilled water at pH 7. Sensing properties were evaluated by mixing a few microliter of the metal cations stock solution to a known volume of the compound **1** solution (2 ml). The total volume of the addition metal cations solution was limited to 0.1 ml, so that the dilution of the compound **1** solution remained insignificant. The colorimetric performance was evaluated by naked eye and quantified by UV-Vis absorption spectroscopy. Absorption spectra were examined in the wavelength interval 280-650 nm. The UV-Vis Shimadzu Lambda 25 spectrophometer was used at room temperature for obtaining the UV-Vis spectra.

RESULTS AND DISCUSSION

Visual Observation of Compound 1 in the Presence of Cations

The colorimetric properties of compound **1** were examined by the addition of various cations such as Fe^{3+}, Cu^{2+}, Ni^{2+} and Zn^{2+} in acetone. The addition of 4 eq Fe^{3+} into compound **1** (1×10^{-5} M) gave a color change from colorless to yellowish while the presence of 4 eq Cu^{2+} caused a color change from colorless to pink. However, the addition of 4 eq Ni^{2+} and Zn^{2+} did not result in a color change of the solution **1**. The color changes of solution **1** after addition of cations were shown in **Figure 2**. The color changes of solution 1 was further investigated by stepwise addition of Fe^{3+} and Cu^{2+}. The naked-eye color changes of solution **1** was detectable upon addition of 1.5 eq Fe^{3+} or 1.5 eq Cu^{2+}. The coloration of the solution was intensified with increasing anions concentration (**Figure 3**).

UV-Vis Spectroscopy Analysis of Compound 1 in the Presence of Cations

Interactions between Fe^{3+}, Cu^{2+}, Ni^{2+} or Zn^{2+} with compound **1** were investigated through UV-Vis spectrophotometer. Preliminary studies were carried out by addition of 4 eq of cation to solution **1** in acetone. A cation which interacts with compound **1** causes shifting of the absorbance peaks. Spectra changes of compound **1** on the presence of cations is presented in **Figure 4**. The addition of Fe^{3+} or Cu^{2+} produced significant changes of the spectra, including shifting and increasing of absorbance. However, the addition of Zn^{2+} or Ni^{2+} only increase the absorbance intensity.

UV-Vis spectroscopy analysis was further carried out by the stepwise addition of Fe^{3+} or Cu^{2+} (0-4 eq) into solution **1** (1×10^{-5} M). UV-Vis spectra show that increasing amount of Fe^{3+} causes peak shifting at 379 to 361 nm and decreasing shoulder at 410-540 nm, gradually (**Figure 5**). This new absorption peak appeared upon addition of 1.5 eq. of Fe^{3+} and the further addition of Fe^{3+} ion did not change the absorbance spectra. These spectral characteristics were also accompanied by a visual color change of the solution from colorless to faint yellow upon addition of Fe^{3+}.

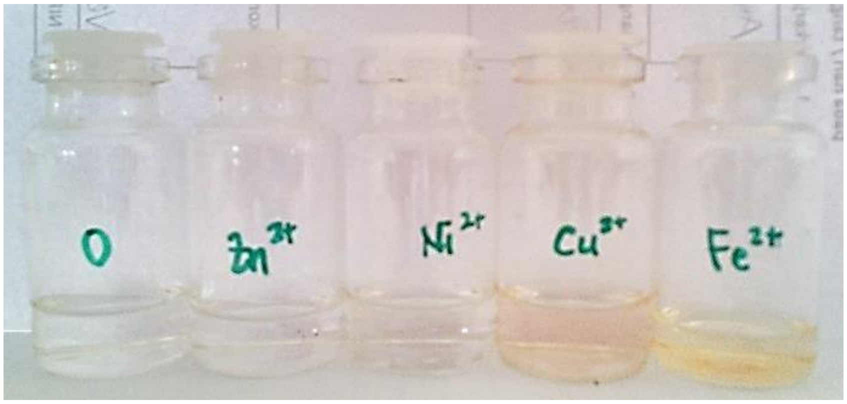


Figure 2. The color changes of compound **1** in acetone was observed upon addition of 4 eq. of various cations, such as Zn^{2+}, Ni^{2+}, Cu^{2+} and Fe^{3+}.

