Study of Interaction between Extrinsic Fluorescence Probe and Dissolved Organic Matter Using Density Functional Theory

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The molecular interaction between an extrinsic fluorescence probe (EFP) and dissolved organic matter (DOM) was calculated using the density functional theory (DFT) at the B3LYP/LANL2DZ level. Eight different types of DOM were selected from the compositions often found in food and beverages. EFP models were obtained from Cambridge Crystallographic Data Centre (CCDC). To avoid problems, all metalloporphyrins and their complexes were optimized at three different spin states. Relative energies indicated that the calculated models possessed the most stable structures at doublet states, except for $ZnP–O_2$. The binding ability representing the sensitivity of the EFP to specific DOM was analyzed using the binding energy. The binding energies were classified into two sensitivity groups with relatively high sensitivity to the binding of O_2, H_2S, and $L_{2,4,5}$, whereas N_2 and $L_{1,3}$ could not easily be detected by a ZnP probe. Our theoretical results may be useful for the design of EFPs.

1. Introduction

Increasing attention has been focused on food freshness and food quality in recent decades due to the improvement of living standards. Food spoilage and freshness loss are rather complex processes that mainly caused by enzymes and microbies. The dissolved organic matter (DOM) in food continuously changes with the loss of freshness and the spoilage of food during storage. Therefore, DOM is considered to be a significant indicator of food freshness and quality. The traditional methods for detecting and evaluating food quality have been based on chemical, physical, and human sensory evaluations. These methods are laborious, destructive, and time-consuming, thus limiting their use in the food industry. Therefore, the demand for highly standardized, sensitive, rapid, and simple measurement is becoming increasingly urgent for quality assurance during production and storage.

Recently, a novel probe-based method has been developed that is based on the strong molecular reaction between a probe and analytes. This method employs a disposable two-

dimensional array of chemoresponsive dyes as the probe, making it particularly suitable for detecting and evaluating the freshness and quality of most food. It has been proved to have huge potential for detecting and evaluating the freshness and quality of certain commodities, for example, fish,[1] soft drink,[2] beer,[3] green tea,[4] and pork.[5]

2. Materials and Methods

2.1 Extrinsic fluorescence probe

The molecular reaction between an extrinsic fluorescence probe (EFP) and analytes is illustrated in Fig. 1. The EFP is created by printing dyes on reverse phase silica gel plates. A color change profile for each sample was obtained by subtracting the before-exposure image from the after-exposure image. This difference image was used as digital data to reflect the quality of analytes. It is important to note that the detection result is almost entirely based on the design of the EFP. The traditional design of an EFP is based on two fundamental requirements: (1) the EFP must contain a specific center to strongly bind analytes and (2) this specific center must be strongly coupled to an intense chromophore.[1,6] These requirements suggest that the interaction of the EFP must not be simple van der Waals interaction and physical adsorption, and that the EFP must not reflect or absorb light in its chemical environment. According to previous reports, three classes of chemoresponsive dyes meet these requirements: (1) Brønsted acidic or basic dyes (i.e., pH indicators) (Fig. 1), (2) Lewis acid/base dyes (i.e., metal-ion-containing dyes), and (3) dyes with large permanent dipoles (i.e., zwitterionic solvatochromic dyes).

2.2 Computational method

All primally initial structures of ZnP and ZnP–DOM were obtained from Cambridge Crystallographic Data Centre (CCDC). The Zn metal atom was moved to the center of the
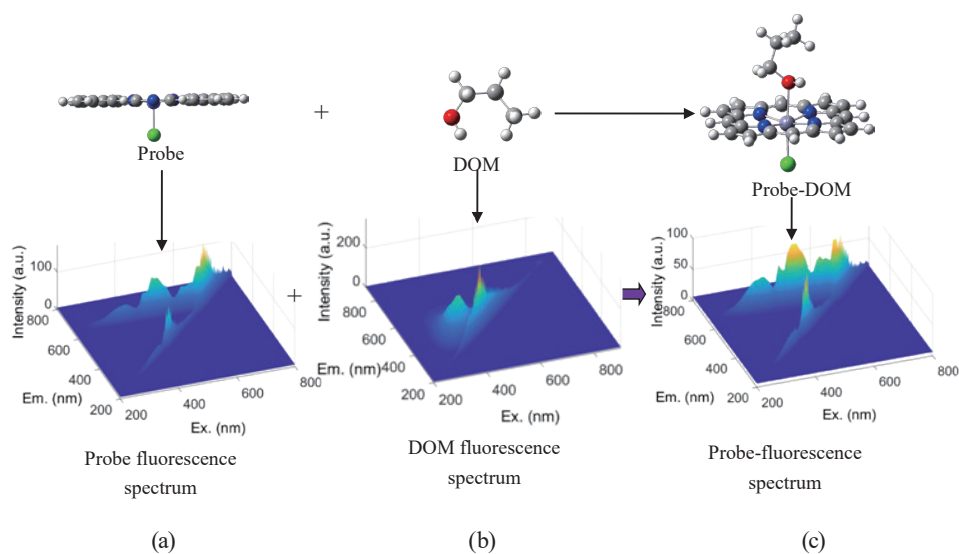

