

## Research Article

### Study on the Property of Colorimetric Sensor Array Binding Volatile Organic Compounds using Density Functional Theory

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**Abstract:** Colorimetric Sensor Array (CSA) has been developed in the application of detection and evaluation of food quality. Theoretical study using Density Functional Theory (DFT) at B3LYP/LANL2DZ level was carried out to investigate the ability of CSA sensor binding Volatile Organic Compounds (VOCs) at molecular level. The binding energy representing the sensitivity of CSA sensor was analyzed. The ability of CSA sensor binding VOCs was classified into three groups by the comparison of binding energy. This study suggests that the theoretical calculation is useful for the optimization of CSA sensor in the further experiment.

**Keywords:** Colorimetric sensor array, density functional theory, food quality, ruthenium porphyrin

## INTRODUCTION

Consumer, industry and government pay more and more attention to food quality and safety in the last decade. They have committed cooperative efforts to make the overall food to be more safety and obtain more quality in China. A series of detection methods based on the detection and determination of VOCs have been used to detect and evaluate food quality and safety (Bhatt and Nagaraju, 2011; Balasubramanian and Panigrahi, 2011). The VOCs from food during the process of storage or shipping is considered to be one of the most useful information to indicate food quality and safety. In the last decade, a series of VOCs detection methods have been developed for the analyses of beverages and food. Traditional methods so-called gas or liquid chromatography is based on component-by-component analysis that will need much money and time (Daz-Maroto *et al.*, 2004; Agüero *et al.*, 2011). Electronic nose and electronic tongue has found some applications in food industry will less expensive and rapid advantages (Rajamki *et al.*, 2006; Iliev *et al.*, 2006). However, these techniques consist of electrochemical sensors or conductive polymers that rely essentially on physical adsorption and van der Waals with least and weakest selective or sensitive of forces between molecules. That means the limitations of such techniques are the lack of chemical discrimination and less sensitivity.

Recently, an optoelectronic approach named Colorimetric Sensor Array (CSA) has been applied to detect, identify and quantify the VOCs from food or

beverages (Rakow and Suslick, 2000). The interaction between VOCs and CSA sensor is always relating to stronger chemical interactions. And this technique is also proved to be anti-interference from changes of humidity and temperature in the environment (Suslick *et al.*, 2004, 2003). Therefore, this helpful method will make the process and result to be more credible. However, the sensor design of this method is based on experience and test that will limit the application and development of this method.

In this study, the process of CSA sensor binding VOCs was studied by Density Functional Theory (DFT) at B3LYP/LANL2DZ level. The further design of CSA sensor will be rapid and simple based on this theoretical study.

## COLORIMETRIC SENSOR ARRAY AND COMPUTATIONAL METHODS

**Colorimetric sensor array:** Figure 1, CSA sensor is constructed by chemoresponsive dyes that were printed on C2 reverse phase silica gel plates using microcapillary pipettes (Huang *et al.*, 2011). The nature of CSA sensor detecting and evaluating food quality is interaction of dyes on the sensor and VOCs from food at molecular level. First, the VOCs combined with metal atom in the center of dye. The ability is always represented by binding energy that is obtained by differentiating the energy from the CSA sensor before and after reacting with VOCs. Second, this molecular interaction must be strongly coupled to an intense chromophore to provide image information from the

