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

1,2 Haiyang Gu, 1,2 Yanhui Sun, 2 Xingyi Huang and 3 Huang Dai
1 School of Bio and Food Engineering, Chuzhou University, Chuzhou, 239000, China
2 School of Food and Biological Engineering, Jiangsu University, Zhenjiang, 212013, China
3 College of Biosystems Engineering and Food Science, Zhejiang University, Hangzhou, 310058, China

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; Aguero 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
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$_2$ and RuP-N$_2$ possess relative smaller energy gaps, followed by RuP-L3, whereas RuP-H$_2$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.
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.
possesses the largest binding energy, followed by RuP4L2, RuP4L4 and RuP4L5, whereas RuP4O2, RuP4N2, RuP4H2S and RuP4L3 possess relative smaller binding energies. All the results mentioned above reveal that the binding energies of the CSA sensor before and after exposure to VOCs were calculated to represent the property of that sensor for further application. According to the previous study, the VOCs binding model from the after-binding model based on DFT method at B3LYPd 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 sensor /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-O2, RuP-N2, RuP-H2S 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.

**CONCLUSION AND DISCUSSION**

The nature of CSA is an array-based chemical sensing that baser binding VOCs based on DFT method at B3LYPd 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 sensor /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-O2, RuP-N2, RuP-H2S 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**

This study was sponsored by the Scientific Research Foundation of Chuzhou University (Project No. 2014qd042); Planning Project for Jianghuai Watershed Coordination Center (Project No. 2014GH37); Anhui Research center for Heat-Sensitive Material Open Fund (Project No. 2015RMY04); Horizontal Subject (Project No. HX201558).
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