Computational simulation in Molecular Recognition and Spectroscopic Characteristics of a Probe for Zn$^{2+}$, Cu$^{2+}$, Hg$^{2+}$, Fe$^{3+}$

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Abstract. Using computer technology and density functional theory methods, the binding and recognition ability of quinoline derivative probes to Zn$^{2+}$, Cu$^{2+}$, Hg$^{2+}$ and Fe$^{3+}$ ions were studied. And the UV-Vis absorption and fluorescence spectra before and after the complexes formed by the probe and Zn$^{2+}$, Cu$^{2+}$, Hg$^{2+}$ and Fe$^{3+}$ were compared and analyzed. Finally, the energy gap of the frontier molecular orbital energy of each complex was explored and compared. The results of the study show that the probe has obvious differences in coordination recognition ability with Zn$^{2+}$, Cu$^{2+}$, Hg$^{2+}$ and Fe$^{3+}$. The binding energy of the probe to Fe$^{3+}$ is much greater than that of other ions. Moreover, the complexes formed by the probe and the metal ion have significant differences in the ultraviolet-visible absorption spectrum and the fluorescence spectrum. These will provide an important reference for the probe molecule’s identification of different metal ions and the qualitative and quantitative detection and analysis of metal ions.

1. Introduction

As a superior metal ion ligand, quinoline molecule and its derivatives can coordinate with a variety of metal ions[1]. Studies have shown that many quinoline derivatives and their metal complexes can not only be used for anti-tumor and antibacterial activities[2], but also widely used in research related to new luminescent materials[3]. This is mainly due to the unique delocalized electronic structure of quinoline molecules, which makes a variety of quinoline molecules and their derivatives have better absorption capacity for light in the ultraviolet-visible wavelength range and can produce strong fluorescence. Gao Xin et al[4] used the condensation reaction of 8-hydroxyquinoline-2-carboxaldehyde and salicylic hydrazide to synthesize a quinoline Schiff base derivative fluorescent molecular probe, which is the abbreviated “probe” in this study. And which studies have found that the probe molecules have very good fluorescence intensity, while, when the probe molecules are combined with Fe$^{3+}$, the fluorescence disappears completely. Considering that quinoline derivatives can coordinately bind to a variety of metal ions, and have certain binding and recognition capabilities for metal ions, and quinoline derivatives have better spectroscopic properties, when quinoline derivatives are combined with other metal ions are combined, they may produce unique spectral characteristics, which can provide a reference for quantitative detection and qualitative analysis of metal ions. With the rapid development
of computer technology, theoretical calculation results can often be directly used to guide experimental research, even replace experimental research, especially the commonly used density functional theory method has been widely used in various fields[5]. In this study, used the condensation reaction of 8-hydroxyquinoline-2-formaldehyde and salicylic hydrazide to synthesize the fluorescent molecular probes, which were computerized with common metal ions Zn$^{2+}$, Cu$^{2+}$, Hg$^{2+}$ and Fe$^{3+}$ in a vacuum model.

2. Research methods
Using the density functional theory (DFT)[6, 7] method in the Gaussian 16 quantum computational chemistry software, at the b3lyp level[8], under the vacuum model, the Zn, Cu, Hg, and Fe atoms are calculated using the pseudopotential (genecep) basis set relativistic effect, the 6-311G* basis set was used for atoms of CO and H [9].

3. Results and analysis

3.1 Configuration and infrared spectrum
The optimized configuration of the probes forming complexes with Zn$^{2+}$, Cu$^{2+}$, Hg$^{2+}$ and Fe$^{3+}$ are shown in figure 1. Through the vibration frequency analysis of the fully optimized probes and the complexes formed by the probe molecules with Zn$^{2+}$, Cu$^{2+}$, Hg$^{2+}$ and Fe$^{3+}$, it is found that all molecular vibrations have no false frequencies, indicating that the complexes are already at the most stable structure. The infrared spectrum of each complex is shown in figure 2. The infrared spectrum data clearly shows that the probe molecule has a very strong O(4)-H stretching vibration at the wavenumbers of 3223cm$^{-1}$. With the combination of the probe and the metal ion, the H atom falls off and the O-H stretching vibration absorption peak of the probe disappears, indicating that the probe has been coordinated with the metal ion.