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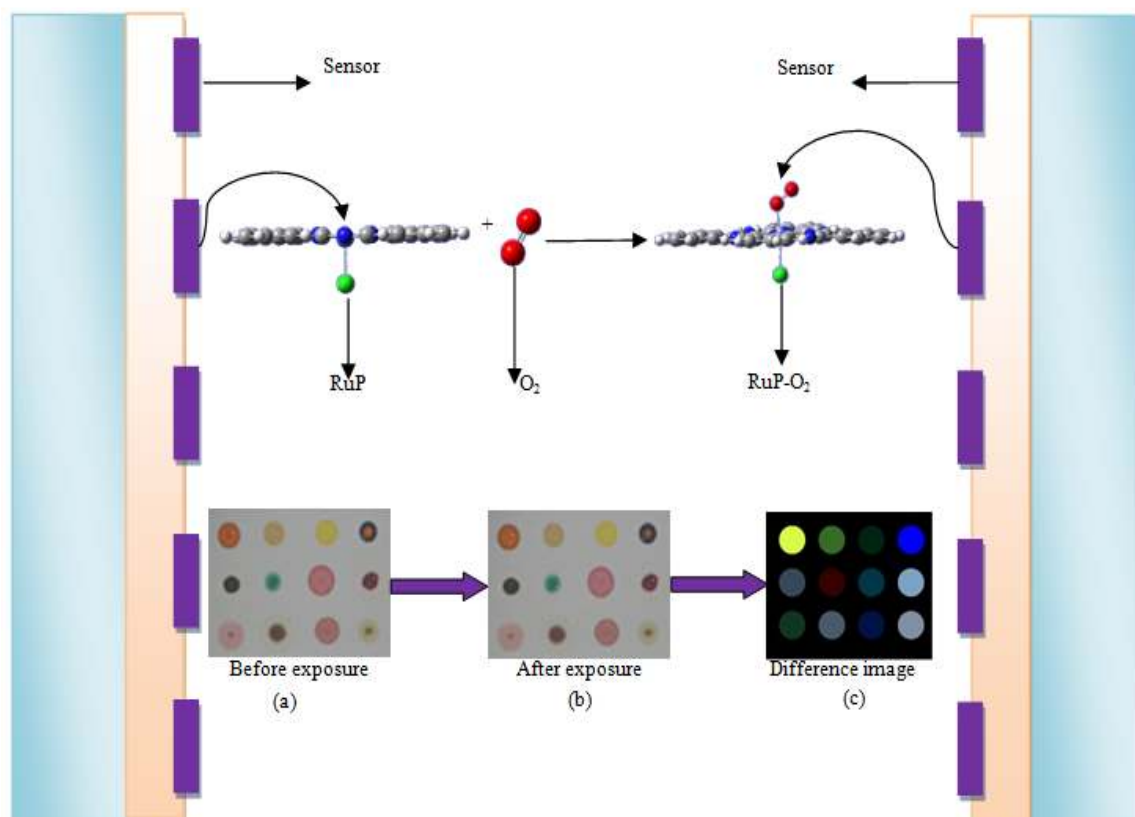


Fig. 1: Schematic of the experimental apparatus consisting of a C2 reverse phase silica gel plates and dyes printed on it. Different image is obtained by subtracting the before-exposure image from the after-exposure image

CSA sensor before and after binding VOCs. The image from the sensor before and after reacting with VOCs was then used to evaluate food quality. According to the previous study, the binding energy is always used to reflect the sensitivity of CSA sensor. Thus, this study is intended to investigate the sensitivity of CSA for a special analyte by the theoretical calculation.

**Computational methods:** The CSA sensor is represented by a simple RuP without any meso substitute. All calculations were carried out at gas phase because of the application of CSA sensor to detect and evaluate food quality is always performed at gas phase. To avoid any shortcomings, all the calculations are performed at the ground state structures. The ground state structures were determined by the comparison of energy for each model at three different spin states (Sun *et al.*, 2009). Calculations of molecule structure, Mulliken charge, relative energy and binding energy for RuP-VOCs were carried out by DFT method at B3LYP/LANL2DZ level. DFT-based method at B3LYP/LANL2DZ has been proved to be very efficient in the calculation of metalloporphyrin and similar complexes (Granados-Oliveros *et al.*, 2010; Huang *et al.*, 2014). Axial ligand below the center of metalloporphyrin plane is selected to be chlorine atom

that is always used in the CSA system. All calculations were carried out using Gaussian 09 program package.

## RESULTS AND DISCUSSION

**Relative energy:** To avoid any shortcomings, all initial structures were optimized at three possible spin states (i.e., the low-spin state, intermediate-spin state and the high-spin state). The ground structure for each model was identified by the energy comparison at three possible states. As it is shown in Fig. 2, for unligated RuP system, quartet is much more stable than doublet and sextet. The energies for doublet and sextet after optimization are 2.915 and 68.389 kcal/mol higher than that of quartet, respectively. According to the previous study, the smaller energy gap between the ground state and other states probably makes the process of RuP binding VOCs to be more than one pathway. It is interesting to notice that RuP-O<sub>2</sub> and RuP-N<sub>2</sub> possess relative smaller energy gaps, followed by RuP-L3, whereas RuP-H<sub>2</sub>S, RuP-L1, 2, 4, 5 possess relative larger energy gaps. The result of relative energies indicates that the relative energy will affect the ability of RuP binding VOCs. Therefore, the relative energy will be considered when the binding energy of RuP for two different VOCs showing same or similar.

