

Insights into the fluoride ions response mechanism for the novel 2,2':6',2''-terpyridine fluorescent sensor

Received Oct. 18, 2017,
Accepted Nov. 29, 2017,

DOI: 10.4208/jams.101817.112917a

<http://www.global-sci.org/jams/>

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Abstract. In this present work, the sensing mechanism of a novel fluoride chemosensor 2,2':6',2''-terpyridine (abbreviated as "2" according to previous experiment) has been investigated based on density functional theory (DFT) and time-dependent DFT (TDDFT) methods. The theoretical electronic spectra (vertical excitation energies and fluorescence peak) reproduced previous experimental results [*RSC Adv.* **2014**, *4*, 4041.], which confirms the rationality of our theoretical level used in this work. The constructed potential energy curve suggest that the non-barrier process could be responsible for the rapid response to fluoride anion. Analyses about binding energies demonstrate that only fluoride anion could be detected for 2 chemosensor in acetonitrile solvent. Comparing with other anions, we confirm the uniqueness of fluoride anion for 2 sensor. In view of the excitation process, the strong intramolecular charge transfer (ICT) process of $S_0 \rightarrow S_1$ transition explain the redshift of absorption peak for 2 sensor with the addition of fluoride anion. This work not only presents a straightforward sensing mechanism of fluoride anion for 2 chemosensor, but also plays important roles in synthesizing and designing fluorescent sensors in future.

1. Introduction

As the smallest anion owning the unique position among all the essential anions, fluoride anion (F⁻) plays an important role in many ranges about chemical and biological fields [1-3]. In fact, even though fluoride ion is beneficial to dental health and treatment of osteoporosis [4], obvious fluoride toxicity can be generally exposed on a less salubrious level to lead to fluorosis in terms of increasing bond density, urolithiasis, and even cancer [5]. Therefore, it has become the high demand to make considerable effects in detecting and recognizing fluoride anions. And lots of attention has been focused on the selective sensing for fluoride ions recently [6-9]. Particularly, it is important to develop novel optical probes revealing high selectivity, good sensitivity and rapid response toward fluoride anions [10-15].

In general, for developing ideal fluoride anion probes, the following characters could be considered. For more legible, it should be the best choice for presenting apparent optical signal modifies to realize the naked-eye detection [16]. It will be better to own optical signals from far-red to near-infrared region to avoid interference from endogenous sensors in biological system [17]. Showing practical applications of detecting fluoride in real samples is also another attractive aspect [18]. To the best of knowledge, at present, the strategies for constructing fluoride probes are mostly based on B-F complexation, F⁻-induced desilylation of Si-O bands and deprotonation via hydrogen bond [19-25]. And generally, the fluorescence transduction processes are involved in photoinduced electron transfer (PET), intramolecular charge transfer (ICT), excited state proton transfer (ESPT), and so on [26-29]. In fact, although more and more work about fluoride anion have been reported, theoretical investigations about fluoride-sensing mechanisms are

rare relatively.

Recently, Cao *et al.* synthesized two novel fluorescent sensors (named as 1 and 2 according to experiment) experimentally [30]. They found that the both 1 and 2 sensors show the colorimetric and luminescent response to the fluoride anion over other anions based on strong hydrogen bonding interaction (O-H...F) in organic solvent. And upon the addition fluoride anions, these two receptor can show the color change from colorless to yellow. In fact, the probe response mechanism of compound 1 could be understood clearly, which can be attributed to that the ESPT process could be inhibited by the fluoride anions [19, 21, 26]. Whereas for sensor 2,2':6',2''-terpyridine (abbreviated as "2" according to previous experiment), the response mechanism seems to be scarce theoretically. To the best of our knowledge, just the indirect information about structural and photochemical properties could be provided in experimental studies. While the calculations of electronically excited states can be adopted to clarify the fundamental aspects about

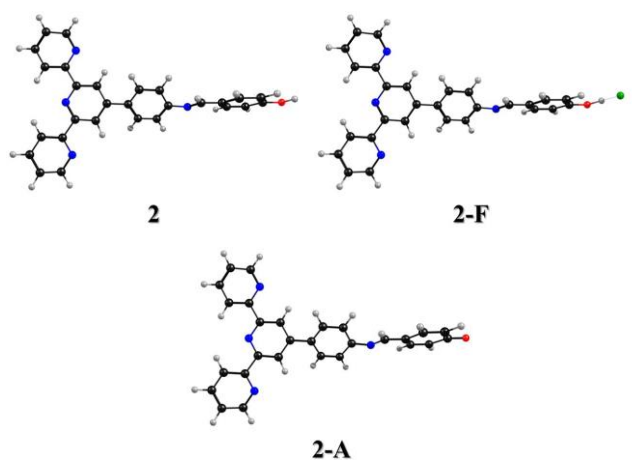


Figure 1: View of the relative structures of 2, 2-F and 2-A. Herein, black: C atoms; gray: H atoms; Blue: N atoms; Red: O atoms; Green: F atom.

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sensing mechanism. Particularly, the mechanism about “on-off” process is the fundamental aspects of 2, which might be useful for understanding and controlling probe response about 2 and its derivatives in future.

In this present work, therefore, the density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods have been adopted to investigate the fluoride sensing performances and the relative mechanism for 2 sensor. On the basis of Kasha’s rule [31], fluorescence radiation happens with an electron relaxes from S_1 state to its S_0 state, therefore, both S_0 and S_1 states of 2 and relative structures are of interest in this work. Based on comparing the structural parameters and reaction energies with other anions, we clarify the ability of F^- for 2 sensor. Particularly, we mainly focus our attention on the changes of photochemical properties and the excited-state charge redistributions upon adding the fluoride anion. Comparing with other anions, we confirm the uniqueness of fluoride anion. We deem the mechanism we put forward is very important for the synthesis and design for fluorescent sensors in future.

