



Three dimethoxy-substituted luminol derivatives: A comparative study using theoretical method



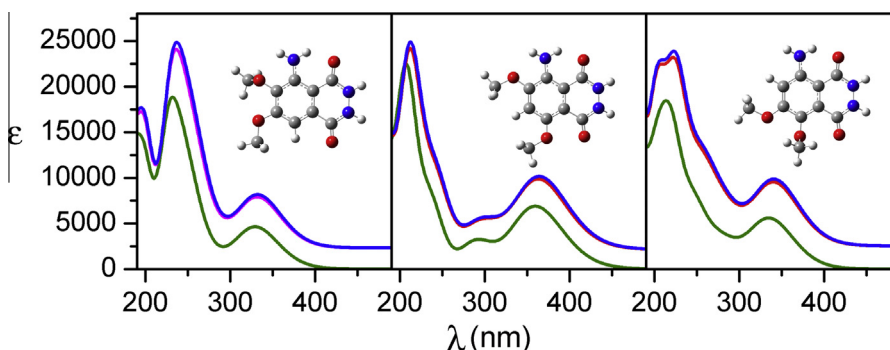
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HIGHLIGHTS

- Three dimethoxy-substituted luminol derivatives are investigated.
- Their structures, electron and spectrum properties are compared.
- A derivative with high chemiluminescent efficiency is suggested.

GRAPHICAL ABSTRACT



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ABSTRACT

In this research, geometrical optimisation, Mulliken charge, molecular electrostatic potential, and the frontier molecular orbitals of three dimethoxy-substituted luminol derivatives were investigated by *ab initio*, density functional, and Møller-Plesset perturbation theory with a 6-311G (d, p) basis set in gas phase, water, and dimethylsulphoxide solution. The UV-vis spectra were calculated by time dependent density functional theory method. The properties of derivatives were compared with luminol at a molecular level to investigate the change induced by the methoxy group. The three derivatives were also compared with the aim of predicting the order of chemiluminescent efficiency. The results showed that methoxy substitution significantly changed the electronic and spectral properties of luminol. Among three derivatives, structure 2 was suggested to have the highest chemiluminescent efficiency. The results may shed some light on the design and selection of chemiluminescent reagents.

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Introduction

Chemiluminescence (CL) is produced when a chemical reaction yields an electronically excited molecule, which emits lights as it returns to its ground state. The attractive features of CL for analytical applications are the simple instrumentation and high

sensitivities [1,2]. In general, it is 10^3 – 10^5 times more sensitive than absorption and fluorescence techniques [3] and has been widely used in the trace detection of food, medical compounds, environmental samples, etc. [4–8].

The classical CL reaction is based on the oxidation of luminol (5-amino-2,3-dihydro-1,4-phthalazinedione, the structure is shown in Fig. 1). Experiments show that the CL quantum yield of luminol is approximately 1–2% [9], which indicates that there is still the possibility to increase CL efficiency and further enhance the sensitivity of this method. Among all the efforts to improve

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CL efficiency, the design and synthesis of luminol derivatives have attracted a lot of attention [10,11]. The modification methods include amino group or benzene ring substitution by other groups, the number of rings increased to enhance conjugation effects [12,13]. Thereinto, the dimethoxy-substitution on the benzene ring was proven to increase CL intensity [14,15]. However, as shown in Fig. 1, the substitution of two methoxy groups at three sites of benzene moiety can obtain three different derivatives, which one own the high CL efficiency has been not clear.

Experimentally, to obtain a new molecule with high CL efficiency, it should be first synthesised, and then the CL intensity verified: this is a complicated process. As excellent alternative methods, theoretical calculations have been proven to be a useful tool for molecule design and property prediction because of their high accuracy and low cost.

In this research, *ab initio* (HF) [16], density functional theory (B3LYP) [17,18], and Møller-Plesset perturbation theory (MP2) [19] calculations were used to investigate the geometrical structures, Mulliken charges, molecular electrostatic potential (MEP), and frontier molecular orbitals (FMO) of three dimethoxy-substituted luminol derivatives in gas phase, water, and dimethylsulphoxide (DMSO) solution. The UV–vis spectra were studied by time-dependent density functional theory (TD–DFT) [20,21]. The properties of three derivatives, as well as derivatives with luminol, were compared at a molecular level to find some clues which related to CL intensity with a view to suggest the best CL reagent among them.

