



Full Length Article

Sensing mechanism for a fluorescent off–on chemosensor for cyanide anion

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ABSTRACT

In this article, the sensing mechanism of cyanide anion chemosensor 2-((2-phenyl-2H-1,2,3-triazol-4-yl)methylene)malononitrile (**M1**) has been investigated through the density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods. The theoretical results demonstrate that the reaction barrier of 13.02 kcal/mol means a favorable response speed of the chemosensor **M1** for cyanide anion. Cyanide anion attacks C=C double bond and hinders the ICT process from the malononitrile moiety to the fluorophore phenyl ring. The high viscosity of DMSO restrains the twisting of the group, inhibits the formation of the ICT state in the first excited state. Due to weak ICT character, the nucleophilic addition product shows the dramatic “off–on” fluorescence enhancement. Meanwhile, intramolecular charge transfer (ICT) mechanism accounts for how different solvents influence the fluorescence spectra. That is, more obvious ICT character of product in EtOH causes fluorescence quenching. The “reaction-based” recognition mode and large bond energy between **M1** and cyanide anion minimize the interference by other anions, such as F[−], AcO[−]. Thus, the chemosensor **M1** has a high selectivity for cyanide.

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1. Introduction

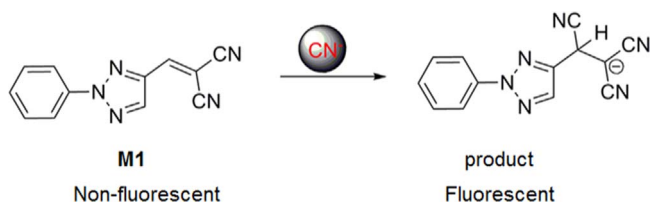
Cyanide anion is of vital importance in industrial processes, such as gold mining, metallurgy and the synthesis of nylon, fiber, and resin [1–3]. Nevertheless, cyanide anion is a sort of hypertoxic anion for human, which could be rapidly absorbed through digestive, respiratory, and cutaneous routes [4]. It could do great harm to brain and heart, and might even cause coma or death. Nevada and Arizona mining operators claim ‘safe concentrations’ of cyanide entering mill tailings ponds should be at or below 50 ppm [5]. And the legal range of the concentration of cyanide in drinking water is from 0.001 to 0.011 ppm in the United States and Canada [6]. Therefore, an accurate method to detect CN[−] becomes undoubtedly crucial.

In recent years, because fluorescent chemosensors have great advantages of low-cost, high sensitivity, good selectivity, rapid response and minimal toxicity to cells [7–9] compared to

titrimetric method [10], electrochemical method [11], and ion chromatography [12], fluorescent chemosensors have attracted considerable attention and have been applied for detection of anion in solution and analysis of a variety of biological events [13–15]. Among various fluorescent chemosensors, those based on nucleophilic addition reaction [16] have been widely concerned. Unlike the ones based on hydrogen-bonding interaction [17] and deprotonation [18], fluorescent chemosensors based on nucleophilic addition reaction can minimize the interference by other anions. In this background, a series of chemosensors based on nucleophilic addition of cyanide anion to alkene [19], boride [20], Schiff base [21], spiro-compound [22], carbonyl [23] have been frequently reported. At the same time, a variety of signaling mechanisms have been suggested for cyanide chemosensor, such as intramolecular charge transfer (ICT) [24], proton transfer (PT) [25] and excited state proton transfer (ESPT) [26]. In the process of sensing, cyanide anion would attack a functional group and cause the change of molecular configuration, charge redistribution and energy redistribution. Then it would bring about fluorescence response and spectroscopic change. Generally, “off–on” fluorescence sensors have obvious advantages over “on–off” ones, which

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Scheme 1. The proposed reaction mechanism of the chemosensor **M1** with CN^- .

have higher signal-to-noise ratio, recognizable optical changes and are suitable for naked-eye observation [27].

Recently, Chen and his coworkers [28] have designed and synthesized 2-((2-phenyl-2H-1,2,3-triazol-4-yl)methylene)malononitrile as a new highly selective fluorescent turn-on chemosensor **M1** for cyanide based on the special nucleophilic addition reaction (see Scheme 1). Upon photoexcitation, the chemosensor **M1** is at the “off” state without emission. After nucleophilic addition of cyanide anion to the chemosensor in DMSO, the product has an apparent fluorescence emission at the “on” state, which realizes the “off–on” signaling. Besides, they proposed a mechanism that addition of cyanide anion broke the conjugated C=C double bond and induced the fluorescence enhancement. However, the mechanism of the high selectivity of the chemosensor for cyanide anion and the sensing behaviors of the chemosensor in different solvents remained unclear. For further comprehension of the sensing mechanism, density functional theory (DFT) and time-dependent density functional theory (TDDFT) can be employed to clarify the fundamental aspects including the geometries and the photophysical properties of the investigated chemosensors [29–34]. For instance, based on this method, Li et al. [35] successfully described the anion-induced PT process via the intramolecular hydrogen bond of a fluorescent chemosensor for cyanide anion based on nucleophilic addition reaction and explained the sensing mechanism. Chen et al. [36] suggested that the excited state hydrogen-bonding and intramolecular charge transfer play an important role for the bi-thiol chemosensor DOC. Herein, we investigated the ground state and the first excited state properties of the relevant molecules involved in the cyanide sensing process of the chemosensor **M1** by employing the DFT/TDDFT methods. The frontier molecular orbitals, electronic transition energies and corresponding oscillator strengths have been calculated for these molecular systems and are taken into consideration in the explanation of sensing mechanism as well. The ^1H NMR spectra were also obtained and analyzed for **M1** and its anion product to confirm the molecular structures. Meanwhile, we still investigated the ICT process of the chemosensor and its nucleophilic addition product in two different solvents of DMSO and EtOH and investigated the solvent effects on sensing mechanism.

