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Computational Studies on Quinoline Based Metal Chemosensors

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Abstract: The design and synthesis of sensors that selectively sense metal ions have a very important place in biological and environmental processes. Fluorescence sensor is one of the most important chemical sensors and is a powerful tool for imaging target molecules and ions in living organisms. Because it has high sensitivity and simultaneous imaging. Although there are many metal sensors available commercially, chemists are still designing sensors that are simpler, easier to synthesize, higher in sensitivity, selectivity and reliability to meet their needs. Hydroxy quinolines are used as fluorophore in metal chemosensors. 8-Hydroxyquinoline (8-HQ), an important fluorophore, exhibits poor fluorescence due to intramolecular proton transfer from oxygen to nitrogen (ESIPT-excited state intramolecular proton transfer). But they show bright fluorescence and photostability after they are attached to metal ions. Thus, the 8-HQ framework is commonly used to construct fluorescence sensors for many important metal ions. However, since the 8-HQ molecule has poor binding selectivity to many metal ions, chemosensors are designed by combining the appropriate binding units (ionophores). Computational calculations of the designed chemosensors have beenperfomed to determine the 3D geometries of the structures, to calculate the spectroscopic properties and to elucidate the mechanism of metal bonding. Calculations will be performed using the Density Functional Theory, the B3LYP hybrid function and the basic set of 6-311++(d,p).

Keywords: Chemosensors, Quinoline, Computational calculations, Metal chemosensors

Introduction

Detecting cations is of great interest to many scientists, including chemists, biologists, clinical biochemists and environmentalists. Sodium, potassium, magnesium, calcium are involved in *biological processes* such as transmission of nerve impulses, muscle contraction, regulation of cell activity, etc. Moreover, various metal ions belong to metalloenzymes. In *medicine*, it is important to control the serum levels of lithium in patients under treatment for manic depression, and potassium in the case of high blood pressure. Regarding aluminium, its toxicity has long been recognized and there is a controversy about its possible implication in Alzheimer's disease. In *chemical oceanography*, it has been demonstrated that some nutrients required for the survival of microorganisms in sea water contain zinc, iron, manganese as enzyme cofactors. Finally, it is well known that mercury, lead and cadmium are toxic for organisms, and early detection in the environment is desirable.

Among the numerous analytical methods that are available for the detection of cations, flame photometry, atomic absorption spectrometry, ion sensitive electrodes, electron microprobe analysis, neutron activation analysis, etc., are expensive, often require samples of large size and do not allow continuous monitoring. In contrast, the methods based on fluorescent sensors [1–6] offer distinct advantages in terms of sensitivity, selectivity, response time, local observation (e.g. by fluorescence imaging spectroscopy). Moreover, remote sensing is possible by using optical fibres with a molecular sensor immobilized at the tip [7]. Therefore, considerable efforts are being made to develop selective fluorescent sensors for cation detection.

Such fluorescent sensors consists of a fluorophore linked to an ionophore and is thus called a fluoroionophore (Fig. 1). In the design of such sensors [8], attention should be paid to both recognition and signaling moieties. The *signaling moiety* acts as a signal transducer, i.e. it converts the information (recognition event) into an

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- Selection and peer-review under responsibility of the Organizing Committee of the Conference optical signal expressed as the changes in the photophysical characteristics of the fluorophore. These changes are due to the perturbation (by the bound cation) of photoinduced processes such as electron transfer, charge transfer, energy transfer, excimer or exciplex formation or disappearance, etc. These aspects are relevant to the field of *photophysics*.

As regards the *recognition moiety*, it is responsible for selectivity and efficiency of binding which depend on the ligand topology, on the characteristics of the cation (ionic radius, charge, coordination number, hardness, etc.), and on the nature on the solvent (and pH, ionic strength in the case of aqueous solutions). These aspects are relevant to the field of *supramolecular chemistry*. It should be noted that the signaling moiety can be linked to the ionophore moiety via a spacer or not. Even in the latter case, some atoms of the fluorophore may participate in the complexation. Therefore, the selectivity of binding often results from the whole structure involving both signaling and recognition moieties.

It should be emphasized that, under the conditions of detection, the dissociation constant of the complex should match the expected range of cation concentration which is very different according to the field. For instance, the concentration of calcium ion inside a living cell is in the micromolar range, whereas in blood plasma and urine it is in the millimolar range. Therefore, the well-known calcium sensors designed by Tsien (Indo-1, Fura-2, etc.) [9] are suitable for cellular biology but not for clinical diagnosis.

Method

The three-dimensional ground state (S_0) geometry of the compound was geometry optimized using Density Functional Theory (DFT) [10] by using the Gaussian 09W [11] package program and the hybrid functional B3LYP. The B3LYP is composed of Becke's three parameter exchange functional (B3) [12] and the nonlocal correlation functional by Lee, Yang, and Parr (LYP) [13]. The basis set used for all atoms was 6-31++G(d,p) in both DFT and time-dependent density functional theory (TD-DFT) method. We have applied default G09 grid for computations.

For the nonel compound, vibrational analyses were carried out using the same basis set employed in the corresponding geometry optimizations. The frequency analysis of none of the compounds yielded any imaginary frequencies, indicating that the structure of each molecule corresponds to at least a local minimum on the potential energy surface. The normal mode analysis was performed for 3N-6 vibrational degrees of freedom, N being the number of atoms in the molecule.

The low-lying triplet (T) and singlet excited states (S) of the compounds were relaxed to obtain their minimum energy geometries using the TD-DFT as implemented in G09 package program [14]. The vertical excitation energies and oscillator strengths were obtained for the lowest triplet and singlet transitions at the optimized ground state equilibrium geometries by using TD-DFT at the same hybrid functional and basis set [14]. Optimized ground state structures were utilized to obtain the electronic absorption spectra, including maximum absorption wavelengths, oscillator strengths, and main configuration assignment by using TD-DFT.

