Light Emission Mechanism of a New Class BDP Fluorescent Probe by Density Functional Theory

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Abstract: BDP Fluorescent probe has the advantages of high sensitivity, specific recognition and light stability, which is widely used in sensors and biometric identification areas, and has become a main testing technique. GaussView software was used to simulate the hydroxyl-substituted BDP fluorescent probe. The basis set B3LYP/6-31G based on the density functional theory (DFT) in a quantum computational software Gaussian 05W was applied. The BDP fluorescent probes molecule structure was optimized to describe the mechanism of fluorescence occurrence and quenching. Additionally, the donor (phenol, phenoxy anion) and the acceptor of the BDP fluorescent probe was optimized, and the HOMO and LUMO orbital value and frequency data were obtained.

Keywords: electron transfer; DFT; structural optimization

1. Introduction

With the rapid development of science and technology, a variety of biological identity methods were emerged. Fluorescent molecular probe is one of the most important identification methods, which has aroused great interest in modern biotechnology and life science research, and have been widely used in a variety of biological substances (such as proteins, DNA and trace metal ions, anions, protons, neutral molecules, etc.). In the past 20 years, the photophysical and photochemical properties of fluorescent probes were improved by structural modification. Many important physiological processes and completion of the chemical reaction of cells and organelles are closely related with pH value [1,2]. Therefore, accurate measurement of pH value in the study of chemical biology is very meaningful [3]. BDP fluorescent probe that we are looking for have the advantages of high sensitivity, specific recognition, and light stability, whose synthesis and application are still worth discussing [4].

In this paper, the hydroxyl-substituted BDP fluorescent probe was optimized by using Gaussian 05w, and IR spectra was drawn and analyzed. Meanwhile, the theory and mechanism of their fluorescence emission were explained. By doing those above on we hope to understand and utilize it better.

2. Principle

Fluorescent probe is an emerging research area, photophysical and photochemical characteristics of probe compounds are utilized to mainly research chemical and physical properties of some system or the sensing structure and materials under some special circumstances at the molecular level. Fluorescent molecular probe is usually made of receptor (the control unit parts), the light emitting group (the activity unit) and spacer (the isolation base), as shown in Figure 1.

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Density functional theory (DFT) with high accuracy, fast calculation speed \(^{(5)}\) is a quantum mechanical method, by which the electronic structure of multi-electron system was investigated. The expression of density functional energy was shown in Equation 1.

\[
E[\rho] = -\frac{1}{2} \sum_{i=1}^{n} \psi^*_i(\eta) \nabla^2 \psi_i(\eta) d\eta - \sum_{X=1}^{N} \int \frac{Z_X}{r_Xi} \rho(\eta) d\eta + \frac{1}{2} \int \int \frac{\rho(\eta) \rho(\eta_2)}{\eta_2} d\eta d\eta_2 + E^{xc}[\rho]
\]  

Where \( \psi_i \) \( (i=1, 2, \ldots, n) \) is the Kohn-Sham track. The first part represents the accurate kinetic energy; the second part is Electron nuclear interactions; the third part is the repulsion between the electrons; the fourth part is the exchange-correlation.

In this paper, probe’s plane structure was plotted by Chemdraw, as shown in Figure 2. Optimization and frequency calculations were conducted by Gaussian 05W. The d function was added, due to the molecule is a large conjugated system contains the heavy atoms such as C and N. The optimized 3D structure was drawn in GaussView, and shown in Figure 3.

\[ \text{Figure 2 Plane structure of the hydroxyl-substituted BDP fluorescent probe} \]

3 Results and discussion

3.1 Fluorescent emission mechanism

In the hydroxyl-substituted BDP fluorescent probe, –OH selectively bonded with median receptor cells phenolic hydroxyl, leading to the –OH group deprotonated into O\(^-\), which is considered to be the root cause of the fluorescence quenching. There is the Steric hindrance between fused phenanthrene ring and middle hydroxy substituent (for position), therefore, the fluorescence characteristics was caused by the mechanism of photoinduced electron transfer (PET). The fluorescence’s on/off effect depends on the highest position of orbital (HOMO) energy levels \(^{(6,7)}\). The calculation showed that when donor site combined with –OH, the OH turned into –O\(^-\), the HOMO orbital energy levels rise from -0.24141 to -0.09424, which was between the orbital energy...
levels of acceptor’s HOMO orbital lead to the fluorescence quenching, which called the fluorescent molecule’s "On - Off" switch. The measurement mechanism of fluorescence emission and quenching were shown in Figure 4. The donor and acceptor’s HOMO and LUMO energy values were obtained and shown in Table 1.

![3D structure of the hydroxyl-substituted BDP fluorescent probe](image)

**Figure 3** 3D structure of the hydroxyl-substituted BDP fluorescent probe

**Table 1** Energy values of the highest occupied orbital (HOMO) and the lowest unoccupied orbital (LUMO) of the compound

<table>
<thead>
<tr>
<th>Compounds</th>
<th>donor Phenol</th>
<th>Phenol anion</th>
<th>acceptor</th>
</tr>
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<tbody>
<tr>
<td>$E_{HOMO}$</td>
<td>-0.24141</td>
<td>-0.09424</td>
<td>-0.11933</td>
</tr>
<tr>
<td>$E_{LUMO}$</td>
<td>—</td>
<td>—</td>
<td>-0.09120</td>
</tr>
</tbody>
</table>

![Figure 4](image)

**Figure 4** The measurement mechanism of fluorescence emission and quenching

3.2 Fluorescence titration study

The fluorescence titration experiment was conducted and the results of emission spectra were shown in the Figure 5. In the alkaline environment, fluorescence’s intensity gradually reduced with the increase of pH. This was mainly due to the addition of alkaline substances, the hydroxyl-substituted BDP’s –OH deprotonated into O-. Whereby electron transfer occurs from O- group to BDP fluorescence, because the electron donating ability of –O- is strong than –OH. Therefore, fluorescence quenching and the experimental curves gradually flatten.
4. Conclusions

Gaussian 05W was applied to optimize the BDP fluorescent probe, the HOMO orbital energy value was obtained. We got that when –OH deprotonated into –O-, the HOMO orbital energy rise from -0.24141 to -0.09424, which is located in the orbital energy levels of acceptor between -0.11933 and -0.09120. The electrons transfer to donor’s HOMO orbital lead to the fluorescence quenching. The fluorescence titration experiments were conducted and the substance was approved to be the purpose product. And the result of emission spectra has a good consistency with the calculation results.

5. References