Computational details

All of the calculations were carried out using the Gaussian 09 [22] software package. HF, B3LYP, and MP2 methods with the 6-311G (d, p) basis set [23] were adopted to optimise the structures in gas phase, water, and DMSO solutions. By fully optimising all possible conformers, the most stable conformations for each compound were found. Frequency analysis was performed at the same level to confirm the optimised structures' stability without imaginary frequency components. Polarizable continuum model

(PCM) [24,25] was used to account for the solvent effect. The most stable compounds were used in the later analysis of items such as the Mulliken atomic charge, MEP, and FMOs. The simulated UV–vis spectra were evaluated using the TD–DFT/B3LYP method with the 6-311G (d, p) basis set. The lowest 20 singlet–singlet excitation energies were calculated.

Results and discussion

Molecular structures

The optimised molecular structures of luminol and its three dimethoxy-substituted derivatives were obtained from HF, B3LYP, and MP2 methods with the 6-311G (d, p) basis set in gas phase, water, and DMSO solution. The results showed that although the structures in gas phase, water, and DMSO solutions obtained by different methods differed in detail, their underlying framework was similar. Therefore, in Fig. 1, only the structures in the gas phase, using MP2 methods, are shown. For convenience in subsequent analysis, the related atoms were numbered, and for simplicity of depiction, luminol was denoted by LH₂, and its three derivatives by the numbers 1, 2, 3.

The calculated relative energies of the three derivatives using HF, B3LYP and MP2 methods in gas phase, water and DMSO solution are shown in Table 1. From Table 1, it can be seen that among the three derivatives, the energies of structure 1 are the lowest regardless of which method was used and which state it existed. The energies of structure 2 are lower than structure 3 when B3LYP method was used, while the energies of structure 3 are lower than structure 2 when MP2 method was used. Hence, the structure 1 is thought to be the most stable.

All the bond lengths of the derivatives were different from those of LH₂ due to the influence of the –OCH₃ substituted group. By analysing the bond length data, it was found that the bond length change was greater when it was located near the –OCH₃ substituted sites than other sites. Thus, the bond lengths of C8–C9, C7–C8, C6–C7, and C5–C6 neighbouring –OCH₃ are listed in Table 2. The relevant atom number is shown in Fig. 1. Here, the values obtained from the MP2 method in the gas phase were used as examples to illustrate the effect of the substituent group. From Table 2, it can be seen that, compared with LH₂, the larger change occurred in the bond length C6–C7 in structure 1, C8–C9 in structure 2, and C7–C8 in structures 3. Even so, the differences were only 0.015, 0.013, and 0.021 Å, which indicated that the change of aromatic ring structure induced by –OCH₃ was not large. This

Table 1

Calculated relative energies (kJ/mol) for three luminol derivatives using HF, B3LYP and MP2 methods in gas phase, water and DMSO solution.

Isomers	HF		
	Gas phase	Water	DMSO
1	0	0	0
2	27.914	29.608	29.829
3	36.699	26.742	26.960
	B3LYP		
	Gas phase	Water	DMSO
1	0	0	0
2	27.610	18.590	18.772
3	36.115	27.447	27.634
	MP2		
	Gas phase	Water	DMSO
1	0	0	0
2	42.614	37.630	37.758
3	34.791	28.046	28.310

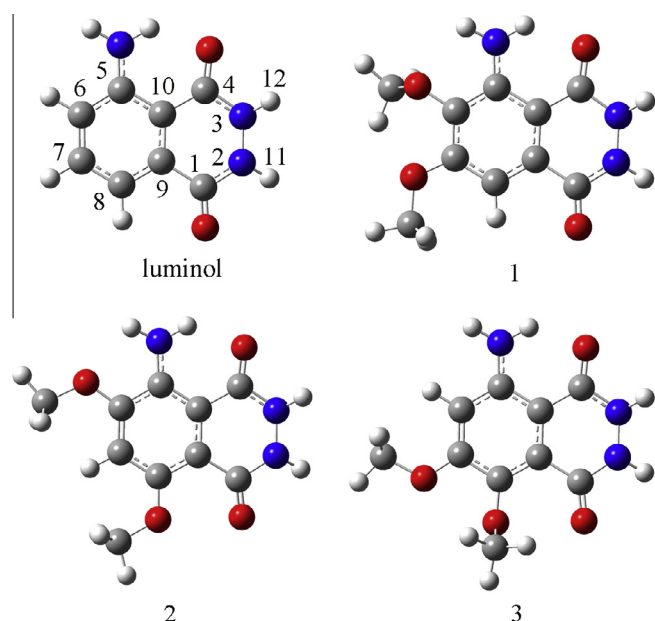


Fig. 1. Molecular structures of luminol and its three derivatives. Grey, white, blue, red ball represent carbon, hydrogen, nitrogen, oxygen atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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