Results and Discussion

In the present study a quinoline based metal chemosensor has been considered for its spectroscopic properties at B3LYP/6-31++G(d,p) level of theory.

First of all, geometry optimization of the quinoline based antracene derivative has been performed to obtain the ground state structure. Front and side view of the structure after geometry optimization can be seen in Figure 1. As can be observed the triazole moiety is directed out of the coordination center which was unfortunate for us since the triazole nitrogen units had been thought to be a very well coordination part of this potential chemosensor. Although the geometry optimized structure has been obtained out of what we were expecting, the coordination computatons for metal till went on because there are more complexation sites (quinoline nitrogen and connecting oxygen) in the structure.

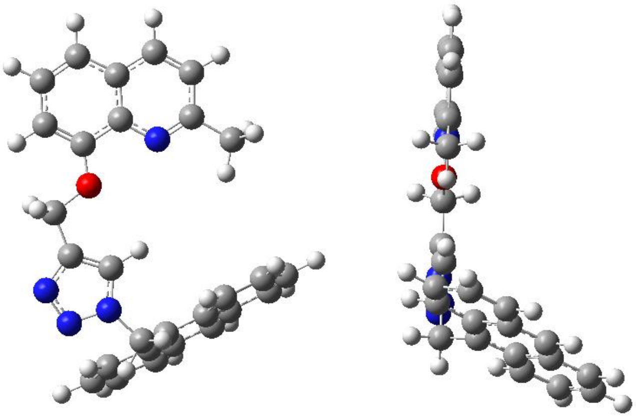

Figure 1. Chemical structure of triazophenone

Geometry optimized structures of the Zn^{2+} and Hg^{2+} coordinated structures are shown in Figure 2. As we performed the ground state search the triazole moiety rotated towards the coordination center which is more obvious in Hg coordination. Moreover anthracene unit came closer to the metal to make a π-π-stacking interaction.

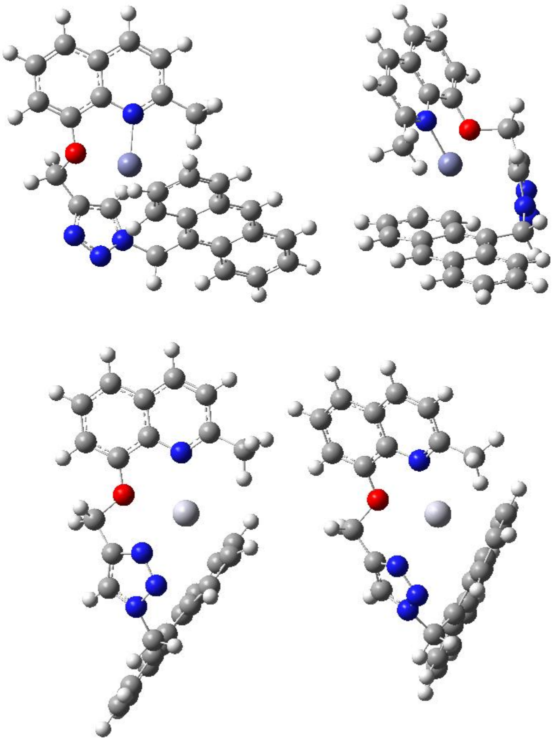

Figure 2. Geometry optimized structure of Zn and Hg complexes

The UV-VIS spectra of the compounds have been obtained by the same method of computation. The non-metal quinoline compound has got two major peaks at around 200-300 nm and a non-intense peak at 390 nm. Zn and Hg complexes possess a new band at around 350 nm and 400 nm, respectively. Moreover the non-intense band of the parent compound shifted to blue in both cases.

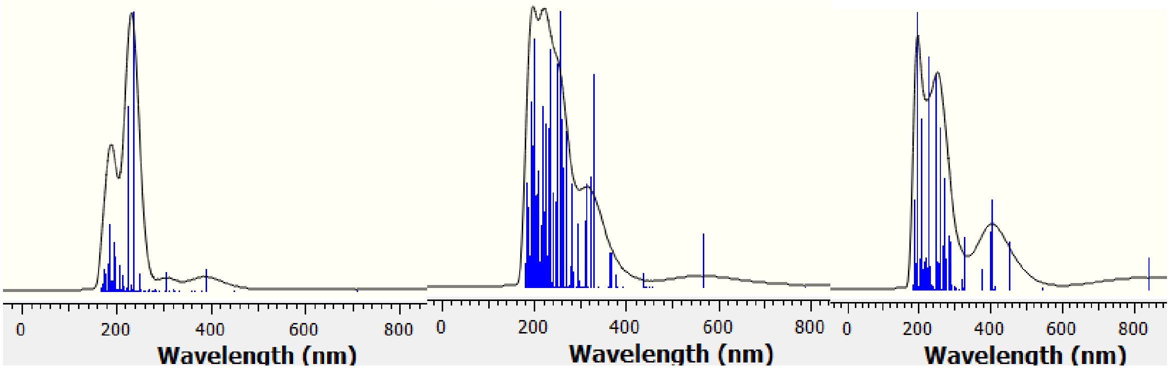

Figure 3. UV-VIS spectra of the present compounds

Conclusion

In the present study, we performed a computational study by the application of Density Functional Theory at B3LYP/6-31++G(d,p) level on a quinoline based anthracene derivative.

The triazole in the parent structure changed conformation towards coordination in the metal complex. The charge on the metal cation decreased from +2 to 0.845 and 0.873 on Zn and Hg, respectively, which proves the coordination.

Moreover, the changes in the UV-VIS spectra clearly indicated the coordination and complex formation.

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