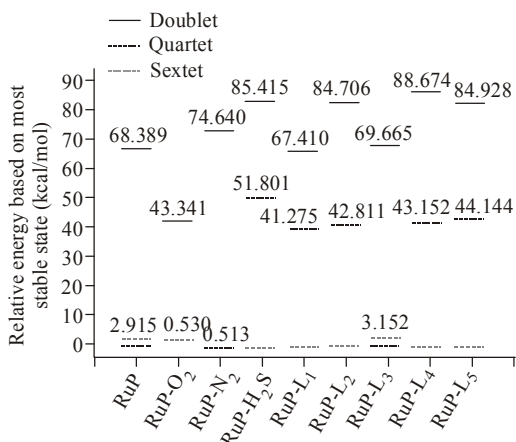


Fig. 2: Relative energies for all RuP-VOCs and RuP relating to the most stable one (Given in kcal/mol). L1 is trimethylamine, L2 is propanol, L3 is propane, L4 is ethyl acetate, L5 is butanone, L6 is propionaldehyde

**Molecular structure:** All calculations were performed on the most stable structure for each model with the lowest energy. The initial structure for RuP and VOCs were obtained from CCDC (i.e., cambridge

crystallographic data centre). Chlorine atom was selected to be axial ligand that is always used in CSA sensor. The distance between metalloporphyrin plane and VOCs was designed between 2-4 Å, which is consistent with the previous study. There are two fashions for metalloporphyrin binding VOCs, namely, end-on bent and the side-on bent. However, the end-on bent fashion is proved to be more stable than side-on fashion by the X-ray structure determinations (Shaanan, 1982; Kitagawa *et al.*, 1982) and theoretical studies (Dube *et al.*, 2008). To avoid any shortcomings, the initial geometry structures were optimized at three different spin states (e.g., low-spin state, intermediate-spin state and high-spin state). Figure 3 shows the optimized structure for each model at three different states. It is interesting to notice that the distance changes of Ru atom moved out of metalloporphyrin plane is much more than the distance of Ru atom and Cl, VOCs atom. On the other hand, the other structures in the metalloporphyrin plane are more stable than Ru atom moved out of metalloporphyrin plane. The above result indicates that the influence of VOCs on metalloporphyrin plane is from RuP atom to other atoms.

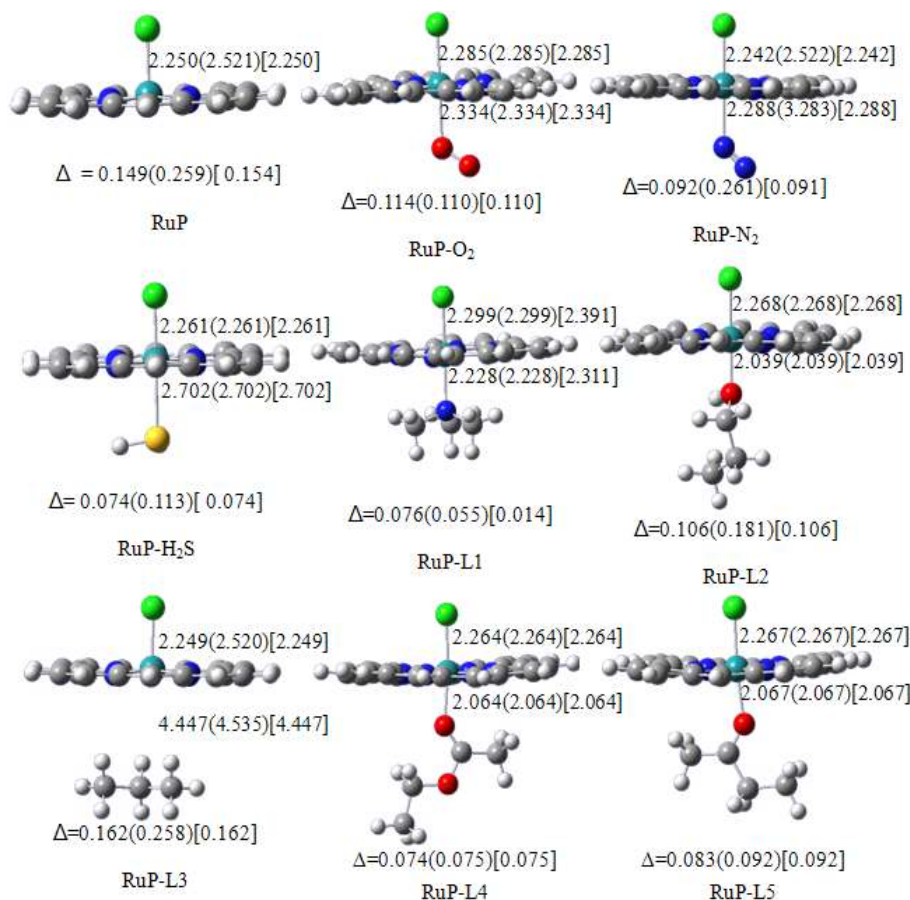


Fig. 3: Optimized structures for RuP-VOCs at three different spin states. Δ is the distance of Ru atom moved out of metalloporphyrin plane. Data for RuP-VOCs at singlet is outside of parenthesis, triplet is in the parenthesis and quintet is in the bracket