At the same time, the main coordination bond lengths of the complexes formed by the probe with Zn$^{2+}$, Cu$^{2+}$, Hg$^{2+}$ and Fe$^{3+}$ are shown in table 1. From the data in table 1, it can be seen that the coordinate bond length between the O and N atoms in the center of the probe and iron is the shortest, and the coordination bond with mercury has the longest. To a certain extent, the bond length can reflect the strength of the interaction between two atoms. Basically, it can be concluded that the probe has the strongest effect on Fe$^{3+}$, while its effect on Cu$^{2+}$ and Zn$^{2+}$ is relatively weak, and its effect on Hg$^{2+}$ is the weakest. This is because Fe atoms become Fe$^{3+}$ lose more electrons. In order to obtain more electrons, they will be more closely bound to the surrounding O and N atoms, which may even destroy the original planar structure of the probe.
Table 1. Binding length of probe with Ions of Zn, Cu, Hg and Fe (nm)

| complexes  | Zn-N(1) | Zn-N(2) | Zn-O(3) | Zn-O(4) |
|------------|---------|---------|---------|---------|
| Probe-Zn   | 0.2089  | 0.2054  | 0.1948  | 0.2027  |
| Probe-Cu   | 0.1980  | 0.1957  | 0.1897  | 0.1978  |
| Probe-Hg   | 0.2541  | 0.2474  | 0.2249  | 0.2274  |
| Probe-Fe   | 0.1970  | 0.1939  | 0.1900  | 0.1979  |

3.2 Binding energy

Binding energy is often used to directly reflect an important indicator of the binding ability of ligand molecules to metal ions [10]. The larger the binding energy, the more difficult it is for the metal ions to be resolved after the probe forms a complex with the metal ion. The binding energy of the probe and each metal ion is shown in Table 2. The molecular binding energy is calculated as shown in formula (1), where $\Delta W_{AB(R)}$ represents the binding energy of ligand A and metal ion B, and $\overline{W}_{AB(R)}$ represents the energy value of ligand A and metal ion B to form a complex, $\overline{W}_{A(R)}$ represents the energy value of the ligand A molecule, and $\overline{W}_{B(R)}$ represents the energy value of the metal B ion. It is obvious from the data in Table 2 that the binding energy of the probe to Fe$^{3+}$ is much higher than that of Zn$^{2+}$, Cu$^{2+}$ and Hg$^{2+}$. It can be seen that the probe has a much stronger ability to recognize Fe$^{3+}$ than other ions. This can also indicate that the probe binds more tightly to Fe$^{3+}$. The binding energy of the probe to each metal ion in descending order is: probe-Fe > probe-Cu > probe-Zn > probe-Hg, which is consistent with the result of the coordination bond length in the complex formed by the probe and the metal ion.

$$\Delta W_{AB(R)} = \overline{W}_{AB(R)} - \overline{W}_{A(R)} - \overline{W}_{B(R)}$$

Table 2. Binding energy of probe with Zn$^{2+}$, Cu$^{2+}$, Hg$^{2+}$ and Fe$^{3+}$

| Probe-X  | probe-Zn | probe-Cu | probe-Hg | probe-Fe |
|----------|----------|----------|----------|----------|
| Binding energy (kJ/moL) | -550.65  | -641.71  | -200.95  | -7143.95 |

3.3 Ultraviolet-visible absorption spectrum

It is obvious from Figure 3 that the probe has good absorption in the ultraviolet region of the ultraviolet-visible light spectrum, and when the probe is combined with each ion, its optimal ultraviolet-visible absorption wavelength and absorption intensity change significantly. When the probe is combined with zinc, its absorption of light undergoes a significant red shift, and has the best absorption value at 504 nm, and the absorption intensity has a certain decrease. When the probe is combined with copper, the ultraviolet-visible absorption also has a significant red shift, and the absorption intensity of light is lower than that of other complexes, and has the best absorption value at 591 nm. However, when the probe is combined with mercury, the degree of light absorption is significantly reduced, and the best light absorption is also found to have a significant red shift. When the probe is combined with Fe$^{3+}$, the absorption in the ultraviolet region is greatly increased, and its optimal absorption wavelength is at 322 nm, and the second strong absorption wavelength appears at 272 nm. The obvious difference of the best absorption wavelength and degree of absorption can be used as a basis for the probe and the determination of Zn$^{2+}$, Hg$^{2+}$ and Fe$^{3+}$. At the same time, it can be clearly seen that the probe can be used for quantitative determination of Fe$^{3+}$, as it has an extremely good UV absorption value for Fe$^{3+}$. 
3.4 Fluorescence spectrum

