



A highly selective fluorescent chemosensor for Mg²⁺ ion in aqueous solution using density function theory calculations



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ABSTRACT

Magnesium is one of the most common metal cations that contributes to the metabolism cycle of living beings as a biological ion so sensing magnesium ions is of great importance. As a catalyst, magnesium plays an essential part in a large number of cellular processes such as enzymatic biochemical reactions, and cell proliferation. Recently chemosensors are widely used in the detection of metal cations. In this study, the sensing ability of Isatin-3-(7'-Methoxychromone-3'-methylidene) (HL) ligands for the bivalent Mg²⁺ and Ca²⁺ cations was studied and compared using density function theory (DFT) method. The main inconvenient factor to detect magnesium is the Ca²⁺ cation. The calculations were performed using the CAM-B3LYP method on an aqueous environment. The analysis of optical data, including fluorescent and electronic absorption and emission indicates more sensitivity and selectivity for the detection of Mg²⁺ compared to Ca²⁺ in a way that energy gap changes of the [HL + Mg] and [HL + Ca] complexes are 0.155 eV and 0.054 eV respectively.

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1. Introduction

Magnesium is the eighth most common element in the crust of the earth, and the fourth most common cation in human body, It is therefore essential to detect and sense it [1–4]. Magnesium is regarded as a vital biological ion for all living beings. The Mg²⁺ cation plays an essential part in a large number of cellular processes such as the biochemical reactions of cell proliferation and the DNA structure stability [5,6]. For instance, mostly ATP is attached to Mg²⁺ in such a way that MgATP²⁻ is the active variant in the enzyme contributing to the positive transfer and muscular contraction [7]. The total concentration of Mg²⁺ in the mammals' cells accounts to 14–20 mM, the most of which is attached to ATP but the least of which occurring in proteins and phospholipids [5].

It is of paramount importance to specify the Mg²⁺ concentration in the presence of other alkaline and earth metal cations like Na⁺,

K⁺ and Ca²⁺ that display a similar chemical behavior to magnesium [8]. There are numerous analytical methods, including atomic absorption, ion-selective electrodes (ISEs) and NMR [9–11], However the optical methods that show the changes in absorption or fluorescence resulting from Mg²⁺ concentration are suitable for specifying Mg²⁺ concentration in biological systems [12–14]. In addition, chemosensors have a high sensitivity and selectivity, and a suitable response time. So, they are cheap and economical. In recent years, different compounds have been studied as chemosensors to detect Mg²⁺. Among these compounds we can mention crown ethers [15,16], diketones [17], and porphyrins [6].

Men and coworkers (2014) designed and synthesized a chemosensor using the 3,5-dichlorosalicylaldehyde compound for Mg²⁺ colorimetry. This chemosensor showed a suitable sensitivity and selectivity for the detection of Mg²⁺ using the Uv–Vis absorption spectrum, and fluorescence. They also used DFT calculations to study this phenomenon [18]. Hamdi and coworkers (2009) used the calixazacrown compound for the detection of Mg²⁺. When Mg²⁺ is attached to calixazacrown the pyrene monomer increases but the excimer emission decreases [19]. Xu and coworkers (2004)

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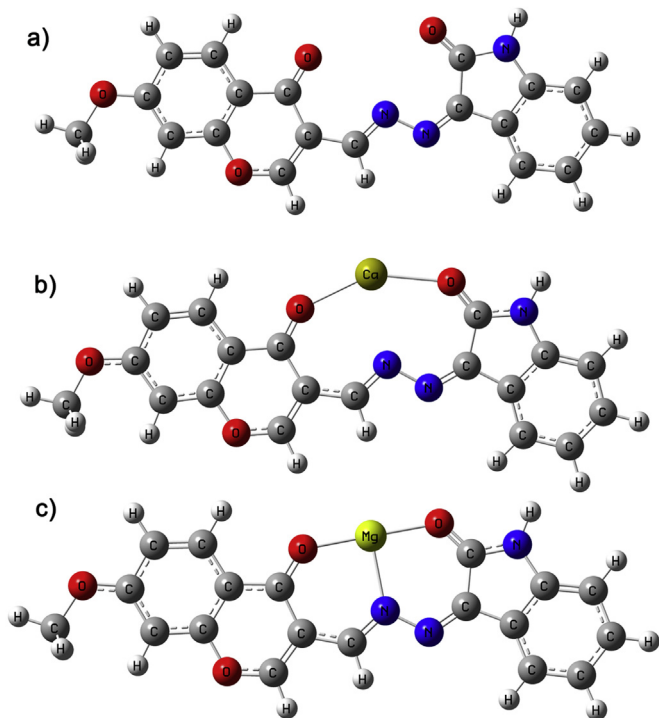


Fig. 1. The HL ligand, [HL + Ca] complex, and [HL + Mg] complex.

Table 1

Electron transfers of non-bonding electron pairs to the bonding orbitals of the HL ligand before and after the formation of the complexes.