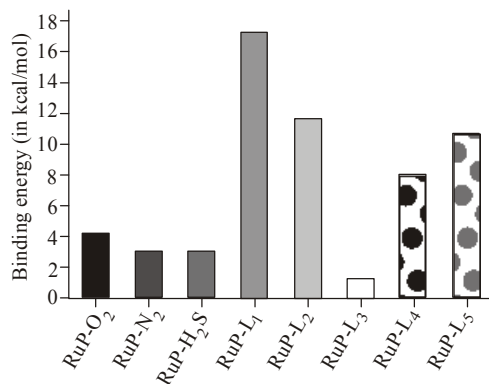


Fig. 4: Binding energies (Given in kcal/mol) for each RuP-VOCs that obtained by subtracting the energy before-binding model from the after-binding model based on the most stable state

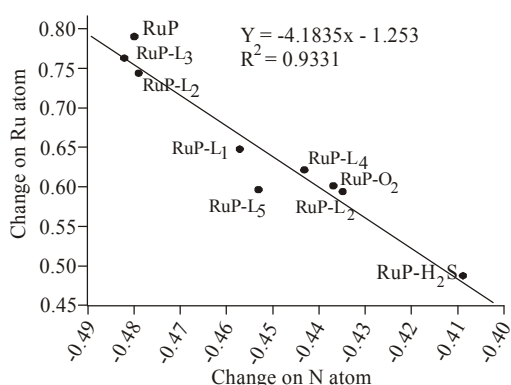
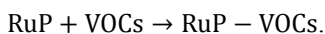


Fig. 5: The strong relationship between charges of nitrogen and Ru atom's charge distribution for RuP coordinating with different VOCs

**Binding energy:** The energy change relating to the process of CSA sensor binding VOCs is always used to indicate the sensitivity of that sensor for special analyte. Therefore, binding energy that was obtained by subtracting the before-reaction energy from the after-reaction energy makes it more convenient to investigate the property of CSA sensor for further application. According to the previous study, the VOCs binding process can be written as:



The binding energy is the energy change relating to this process. The binding can be calculated as below:

$$\text{BE} = E_{\text{VOCs}} + E_{\text{RuP}} - E_{\text{RuP-VOCs}}$$

Figure 4 shows the binding energy (kcal/mol) for each RuP-VOCs. It is interesting to notice that RuP-L1 possesses the largest binding energy, followed by RuP-L2, RuP-L4 and RuP-L5, whereas RuP-O<sub>2</sub>, RuP-N<sub>2</sub>, RuP-H<sub>2</sub>S and RuP-L3 possess relative smaller binding energies. All the results mentioned above reveal that the

CSA sensor containing RuP dye is helpful to detect L1, L2, L4, L5 and the similar VOCs and that CSA sensor is insensitivity to O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>S and L3. This theoretical study will be used to improve the detection ability of the CSA sensor for a special analyte.

**Charge distribution:** The linear relationship of charge distribution between metal ions Ru and N atoms in the center of metalloporphyrin plane was plotted in Fig. 5. It is interesting to notice that the larger positive charges on Ru atoms and more negative charges on N atoms, which are reflected by RuP, RuP-N<sub>2</sub> and RuP-L3 at the top left of the line. On the other hand, the metal ions have less positive charges on Ru atoms and less negative charges on N atoms that reflected by the Ru atom and N atom sitting at the lower left-hand corner of the liner. As shown in Fig. 5, Ru atoms and N atoms display strong linear relationship with the square of correlation coefficient ( $R^2$ ) = 0.9331. It is generally accepted that the electron transfer is reflected by the charge distribution. The VOCs effect has a significant effect on the Ru atoms and N atoms, making the Ru atoms have more electron and N atoms have less electron. All the results mentioned above also reflect that the influence of VOCs was through Ru atom to metalloporphyrin plane. Therefore, the color on the CSA sensor is changed that will reflect the information of VOCs from food.

## CONCLUSION AND DISCUSSION

The nature of CSA is an array-based chemical sensing that baser binding VOCs based on DFT method at B3LYP/d on strong molecular interaction between sensor and analyte with both excellent selectivity and sensitivity to a broad range of VOCs. This present study focused on the ability of CSA senso /LANL2DZ level. The binding energies of the CSA sensor before and after exposure to VOCs were calculated to represent the ability of RuP binding VOCs. The analysis of binding energy shows that RuP-L1 possesses the largest binding energy, followed by RuP-L2, RuP-L4 and RuP-L5, whereas RuP-O<sub>2</sub>, RuP-N<sub>2</sub>, RuP-H<sub>2</sub>S and RuP-L3 possess relative smaller binding energies. Results suggest that theoretical study is helpful for the optimization of CSA sensor. This theoretical study maybe also helpful for other similar VOCs volatilized from food during the storage.

## ACKNOWLEDGMENT

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