2. Theoretical Methods

In this work, all the simulated calculations have been carried out using Gaussian 09 program [32]. Within the framework of DFT and TDDFT methods, the hybrid exchange-correlation functional B3LYP and the triple- ζ valence quality with one set of polarization functions (TZVP) basis set have been selected in all calculations [33-39]. In view of the solvent effect, acetonitrile (the dielectric constant: 35.688) solvent has been adopted within the model of Polarizable Continuum Model (PCM) using the integral equation formalism variant (IEFPCM) [40-42], which considers the solute in the cavity of overlapping solvent that own apparent charges to reproduce the electrostatic potential because of the polarized dielectric within the cavity. The ground-state geometries for all the species have been optimized without constraint. And the vibrational frequencies have been also analyzed at the optimized structures to ensure these structures corresponded to the local minima on the S_0 state potential energy surface. The vertical excited energies have been performed from the ground state stable form using TDDFT, and six low-lying excited states are predicted in this work. The excited-state structures have been calculated starting from the S_0 -state stable configuration with analyzing vibrational frequencies to confirm the stability. The calculations about potential energy curves for the probe response process have been also carried out to explain the mechanism. All the stationary points along with reaction coordinate were optimized in acetonitrile solvent. Analyses of frequency can obtain the thermodynamic corrections in the corresponding electronic states. Zero-point energy correction and

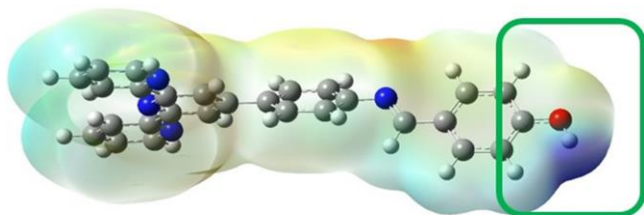


Figure 2: View of the electrostatic potential surface of 2 sensor in the S_0 state.

thermal corrections to the Gibbs free energy were also performed according to the harmonic vibrational frequencies.

Fine quadrature grids of size 4 were employed. The self-consistent field (SCF) convergence thresholds of the energy for both the ground state and excited state optimization were set at 10^{-8} (default settings are 10^{-6}). Harmonic vibrational frequencies in the ground and excited state were determined by diagonalization of the Hessian. The excited-state Hessian was obtained by numerical differentiation of the analytical gradients using central differences and default displacements of 0.02 Bohr. The infrared intensities were determined from the gradients of the dipole moment.

3. Results and discussion

The geometries of the chemosensor 2, the fluoride complex 2-F form and the anion product 2-A structure have been optimized based on the B3LYP/TZVP theoretical level within the framework of the IEFPCM solvent model (see Figure 1). In the process of investigating the possible correlation of electrostatic potential with hydrogen bonding interactions (shown in Figure 2), the regions of the negative electrostatic potential (denoted by red) are usually used to identify the hydrogen bond acceptor sites. Whereas for describing the hydrogen bond donating sites, the regions of positive potential (denoted by blue) are prominent [29]. Obviously, the positive electrostatic potential around H atom of oxhydryl exists in 2 chemosensor. The corresponding natural bond orbital (NBO) charge analyses also reveal that the hydrogen atom should be the most possible reactive site of 2 sensor for attracting fluoride ion. Therefore, the fluoride complex 2-F form can be reasonably obtained via optimizing corresponding stable structure. And for complex 2-F, a relatively effective method (i.e., the quantum theory of atoms in molecules (AIM)) was used in this work to investigate hydrogen bonds of the normal DOX configuration in the S_0 state. Given the AIM theory, identification of a critical point (CP) and the existence of a bond path in equilibrium geometry are necessary and sufficient conditions for assigning an interaction between two primary atoms [43]. And the AIM analysis of the title compounds ensure the presence of an appreciable interaction in between the atoms concerned. The relevant AIM topological parameters involved in the optimized geometries show that the $\rho(r)$ at the bond critical point (BCP) for the S_0 -state 2-F geometry is around 0.037 a.u. respectively, which is close to the 0.040 a.u. (the maximum threshold value proposed by Popelier to ensure the presence of hydrogen bond [44]). It justifies the presence of intermolecular hydrogen bonds (O-H...F), which is further substantiated from the corresponding $\nabla^2\rho_c$ value (0.124) being well within the range (0.02 ~ 0.15 a.u.) [43, 44]. Therefore, it can be further demonstrated that hydrogen bond should be formed for 2-F in the S_0 state.

One thing is interesting that the fluoride anion-added deprotonation forming 2-A form via hydrogen bond can be used to interpret this kind of response mechanism of fluoride ion probe as mentioned in experiment [30], however, why other anions could

Table1: The theoretical binding energies (kcal/mol) for 2 chemosensor with different anions using the B3LYP/TZVP theoretical level in acetonitrile solvent

| F | Cl | Br | $H_2PO_4^-$ | CH_3COO^- | CN $^-$ | HSO_4^- | ClO_4^- | NO_3^- |
|-------|------|------|-------------|-------------|---------|-----------|-----------|----------|
| 21.54 | 8.49 | 6.48 | 6.05 | 6.49 | 8.46 | 7.38 | 9.51 | 8.14 |