Fig. 1.   (Color online) Process of EFP binding with DOM from oil.

porphyrin plane and the DOM was added 3 to 4 Å above the center of the porphyrin plane in accordance with a previous study.[7] The initial molecular structures were optimized using the density functional theory (DFT) at the B3LYP/LANL2DZ level. DFT-based methods have been proven to be very suitable for metalporphyrin and its similar complexes.[8] To avoid any problems, initial geometric optimizations were carried out at three possible spin states (i.e., low-, intermediate-, and high-spin states) in the gas phase. The most stable structure was obtained by comparing the system energy at the three possible spin states. Further calculations were carried out using stable structures. All calculations were performed using the Gaussian 09 program package on the Windows 7 system.

3.   Results and Discussion

3.1   Relative energy

The most stable metalloporphyrin and its complexes served as a starting point to calculate the ability of metalloporphyrin binding to different types of DOM. To avoid any problems, all metalloporphyrins and their complexes were optimized at three different spin states (i.e., doublet, quartet, and sextet). Figure 2 displays energy gaps of the metalloporphyrins and their complexes among the doublet, quartet, and sextet states. Note that the most stable states are doublet states, except for $ZnP–O_2$, which is similar to $FeP–O_2$ in a previous theoretical study.[9] In addition to the most stable state, energy gap also affects the ability of metalloporphyrins to bind to DOM. As shown in Fig. 2, energy gaps may be grouped into two classes. Note that ZnP, $ZnP–O_2$, $ZnP–N_2$, and $ZnP–L_{1,3,5}$ exhibit relatively large energy gaps, followed by $ZnP–H_2S$ and $ZnP–L_{2,4}$ with relatively small energy gaps. It is generally accepted that a smaller energy gap results in binding processes between metalloporphyrins and DOM through more than one pathway.[10] Therefore, the energy gap is an important factor in the investigation of the ability of metalloporphyrins to bind to DOM.
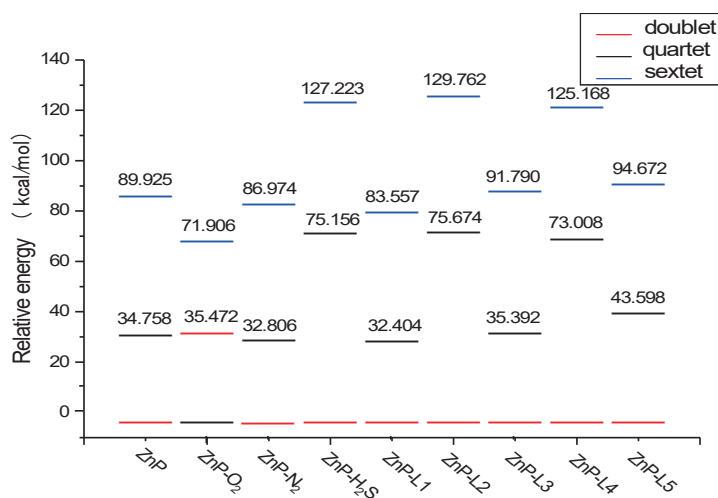

Fig. 2.   (Color online) Energy gaps corresponding to all the calculated models relative to the most stable one (given in kcal/mol). L_1 is trimethylamine, L_2 is propanol, L_3 is propane, L_4 is butanone, and L_5 is propaldehyde.

