Sensing mechanism of a new fluorescent probe for hydrogen sulfide: photoinduced electron transfer and invalidity of excited-state intramolecular proton transfer†

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It is of great significance for biological research to develop efficient detection methods of hydrogen sulfide (H₂S). When DFAN reacts with H₂S, 2,4-dinitrophenyl ether group acting as an electron acceptor generates a hydroxyl-substituted 2,4-dinitrophenyl ether group, resulting in the disappearance of photoinduced electron transfer (PET), and the new formed DFAH can be observed, while being accompanied by a significant fluorescence. In the present study, the PET sensing mechanism of probe DFAN and the excited state intramolecular proton transfer (ESIPT) process of DFAH have been explored in detail based on the density functional theory (DFT) and time-dependent density functional theory (TD-DFT) methods. Our theoretical results show that the fluorescence quenching of DFAN is caused by the PET mechanism, and the result of ESIPT mechanism is not due to the large Stokes shift fluorescence emission of DFAH. We also optimized the geometric structure of the transition state of DFAH. The frontier molecular orbitals and potential barrier show that the ESIPT process does not easily occur easily for DFAH. The enol structure of DFAH is more stable than that of the keto structure. The absence of the PET process resulted in the enol structure emitting strong fluorescence, which is consistent with the single fluorescence in the experiment. Above all, our calculations are sufficient to verify the sensing mechanism of H₂S using DFAN.

1. Introduction

H₂S, the smallest member among intracellular sulfur species, following nitric oxide (NO) and carbon monoxide (CO), has been identified as being the momentous gaseous signaling molecule.¹ ² H₂S can be biosynthesized from 3-mercaptopyruvate thiotransferase,³ and it plays critical roles in numerous biological processes such as the anti-inflammatory action,⁴ mitochondrial energy production, relaxation of blood vessels and the suppression of oxidative stress.⁵ Importantly, an imbalance of hydrogen sulfide in living systems causes a variety of diseases such as Huntington’s,⁶ liver cirrhosis,⁷ low intelligence,⁸ Down’s syndrome⁹ and Alzheimer’s diseases.¹⁰ The amphoteric effects of H₂S make it very important to monitor the concentration of H₂S in vitro and in vivo. Therefore, the real-time detection and analysis of H₂S are of considerable significance for disease diagnosis in the related biomedicine.

To date, numerous analysis approaches for tracing and measuring H₂S have been employed, including metal-induced precipitation,¹¹ ¹² electrochemical analysis,¹³ ¹⁴ gas chromatography¹⁵ ¹⁶ and fluorescence spectrometry.¹⁷ ²² In particular, due to high sensitivity,¹⁸ ²³ noninvasive property,²¹ real-time spatial imaging²² and high throughput,²² ²⁸ fluorescent techniques are extremely attractive, which have been considered to be a reliable detection technique. It is different from traditional analytical methods; the advances in fluorescent probes can sense H₂S inside the living cells, particularly, transduce the nanoscale biochemical processes into optical signals. In the biology field, based on the nucleophilic reaction, good reducibility towards azide compounds²⁶ ²⁹ and high binding affinity towards copper ions,¹¹ ¹³ fluorescent probes for hydrogen sulfide are used. Moreover, it is difficult to design fluorescent probes to sense H₂S from other biological mercaptans (biological nucleophile). It is worth noting that H₂S has the smaller steric hindrance than other biological mercaptans and is a stronger nucleophile under physiological conditions. For instance, comparing 100 μM H₂S with 1 mM GSH or cysteine, the selectivity of 7-azidocoumarin to H₂S was obviously better.²⁴