2. Theoretical methods

In this article, we used DFT/TDDFT methods and Gaussian 09 program to calculate all the structures including those of the ground state and the excited state. A number of functions, including B3LYP (the percentage of Hartree-Fock exchange is 20 %) [37–39], PBE/PBE (25 %) [40], TPSS/TPSS (25 %) [41], MPW1PW91 (42.8 %) [42], and M062X (54 %) [43], have been used in this study, among which the MPW1PW91 function gave the most satisfactory agreement with the experimental results. Therefore, the MPW1PW91 functional was used to study the properties of the ground state and the first excited state in the DFT/TDDFT methods. In addition, the long-range-corrected (LRC) functionals, i.e., CAM-B3LYP [44] and wB97XD [45], were used to correctly describe the properties of the

charge transfer excited state. The 6-31+G(d) [46,47] was chosen as the basis set for the optimized the ground state and the excited state optimizations. Given the range of the 6-31+G(d) basis set, the TZVP [48,49] basis set was suitable and chosen for calculating the bond energy between **M1** and CN^- , F^- , Cl^- , Br^- , AcO^- , OH^- , NO_3^- .

Considering that the solvent environment may influence the optical response of **M1** toward CN^- , chen et al. [28] investigated the sensing behaviors with the addition of CN^- to different solutions of **M1** in DMSO, THF, EtOH, CH_3CN and DMF. They found the fluorescence enhancement with the addition of CN^- in DMSO solvent but the fluorescence quenching in THF, EtOH, CH_3CN and DMF solvents. In order to understand the solvent effect on fluorescence sensing of **M1**, we conducted the theoretical investigation by employing the integral equation formalism (IEF) [50,51] version of polarizable continuum model (PCM) [52] for two different solvents, DMSO with the dielectric constant $\epsilon=46.8$ and EtOH ($\epsilon=24.8$).

All electronic structure calculations were completed with no constraints for symmetry, and all the local minima were confirmed with the absence of imaginary mode in vibrational frequency analysis calculations. We also located the transition state (only one imaginary frequency) by scanning the potential energy surface, and the intrinsic reaction coordinate (IRC) calculations have been performed to make sure that the transition state connects the intermediate and the proper products. Based on the above calculations, the free energy profile for the nucleophilic addition reaction was displayed with Gibbs free energy correction. For the purpose to compute the bond energy between **M1** and different anions, complexes consisting of **M1** and CN^- , F^- , Cl^- , Br^- , AcO^- , OH^- , NO_3^- have been optimized at the MPW1PW91/TZVP level with the consideration of basis set superposition error (BSSE) correction in energies using the counterpoise method [53]. Furthermore, the ^1H NMR spectra of **M1** and its nucleophilic addition product were calculated with the MPW1PW91 function and the 6-311+G(2d,p) basis set.

3. Results and discussion

3.1. Ground state structures

Fig. 1 shows the optimized ground state structures at the DFT/MPW1PW91/6-31+G(d) level of the chemosensor **M1** and its nucleophilic addition product with cyanide anion in DMSO. It can be clearly seen that **M1** has nearly planar conformation, which provides π -conjugation and ICT transition from the phenyl group to the dicyanovinyl moiety [24]. After the addition of cyanide, the C2–C4 bond is lengthened from 1.36 Å to 1.52 Å and the dihedral angle C1–C2–C3–N has changed to 15.75°. This indicates that the added CN^- reacts with **M1** in such a way that it breaks the C=C double bond of the dicyanovinyl group and cuts off the conjugated structure of the chemosensor **M1**.

To further understand the nucleophilic addition process, we displayed the free energy profile for the nucleophilic addition reaction in DMSO solvent (see Fig. 2). Using the reagent energy as a benchmark, all Gibbs free energies computed were relative energies (the raw data are given in Table 1). As seen, the formation of the intermediate is endergonic by 3.56 kcal/mol, and the reaction barrier for the C=C double bond cleavage and CN–C bond formation is 13.02 kcal/mol. The transition state indeed connects the intermediate and the product by performing the IRC calculations. In addition, the $\text{CN}\cdots\text{C}$ distance is shortened from 5.06 Å (in intermediate) to 2.32 Å (in transition state). The Gibbs free energy difference between the transition state and the reactants is 13.02 kcal/mol and such reaction barrier of 13.02 kcal/mol implies that the nucleophilic addition reaction could take place in the

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