3.2 Optimized geometry structure

Figure 3 displays the molecular changes before and after binding to DOM at different spin states. Unligated and unoptimized metalloporphyrins serve as the initial geometric model from CCDC. To obtain the most stable geometric structures, metalloporphyrins before and after binding to DOM were optimized at doublet, quartet, and sextet states. The distance between Zn and Cl in the ZnP model is 2.250 Å for the doublet, quartet, and sextet. Note that the distances between Zn and Cl in all metalloporphyrin complexes are larger than that in ZnP, except for ZnP–L_3. When DOM is a good electron donor, it pulls the Zn atom away from the metalloporphyrin plane, increasing the distance between Zn and Cl. Note that the largest distance between the Zn atom and the metalloporphyrin plane is observed for doublets, except for ZnP–O_2. This may be the reason why ZnP–O_2 possesses the most stable molecule at the quartet state, whereas the doublet is the most stable state for the other ZnP complexes and their complexes. In addition to Zn–Cl distance and the Zn atom distance moved by the addition of DOM out of the metalloporphyrin plane, the distance between DOM and the metalloporphyrin plane is also important in analyzing the ability of ZnP to bind to DOM. The distances between the DOM and the center of the metalloporphyrin plane range from 2.032 to 4.604 Å, consistent with a previous theoretical report.[11]
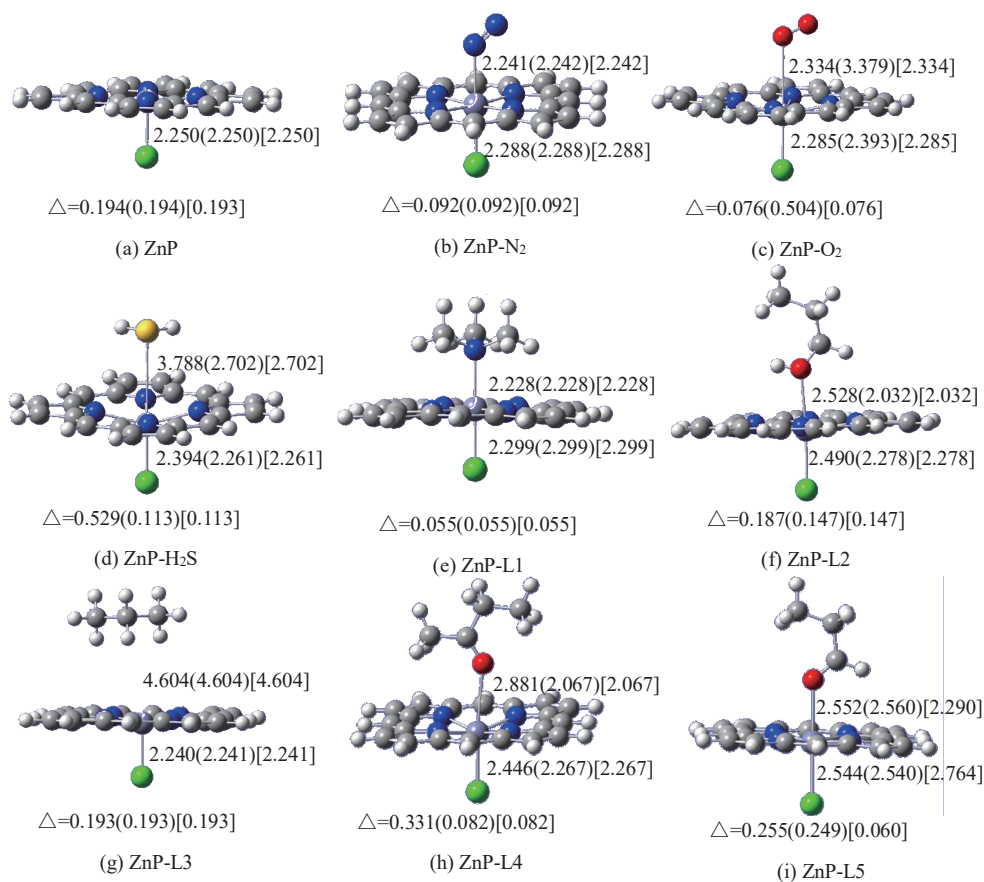

Fig. 3. (Color online) Optimized structures for ZnP–DOM models at three different spin states. △ is the distance between Zn atom and porphyrin plane. Data outside the parentheses are for the doublets, whereas those in parentheses and brackets are for quartets and sextets, respectively.

3.3 Mulliken charge

As shown in Fig. 4, the charge relationship between the nitrogen atom in the center of the metal porphyrin plane and the Zn atom was analyzed using the Origin 86 program package. It is clear that Zn atoms possess larger positive charges and smaller negative charges on the N atom, in the cases of ZnP–L_2, ZnP–L_1, and ZnP at the top right of Fig. 4. On the other hand, the Zn and N atoms have smaller charges at the lower left of the figure represented by ZnP–N_2, ZnP–O_2, and ZnP–L_5. According to a previous study, the chemical reaction and bonds involve the sharing of electrons. The reason for the change in charge on N and Zn atoms may be that the sharing of electrons from DOM results in the N and Zn atoms possessing more electrons and having larger negative charges.