	HL	HL + Ca	HL + Mg
LP ₍₁₎ N ₁₁ → σ* C ₂₆ -H ₃₇	10.33	7.96	7.44
LP ₍₁₎ O ₂₂ → σ* C ₈ -N ₉	2.32	1.51	—
LP ₍₂₎ O ₂₂ → σ* C ₇ -C ₈	27.35	21.11	9.92
LP ₍₂₎ O ₂₂ → σ* C ₈ -N ₉	30.69	24.73	21.33
LP ₍₁₎ O ₂₄ → σ* C ₁₆ -C ₁₇	2.42	1.35	0.72
LP ₍₂₎ O ₂₄ → σ* C ₁₂ -C ₁₇	23.88	17.78	5.03
LP ₍₂₎ O ₂₄ → σ* C ₁₆ -C ₁₇	21.62	17.72	13.47

studied a new chemosensor to detect Mg²⁺ using an SU-CM complex that included a coumarin component. The results showed that there were great changes in the color and luminance intensity of the complex with Mg²⁺ concentration [20]. Hariharan and co-workers (2014) used the *N,N*-bis-(salicylidine)-*O*-phenylenediamine compound in the DMF and DMSO solvents for the detection of Mg²⁺ and Ca²⁺. They could not observe any significant effect in the selectivity of this compound since Ca²⁺ tends to act as an inconvenient ion in sensing the fluorescent Mg²⁺ [5]. Yang and coworkers (2015) in the experimental work, used the Isatin-3-(7'-Methoxychromone-3'-methylidene) (HL) as high selective fluorescence chemosensor for Mg²⁺ detection in the presence of other

Table 2

Electron transfers of non-bonding electron pairs to the magnesium and calcium orbitals after the formation of the complexes.

	HL + Ca	HL + Mg		HL + Ca	HL + Mg
LP ₍₁₎ N ₁₁ → LP* ₍₁₎ M	8.30	30.81	LP ₍₁₎ O ₂₄ → LP* ₍₁₎ M	5.38	4.53
LP ₍₁₎ N ₁₁ → LP* ₍₃₎ M	0.72	5.94	LP ₍₁₎ O ₂₄ → LP* ₍₂₎ M	5.78	10.01
LP ₍₁₎ O ₂₂ → LP* ₍₁₎ M	4.76	5.92	LP ₍₁₎ O ₂₄ → LP* ₍₃₎ M	1.91	3.44
LP ₍₁₎ O ₂₂ → LP* ₍₂₎ M	6.11	12.96	LP ₍₂₎ O ₂₄ → LP* ₍₁₎ M	1.65	19.89
LP ₍₂₎ O ₂₂ → LP* ₍₁₎ M	1.29	16.20	LP ₍₂₎ O ₂₄ → LP* ₍₂₎ M	0.45	14.43
LP ₍₂₎ O ₂₂ → LP* ₍₂₎ M	0.48	11.25	LP ₍₂₎ O ₂₄ → LP* ₍₃₎ M	0.17	1.06

cations especially Ca²⁺ [21].

In the present study, an optical and electronic study was carried out using the DFT method for the HL Schiff base for detecting Mg²⁺ and Ca²⁺ ions. Their optical and electronic data were compared to specify the selectivity between these two ions.

2. Computational details

In the present study, the HL ligand was used as a chemosensor to detect and compare its selectivity for the Mg²⁺ and Ca²⁺ cations. Ca²⁺ is the main inconvenient factor to sense Mg in aqueous environments. The structure optimization was done using the DFT method with the CAM-B3LYP hybrid function, and the Lan12dz potentials in the aqueous solution with the CPCM [22,23] solvation model in the 298.25 K temperature, and 1 atm pressure for the HL ligand structure and [HL + Mg] and [HL + Ca] complexes (Fig. 1). CAM-B3LYP is a new hybrid of the exchange correlation correction function that gives a more suitable estimation of electron transfers in the excited state [24,25]. Unlike the semi-empirical methods that totally ignore the effects of core electrons, the ab initio methods take such effects into account. In core potentials like Lan12dz, this becomes possible by substituting core electrons and the related potentials in the wave function via defining the potential expression in the Hamiltonian [26,27]. The excited state calculations of the absorption [28], fluorescence [29], and analysis of NBO [30] were done with the same method. All the calculations were done using the Gaussian 98 software package. The UV–Vis absorption spectrum, fluorescent emission spectrum, states density graph, and electron transfers were studied. The Multiwfn software was used to study the excited state transfers, involved levels, and electron density images [31,32]. The DOS spectrum data were extracted using the Gausssum software [33].

3. Results and discussion

3.1. Electron analysis

Tables 1 and 2 show the NBO data analysis related to the O₂₂, O₂₄, and N₁₁ that are atoms directly contributing to the formation of complex as the ligand dents. Table 1 shows the transfer of these atoms to their adjacent bonds inside the ligand, including the transfers to fluorophore before and after the formation of the complex with Ca²⁺ and Mg²⁺. Electron transfer from oxygen electron pairs is more than electron transfers from nitrogen electron

Table 3

Order of the organic-metal bonds after the formation of complexes.

Bond order	HL + Mg		HL + Ca		
	HL + Mg	HL + Ca	HL + Mg	HL + Ca	
O ₂₂ -M ₂₇	0.600	0.435	N ₁₁ -C ₂₃	1.814	1.849
O ₂₄ -M ₂₇	0.621	0.448	O ₂₂ -C ₈	1.245	1.835
N ₁₁ -M ₂₇	0.467	0.312	O ₂₄ -C ₁₇	1.22	1.820
N ₁₁ -N ₁₀	1.201	1.206			

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