ESIPT, which takes place through intramolecular hydrogen bond X-H···Y, refers to a photochemical process in which a class of photoinduced enol-keto tautomerization occurs (Fig. S1†). Upon optical excitation, a new hydrogen bond X···H--
Y is formed, after H transfers from X to Y.\(^{49-51}\) Due to the significant Stokes shift emission, ESIPT has attracted considerable attention in the fields of solar energy capture, optical storage,\(^{36}\) dual band emission\(^{37}\) and green fluorescent proteins.\(^{38}\) There are numerous fluorescent compounds with ESIPT properties, such as 2,6-diazabindole,\(^{4,4'}\)dimethylamino-3-phenoyloxy-1,3-bis(2-pyridylimino)isoindoline and 3-hydroxyl-flavone derivatives.\(^{39-41,42}\) Recently, the hydrogen bond enhancement theory in the excited sate was proposed by Han et al.\(^{47,48}\) Based on the hydrogen bond strengthening theory and PET (Fig. S2†),\(^{45}\) a new novel fluorescent probe with the weak fluorescence was synthesized.\(^{49}\) The 2,4-dinitrophenyl ether group masks the cyan-appended benzene unit and causes fluorescence quenching. After sensing H\(_2\)S, the 2,4-dinitrophenyl ether group of DFAN was replaced by the hydroxyl group, forming a new compound DFAH and restoring the fluorescence characteristics (Scheme 1). In the experiment, the fluorescence quenching mechanism of the probe and the causes of the fluorescence emission of DFAH were not proposed.\(^{54}\) Thus, in this study, based on DFT and TD-DFT, we will investigate the fluorescence quenching of DFAN (probe) and the ESIPT of DFAH (reaction product). We have studied the variation of the hydrogen bond strength by analyzing the geometric parameters of hydrogen bond, infrared vibration spectrum (IR) and reduced density gradient (RDG). In order to study the proton transfer (PT) process, the potential energy curves of the ground and excited states of DFAH are constructed. The charge distribution is analyzed by the potential energy curves of the ground and excited states of DFAH using B3LYP function (Hybrid Becke, 3-parameter, with 20% Hartree–Fock exchange energy) with the TZVP basis set.\(^{52,53}\) In order to accurately grasp the hydrogen bonding behavior, the dispersion term is also considered. The integral equation formalism (IEF) version of the polarisable continuum model (PCM) is used to simulate the experimental environment.\(^{46}\) In order to determine the local minimum of the ground state (S\(_0\)) and the first excited state (S\(_1\)), the vibration frequency of the optimized structure is analyzed. The potential energy curves are scanned in S\(_0\) and S\(_1\) states by fixing the bond length of the hydroxyl group (H\(_2\)-O) in the DFAH molecule and restoring the fluxion energy quenching mechanisms. We have used the Multiwfn software to analyze Mulliken’s charge situation and to study the type of hydrogen bond interaction by applying RDG function using the Multiwfn software.\(^{40,44}\) The formula is as follows:

$$\text{RDG}(r) = \frac{1}{2(3\pi^2)^{1/3}} \frac{\Delta \rho(r)}{\rho(r)^{1/3}}$$

The weak interactions depend on the \(\lambda_2\) of eigenvalue and the \(\rho\) of electron density in view of Bader’s atoms-in-molecules (AIM) theory. The relationship between them is as follows:

$$\Omega(r) = \text{sign}(\lambda_2(r))\rho(r)$$

In order to ascertain B3LYP/TZVP, we have used other functionals and basis set to achieve the electronic spectrum information, and the details are listed in Table 1.

### 2. Computational details

In this study, theoretical calculations were conducted via DFT/TDDFT and Gaussian 16 program suite.\(^{25}\) The geometric structures and reaction pathways are calculated without constraint using B3LYP function (Hybrid Becke, 3-parameter, with 20% Hartree–Fock exchange energy) with the TZVP basis set.\(^{52,53}\) In order to accurately grasp the hydrogen bonding behavior, the dispersion term is also considered. The integral equation formalism (IEF) version of the polarisable continuum model (PCM) is used to simulate the experimental environment.\(^{46}\) In order to determine the local minimum of the ground state (S\(_0\)) and the first excited state (S\(_1\)), the vibration frequency of the optimized structure is analyzed. The potential energy curves are scanned in S\(_0\) and S\(_1\) states by fixing the bond length of the hydroxyl group (H\(_2\)-O) in the DFAH molecule and restoring the fluxion energy quenching mechanisms. We have used the Multiwfn software to analyze Mulliken’s charge situation and to study the type of hydrogen bond interaction by applying RDG function using the Multiwfn software.\(^{40,44}\) The formula is as follows:

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### 3. Results and discussion

#### 3.1 Geometric structures, IR vibrational spectra and RDG isosurfaces

We have optimized the S\(_0\) and S\(_1\) states of DFAN and DFAH (enol and keto forms) geometries at the B3LYP/TZVP level. The optimized geometric structures are shown in Fig. 1. In Table 2, we also listed the related bond lengths and angles of enol, keto and transition state structures of DFAH. For DFAH-enol, the O\(_1\)-H\(_2\) bond length is 0.987 Å in the S\(_0\) state, which increases to 0.993 Å

| Method     | DFAN-abs | CAM-B3LYP | M06-2X | B1B95 | PBEPBE | WB97XD | Exp. |
|------------|----------|-----------|--------|-------|--------|--------|------|
| B3LYP      | 382(0.006) | 325(0.003) | 338(0.001) | 347(0.014) | 345(0.253) | 429(0.226) | 314(1.105) | 405   |
| DFAH(N)-abs| 362(1.233) | 318(1.193) | 313(1.266) | 345(1.253) | 429(0.226) | 314(1.105) | 314(1.105) | 405   |
| DFAH(N)-flu | 437(1.829) | 398(1.832) | 390(1.866) | 420(1.843) | 494(0.535) | 392(1.825) | 405   |

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in the S₁ state, and the bond length is growing 0.006 Å; the hydrogen bond length of H₂–O₃ decreases from 1.741 Å in the S₀ state to 1.693 Å in the S₁ state. Moreover, the bond angle of O₁–H₂–O₃ changes from 146.90° in the S₀ state to 149.50° in the S₁ state, which extends by 2.60°. It can be seen from the calculation results that the intramolecular hydrogen bond is strengthened in the S₁ state. In particular, the DFAH-keto geometry in the S₀ and S₁ states are also optimized. Unexpectedly, after optimizing the S₀ state, the stable structure is not obtained because of the high energy. In Table 2, we listed main bond lengths and angles of DFAH-keto in the S₁ state. The change in the geometric structures of DFAH indicates that the photo excitation dominates the enhancement for the hydrogen bonds. Then, we also calculated the electron energies of DFAN and DFAH, which are listed in Table 2.