3.4 Binding energy (BE)

The reaction process between the EFP and DOM can be described as ZnP + DOM → ZnP − DOM. The binding ability of the EFP, corresponding to the BE, was calculated using BE = E_{DOM} + E_{ZNP} − $E_{ZNP–DOM}$. Figure 5 displays the BEs (kcal/mol) of all the ZnP complexes and their complexes. Note that ZnP–L_2 possesses the largest BE, followed by ZnP–O_2, ZnP–H_2S, and ZnP–$L_{4,5}$, whereas ZnP–N_2 and ZnP–$L_{1,3}$ have smaller DOM BEs. It is generally accepted that the more energy released from a reaction process, the more stable state the product will have. It is easy to conclude that ZnP is suitable for binding O_2, H_2S, and $L_{2,4,5}$, whereas N_2 and $L_{1,3}$ are not easily detected by ZnP. It is generally considered that O_2 and N_2 in the atmosphere are especially problematic because they interfere with the process of detecting other types of DOM from food. From the results of the analysis of BEs, we conclude that N_2 can be used as a carrier gas to move DOM from the sample chamber to the reaction chamber to avoid interference from the environment.
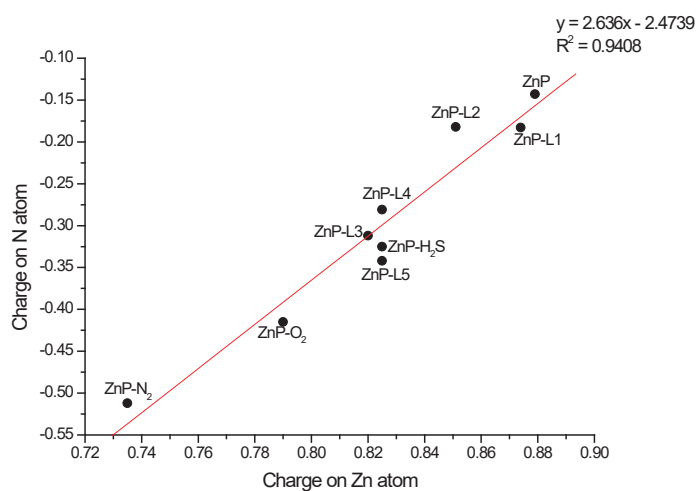

Fig. 4. (Color online) Linear relationship between charge distributions of ZnP and DOM at the most stable state.
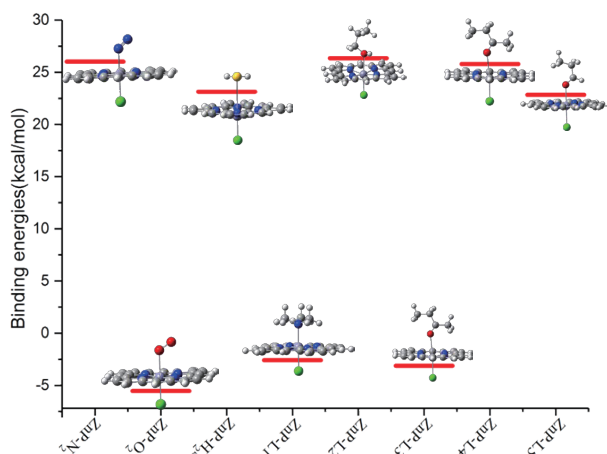
Fig. 5.   (Color online) BEs of ZnP for coordinating different types of DOM.

4.   Conclusions

A theoretical study was performed to investigate the molecular reaction between an EFP and DOM. Theoretical models were optimized at three different spin states to obtain the most stable structures. The ability of the EFP to bind different types of DOM was represented by the BEs obtained by calculating the different energies of the EFP before and after exposure to DOM. The BEs were classified into two sensitivity groups with a relatively high sensitivity to binding O_2, H_2S, and $L_{2,4,5}$, whereas N_2 and $L_{1,3}$ could not easily be detected by ZnP. Our results suggest that an EFP containing ZnP dye is feasible for the detection of O_2, H_2S, and $L_{2,4,5}$. This theoretical method may also be useful for other types of EFP containing other dyes. Further experiments are needed to determine whether the EFP designed by this theoretical study is suitable for the detection of food quality.

Acknowledgments

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