

REGULAR ARTICLE

A TD-DFT Study on Fluorescent Chemosensor for Fluoride Anion Based on Dipyrrolyl Derivatives

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Abstract: Time-dependent density functional theory (TD-DFT) method was used to study the excited-state hydrogen bonds between dipyrrolyl derivatives and fluoride anion (F⁻). The geometric structures, charge density distribution and electronic spectra of two dipyrrolyl derivatives and their doubly hydrogen-bonded complexes with F⁻ were calculated by the DFT and TD-DFT methods. The intermolecular hydrogen bonds in ground states were proposed to be the main reasons for the gradual spectral shifts in the absorption spectra. The excited-state proton transfer (ESPT) was used to explain well fluorescence emission features of their hydrogen-bonded complexes. Furthermore, the radiationless deactivation via internal conversion (IC), which gives rise to fluorescent quenching of dipyrrolyl derivatives, could be facilitated by the ESPT process.

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1. Introduction

Hydrogen bonding is a contemporary research interest because of its universal importance in physics, chemistry, biology and other many branches of science [1-4]. Intermolecular hydrogen bonding has been recognized to play a fundamental role in molecular and supramolecular photochemistry [4-9]. Excited-state hydrogen bonds have been investigated

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experimentally and theoretically in some photophysical and photochemical processes of hydrogen bonding systems [6, 10-18].

Upon photoexcitation of hydrogen-bonded systems, the hydrogen donor and acceptor molecules reorganize due to the significant difference in the charge distribution of different electronic states [5, 7, 17-20]. In a number of cases, these reorganizations can strengthen the intermolecular hydrogen bonding in the electronically excited state and facilitate the radiationless deactivation, i.e. internal conversion (IC) process [6, 10, 21, 22]. This mechanism has been used to explain many photophysical processes, such as fluorescence quenching [8, 10, 23, 24], ultrafast internal conversion [6, 23, 25], etc.

Furthermore, more and more attention has been paid to the role played by hydrogen bond for the design of efficient anion chemosensor. Many neutral organic molecules containing N-H functional groups represent the most commonly seen anion interacting moieties. It is noted that a π -system bearing an N-H moiety may be an appropriate candidate for designing anion chemosensors [26-29]. For this kind of receptors, the hydrogen bond-induced π -electron delocalization or basic anion-induced N-H deprotonation serves as the signaling output of the anion-receptor interaction [30, 31]. In recent years, many studies have focused on the mechanism of such processes [4,6, 30, 32].

Recently, pyrrolyl derivatives as anion-binding motif have attracted considerable attention [9]. Pyrrole is an ideal group for the construction of anion receptors. For example, Ghosh and Maiya reported that an easy-to-prepare dipyrrolyl derivative endowed with electron-withdrawing dicyano groups permit the detection of fluoride anion visually and optically [33, 34]. In particular, pyrrole does not contain an intramolecular hydrogen-bonded acceptor that could compete with anion recognition. A pyrrole N-H proton has a lessened dependence on the pH value of the environment. Over the last decades, pyrrole has emerged as an important structural motif that may be used to construct receptor system capable of interacting effectively and selectively with a range of anionic substrates in many instances [33-37]. However, up to now, there have been few theoretical studies on the hydrogen-bonded interactions of pyrrolyl derivatives with anions and photophysical properties of these systems.

In this paper, we report a theoretical study on the isolated dipyrrolypyrazine (DPP) and dipyrrolyldicyanopyrazine (DPDCP) (see **Figure 1**) as fluorescent chemosensors for fluoride anion. In particular, we have focused our attention on the mechanism relating to the gradual spectral shifts and the fluorescence quenching by the hydrogen-bonding interaction between two chemosensors and fluoride anion in both the ground state and the excited state. Furthermore, the dipyrrolyl derivative DPDCP endowed with electron-withdrawing dicyano groups was verified to be more efficient chemosensor for fluoride anion than DPP.