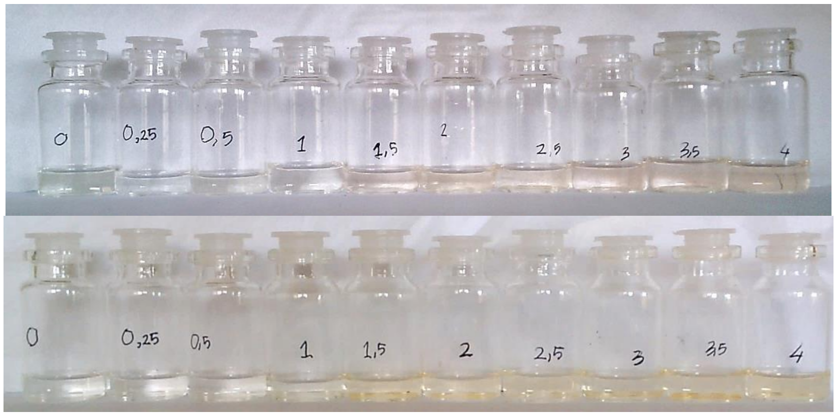


Figure 3. The color changes of compound **1** in acetone was observed upon addition of the cations as nitrate salts: Cu^{2+} (upper) and Fe^{3+} (lower).

The phenomenon occurring in these experiments were similar to some compounds which act as cation sensors for Fe^{3+}. Compound 1,1′-((1E, 1′E)-((thiobis(ethane-2,1-diyl))bis(azanylylidene))bis(methanylylidene))bis(naphthalen-2-ol) gives absorbance at 400 nm, while its interaction with Fe^{3+} forms a peak at 600 nm and changes color from colorless to pale purple (Lee, Yang, & Kim, 2018). Naphthalene diimide amphiphile (NDI-A) based compounds give absorbance at 350 nm, 380 nm and 430 nm, while its interaction with Fe^{3+} formed spectra with a significant decrease in intensity at the wavelength section of 430 nm and changing the color from yellow to colorless (Ghule, Bhosale, Puyad, & Bhosale, 2016). The cation Fe^{3+} in this case removes the color from the receptor. Boron-dipyrromethene (BODIPY) based compounds with phenols as binding sites forms absorbance at 534 nm and 571 nm, while interactions with Fe^{3+} formed a wavelength at 502 nm, changing color from pink to yellow (Wang, Fang, & Cao, 2015).

The addition of Cu^{2+} results in peak shifting from 379 to 366 nm and increasing in absorption intensity at 460-550 nm, gradually (**Figure 6**). This absorption peaks existed upon addition of **1** eq. Cu^{2+} and the further addition of Cu^{2+} did not change the absorbance spectrum. The color change from colorless to pink could also be detectable by naked eye for the solution **1** along with the addition of Cu^{2+}. Behaviors evolving for compound **1** were similar to those reported Cu^{2+}cation sensors. A diarylethene-based compound gives absorbance at 344 nm, while its interaction with Cu^{2+} formed a peak at 412 nm, changing color from colorless to yellow (Liu, Cui, Shi, & Pu, 2019). A coumarin based compound produces a peak at 335 nm, while its interaction with Cu^{2+} formed a peak at 418 nm, changing the color from yellow to colorless (Li et al., 2019). A benzimidazole-quinoline-based compound (BMQ) results peaks at 342 nm and 418 nm, while the interaction with Cu^{2+} forms spectra at 550 nm, changing color from yellow to purple (Liu et al., 2017).

Alike phenomena of UV-Vis absorption were observed upon addition of Fe^{3+} and Cu^{2+} into solution **1**. The observed hypsochromic absorption spectral shift might be due to the formation of cation and sensor complex (Takagi, 1990). The hypsochromic shifting which is the shifting of peak to shorter wavelengths, indicating that dipole charge interaction in excited state is greater than that of in ground state. When the cation interacts with a free electron pair donor group, intramolecular charge transfer occurs so that the excited state becomes increasingly unstable. This has an impact on the formation of new absorbance bands on the hypsochromic shift of the UV spectrum.

