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REGULAR ARTICLE

Time-Dependent Density Functional Theory Study on a Fluorescent Chemosensor Based on C–H···F Hydrogen-Bond Interaction

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Abstract: A new fluorescent chemosensor bearing two imidazolium groups was designed and investigated by DFT/TDDFT method. The fluoride-sensing mechanism of the chemosensor was studied by the geometry optimization, two-dimensional potential energy surface (PES) scan, absorption/emission spectra simulation, and frontier molecular orbital (FMO) analysis. The calculations show that this chemosensor displays an emission band at 407 nm. PES scan confirmed that the excited state proton transfer (ESPT) process of the chemosensor-fluoride complex is barrierless. The ESPT process took place in the C–H•••F hydrogen bond with C–H moiety acting as a proton donor and the fluoride anion acting as a proton acceptor. This process proved that addition of fluoride anion could lead to the formation of the carbene form of the chemosensor. Due to the nπ-type transition mode obtained by FMO, the carbene form has a red-shift emission band at 523 nm.

AMS subject classifications: 65D18, 68U05, 68U07

Key words: Chemosensor, Hydrogen bond, TDDFT, ESPT, Fluorescence

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1 Introduction

Hydrogen bond (H-bond) occurs in both inorganic molecules [1] and organic molecules. Especially, it plays a key role in determining the three-dimensional structures of proteins [2] and DNAs [3]. In these macromolecules, the H-bond between parts of the same macromolecule causes it to fold into a specific shape, which helps the molecule determine its biochemical role. According to the definition from IUPAC, H-bond is an attractive interaction between a hydrogen atom from an X–H group (H-bond donor) and an atom or a group with high electron density (H-bond acceptor) [4]. The X atom in H-bond donor or H-bond acceptor is always an electronegative atom, such as N, O, or F. So H-bonds involved N, O, or F are most frequently studied [5-7]. For some time there were researches on C–H moieties with electron-withdrawing groups, which were proved to be able to act as H-bond donors [8]. This is because the electron-withdrawing moieties lead to the electron pair in C–H moiety close to the carbon atom.

Due to the fundamental roles that anions play in a wide range of chemical and biological processes，numerous efforts have been devoted to the design of chemosensors capable of selectively sensing anions. The development of selective sensors for fluoride anions is of particular interest because they play vital roles in a wide range of our life，such as food science, dental care, and the treatment of osteoporosis [9-11]. midazolium cation can be formed by protonation or substitution at nitrogen atom of imidazole. It has been used as ionic liquids and precursors to stable carbenes [12]. As mentioned above, the C–H moiety between two nitrogen atoms in imidazolium cation is likely to form H-bond with electronegative atoms or anions [13-16]. The H-bond could be strengthened or weakened upon excitation [17-19] and can be monitored by fluorescent spectra. Accordingly, we can design a fluorescent chemosensor for fluoride anions. In general, free imidazolium do not have visible light absorption [20-23]. To improve the photoabsorption properties of imidazolium cations, some groups with conjugated structures can be introduced into the imidazolium skeleton [24,25]. Thus, the fluoride anion can be easily discerned by virtue of the distinct fluorescence wavelengths that they elicit.

Based on C–H•••F H-bond interaction, we designed a fluorescent chemosensor for fluoride anion, 1,1′-butane-1,4-diylbis(3-methylbenzimidazolium), (see **Figure 1**, abbreviated as b). This chemosensor can be easily synthesized by methylation of corresponding imidazole compound that is only slightly soluble in water. Forming imidazolium cation could increase the solubility of the chemosensor, which is favorable to sense the fluoride anions in aqueous solutions. The quantum-chemical calculations are performed to investigate molecular spectra and the structural parameters of the molecule. The