The fluorescence spectra of the probe and the complex formed by the combination of the probe and Zn$^{2+}$, Cu$^{2+}$, Hg$^{2+}$ and Fe$^{3+}$ are further calculated, as shown in Figure 4. It can be seen from the data in the figure that the probe can emit significant fluorescence. When the probe is combined with Fe$^{3+}$, the fluorescence will be quenched completely, which is consistent with the experimental results of Gao Xin et al.[4]. It also shows that the experimental results are highly consistent with the theoretical research results. This is because when the probe is combined with Fe$^{3+}$, on the one hand, the coordination bond formed by the coordination atom of the probe molecule and Fe$^{3+}$ is too short, which breaks the original planar structure of the probe molecule. On the other hand, the trivalent iron ion loses more electrons than the divalent ion. After the probe forms a complex with Fe$^{3+}$, it directly destroys the probe's electron delocalization orbital. Therefore, when the probe is coordinated with Fe$^{3+}$, the fluorescence disappears completely. However, when the probe is combined with Zn$^{2+}$, Cu$^{2+}$ and Hg$^{2+}$, the structure of the probe is changed slightly, but the planar structure and electron delocalization orbits are not destroyed. This makes the fluorescence intensity weakened to a certain extent after the probe is combined with Zn$^{2+}$, Cu$^{2+}$ and Hg$^{2+}$, and the fluorescence wavelength has a significant red shift instead of being quenched directly.

Interestingly, from the data in Figure 4, it can be seen that when the probe is combined with Zn$^{2+}$, it has the best fluorescence intensity at the wavelength of 504.8nm, when the probe is combined with Cu$^{2+}$, it has the best fluorescence intensity at the wavelength of 694nm, and when the probe binds to Hg$^{2+}$, it has the best fluorescence intensity at a wavelength of 954nm. It can be seen that the strongest fluorescence wavelength formed by the probe and each metal ion will have a significant difference. If combined with the changes in the characteristics of the ultraviolet-visible absorption spectrum, it may be extended to the quantitative detection and qualitative analysis of the complex formed by the probe and other metal ions.

3.5 Frontier molecular orbital energy levels

The frontier molecular orbital energy and energy gap formed when the probe is combined with Zn$^{2+}$, Cu$^{2+}$ and Hg$^{2+}$ are shown in Table 3. The $E_{\text{HOMO}}$ represents the energy value of the highest occupied orbital, $E_{\text{LUMO}}$ represents the energy value of the lowest empty orbital, and $E_{\text{LUMO-HOMO}}$ represents the lowest energy required for the corresponding complex from the ground state to the excited state[11]. If the $E_{\text{LUMO-HOMO}}$ value is lower, the complex is the easiest to be activated. From the data in Table 3, it is obvious that the energy gap of probe-Fe is the lowest, which means that when the probe is combined with Fe$^{3+}$, compared with the formation of complexes with other three metal ions, the probe activity is catalyzed and is more likely to occur. Other reactions only need to absorb energy of -0.1008eV to activate from the ground state to the excited state. The values in Table 3 can be drawn that the activation of the complexes is as follows: probe-Fe < probe-Cu < probe-Zn < probe-Hg.
| probe-X | probe-Zn | probe-Cu | probe-Hg | probe-Fe |
|---------|----------|----------|----------|----------|
| $E_{\text{HOMO}}$ | -0.20385 | -0.20808 | -0.19941 | -0.20515 |
| $E_{\text{LUMO}}$ | -0.10171 | -0.10715 | -0.0908  | -0.10507 |
| $E_{\text{LUMO-HOMO}}$ | 0.10214  | 0.10093  | 0.10861  | 0.10008  |

4. Conclusion
The binding and recognition ability of the probe to Fe$^{3+}$ is significantly greater than that of Zn$^{2+}$, Cu$^{2+}$ and Hg$^{2+}$, and the binding ability to Cu$^{2+}$, Zn$^{2+}$ and Hg$^{2+}$ is also quite different. The optimal absorption wavelength and absorption degree of the ultraviolet-visible spectrum of the probes forming complexes with Zn$^{2+}$, Cu$^{2+}$, Hg$^{2+}$ and Fe$^{3+}$ are significantly different. At the same time, in the complexes formed by the probe and Zn$^{2+}$, Cu$^{2+}$, Hg$^{2+}$ and Fe$^{3+}$, there is a significant difference in the wavelength with the strongest fluorescence intensity. The difference in the ability of the probe to recognize these metal ions, and the difference in the ultraviolet-visible absorption spectrum and fluorescence spectrum of the complex formed by the probe with each metal ion, which can indicate that the probe can qualitatively and quantitatively detect certain metal ions. It can provide an important reference for the detection of metal ions.

Acknowledgments
This work was supported by National Natural Science Foundation and National Social Science Foundation Key cultivation projects of Xiannan University [grant number 2020XJ08], the Chenzhou City Heavy Metal Pollution Health Risk Assessment Technology Research and Development Center, and the Chenzhou City Science and Technology Innovation Ability Cultivation Project [zdyf201912].

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