The new peaks in UV-Vis spectra might be accredited to a metal-to-ligand-charge-transfer (MLCT) which was responsible for the faint yellow and pink colors of the solution **1** upon addition of Fe^{3+} or Cu^{2+}. Metal complex formation is on enlightenment of the coordination of metal ions with the lone-pair electrons of the nitrogen and oxygen atoms which are known as centers to coordinate with different transition metal ions. After binding with Fe^{3+} or Cu^{2+}, the charge density in the whole compound **1** changed and transferred thoroughly which will generate new absorption peaks in the UV-Vis spectra and naked eye color changes (Austin, Chen, & Rodgers, 2012; Chen et al., 2015; Devaraj et al., 2012; Erdemir & Malkondu, 2015; Janakipriya et al., 2015; Sherman, 1985). Clearly, compound **1** which were bound with metal ions with different charge density (Fe^{3+} and Cu^{2+}) provided different absorption peaks in UV-Vis spectra. Hence, compound **1** was supposed to be an efficient colorimetric sensor to identify Cu^{2+} and Fe^{3+} metal ions. Therefore, compound **1** could be named as a chromoionophore, since this compound having electron donors changed its color upon complexation with analytes, in this case is Fe^{3+} or Cu^{2+}. This study is the first established principle in the development of chromoionophore based on nitrophenyl cynnamaldehide derivative.

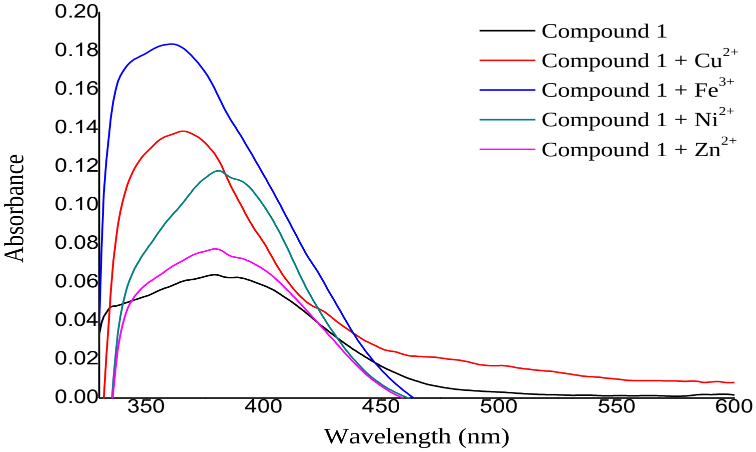


Figure 4. The absorption spectra of compound **1** (1×10^{-5} M) in acetone upon the addition 4 eq. of metal ions solutions.

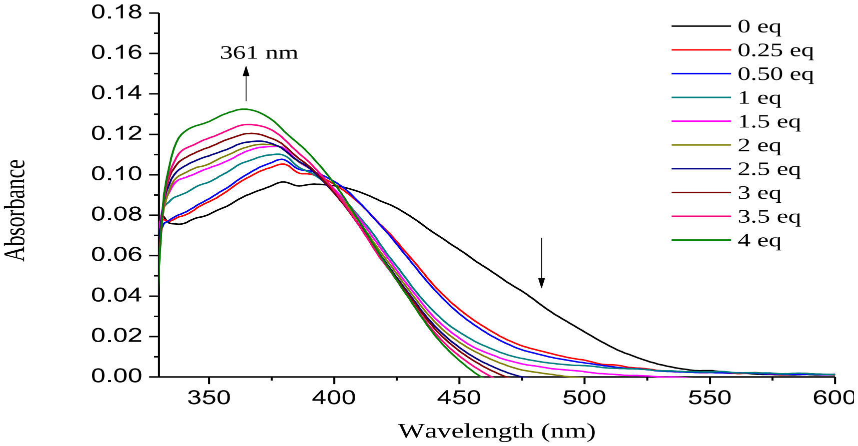


Figure 5. The absorption spectra of compound **1** (1×10^{-5} M) in acetone upon the addition 0-4 eq. of Fe^{3+}.

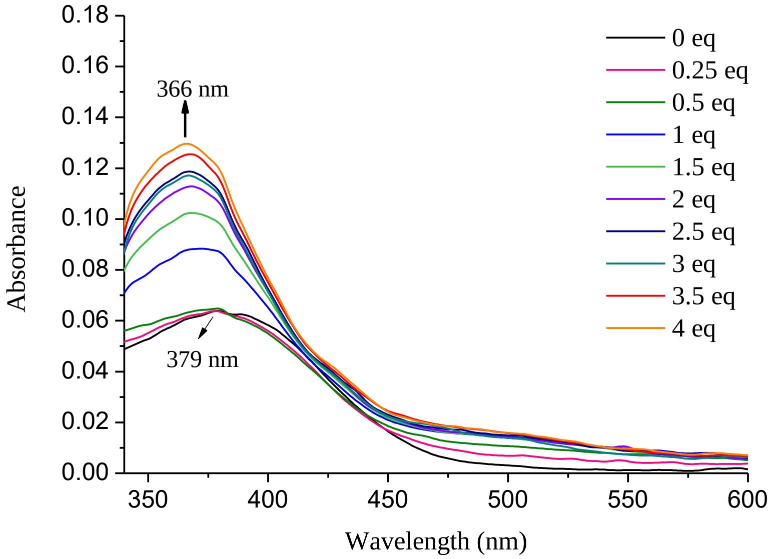
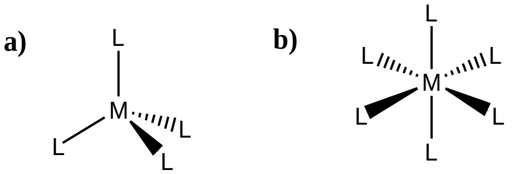


Figure 6. The absorption spectra of compound **1** (1 x 10^{-5} M) in acetone upon the addition 0-4 eq. of Cu^{2+}.

The calculation formula of limit of detection (LOD) = 3*Sd*/s and limit of quantification (LOQ) = 10*Sd*/s, where *Sd* and *s* are the liner curve slope and standard deviation, respectively, were applied (Zou et al., 2015; Saleh et al., 2019). The LOD and LOQ of compound **1** were determined to be 4.19 x 10^{-5} M and 1.39 x 10^{-4} M for Fe^{2+} and 2.66 x 10^{-5} M and 8.88 x 10^{-5} M for Cu^{2+}, respectively. The selectivity sensing of compound **1** for Fe^{3+} and Cu^{2+} was probably due to the cooperation of combined effects, such as the proper radius, the suitable coordination geometry and charge density of the tested metal ions (Geng, Wang, Zhu, Jiang & Wang, 2017). Among the tested cations, the order of diameter of cations was $Fe^{3+}<Cu^{2+}<Ni^{2+}<Zn^{2+}$ (Luo et al., 2011). As the diameter of Fe^{3+} and Cu^{2+} are shorter than that of Ni^{2+} and Zn^{2+}, they provide appropriate radius for electrostatic interactions and undergo complexation reactions with compound **1**. Interestingly, the complexation of compound **1** took place at higher concentrations of Fe^{3+} than that of Cu^{2+}. This was an unexpected result as the Fe^{3+} has shorter diameter than that of Cu^{2+} which should has considered greater electrostatic interactions to compound **1**. This result can be explained on the basis of charge density and the suitable coordination geometry.

Factors which can affect the coordination bonds between compound **1** with Fe^{3+} or Cu^{2+} are the electrostatic repulsion between ligands, the shape of the ligand and metal bonds (Sacconi, 2009). Fe^{3+} and Cu^{2+} have *d*5 and *d*9 orbitals, respectively. These *d* orbitals have empty orbitals which allow for *d-d* transitions with ligand electrons to create energy gaps. The number of electrons involved influences the coordination geometry that will be generated. The possible coordination geometry that can be formed for the complexes of compound **1** and Fe^{3+} or Cu^{2+} is tetrahedral or octahedral (**Figure 6**). In the presence of water, the coordination bonds may include water (H_2O) because it has lone pair electrons which can act as a ligand for binding with cations. The complex structure of the compound **1** and Fe^{3+} or Cu^{2+} need to be further explore using computer modelling.



L = ligand (Compound **1** or H_2O)
M = cation (Fe^{3+} or Cu^{2+})

Figure 6. The possible coordination geometry for the complexes of compound **1** and Fe^{3+} or Cu^{2+}: (**a**) tetrahedral or (**b**) octahedral.

CONCLUSIONS

We have developed a novel cation sensor 1 based on organic compound from cynnamaldehide having an aminophenol moiety as a receptor for metal analyte. Sensors 1 were selective for Cu^2 and Fe^{3+} over Ni^{2+} and Zn^{2+} ions. A metal-to-ligand-charge-transfer (MLCT) had occurred and the complexation between the cations with the sensor 1 was formed. The subsequent charge density of the sensor changed resulting in the visible color and UV-Vis spectral changes. These results suggested that an organic compound based cinnamaldehyde derivative could provide very important application in cation recognition and sensing of chemical, environmental and biological systems. Further studies using computational methods need to be done for assessing a metal-to-ligand-charge-transfer (MLCT) process and predicting the complexation structure of the cations with the sensor 1. Additionally, the development of chromoionophore based on nitrophenyl cynnamaldehide derivative need to explore further.

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