As shown in Fig. 2, the infrared vibration spectra of the main hydrogen bonds involved in the S₀ and S₁ states have been computed. The IR vibration frequency of H₂–O₃ is 3342 cm⁻¹ and 3218 cm⁻¹ in S₀ and S₁ states, respectively. In particular, from the S₀ state to S₁ state, the IR vibrational frequency of the H₂–O₃ bond of DFAH has a red-shift of 124 cm⁻¹. Obviously, in the S₁ state, the intramolecular hydrogen bond is strengthened.

The RDG function has been used to further verify hydrogen bond properties. In Fig. 3 the color scale is blue, green and red from left to right, representing strong attraction, van der Waals force and strong mutual exclusion, respectively. The RDG isosurface range is from −0.04 to 0.02, and the isosurface of the hydrogen bond is blue. In the AIM theory, ρ(r) at the critical point of weak interactions is one of the important indexes to measure the strength of interaction, and there is a positive correlation between its value and bond strength. The larger ρ(r) of the blue region and sign(∇²ρ) = −1, the stronger and more attractive weak interaction appears. In Fig. 3, it can be directly observed that the stronger the weak hydrogen bond interaction, the bluer the isosurface is, which proves the phenomenon of hydrogen bond enhancement in the excited state.

### 3.2 Potential energy curves of the proton transfer reactions analyses

Moreover, for the lack of analyzing PT and ESIPT processes, we further plotted the potential energy curves (PECs) of the S₀ and S₁ states along the H₂–O₃ bond. As shown in Fig. 4, along the

| Table 2 | Calculated primary bond lengths (Å) and angles (°) for the enol, keto and transition-state configurations of DFAH in the S₀ and S₁ states |
|---------|------------------|------------------|------------------|
| Parameter | S₀   | S₁   | Keto (S₁) | Transition-state (S₁) |
| O₁–H₂   | 0.987 | 0.993 | 1.618     | 1.219                  |
| H₂–O₃   | 1.741 | 1.693 | 1.016     | 1.224                  |
| δ(O₁–H₂–O₃) | 146.90 | 149.50 | 150.10     | 158.40                  |

Fig. 1 Optimized geometries of DFAN and DFAH in the S₀ and S₁ states. (a) and (b) The S₀ states of DFAN and DFAH-enol, respectively. (c)–(e) The S₁ states of DFAN, DFAH-enol and DFAH-keto, respectively. The labeling of atomic color: C: blue; H: gray; O: red; N: purple.

Fig. 2 Calculated IR spectra of the normal form of DFAH in the relevant spectral region of the O₁–H₂ stretching band in the S₀ and S₁ states.

Fig. 3 The visual diagram of the RDG isosurface and color gradient axis. Blue indicates strong attractive interactions, and red indicates a strong bond-free overlap.
reaction pathway, the energy of DFAH system rises in the S0 state in the S0 state. Thus, the PT process is endothermic, and keto con...5.49 kcal mol−1/C01, and is higher than the corresponding energy of the inverse reaction, which is only 2.24 kcal mol−1/C01. In the S1 state, DFAH-keto is less stable than DFAH-enol, which can be easily converted into an intramolecular proton transfer enol configuration. Therefore, fluorescence can only be emitted by the enol configuration rather than the keto form, which is also consistent with the conclusion of the experiment.

3.3 Electron spectral analysis and charge population

The absorption of DFAN and DFAH and the emission spectra of DFAH have been measured in the experiment. In order to compare with the experimental data, we calculated the absorption and emission spectra of DFAN and DFAH at the B3LYP/TZVP level (Fig. 5). In addition, the corresponding oscillator strengths for the orbital transitions and CI values involved are also listed (Tables 3 and 4). The main absorption band of DFAN is located at 382 nm, which is relatively consistent with the experimental absorption peak (350 nm). The calculated absorption peak of DFAH is located at 380 nm, which is close to the experimental value (405 nm). Kasha’s rule points out that the fluorescence of the condensed matter is from S1 state. After light excitation, the calculated normal fluorescence peak of DFAH is located at 437 nm. Thus, the calculated results of the absorption spectrum and emission spectrum are in good agreement with the experiment.

As shown in Fig. 6, the negative charge on O1 changed from −0.278 (S0) to −0.277 (S1), and from −0.399 (S0) to −0.408 (S1) for O3, respectively. Therefore, for DFAH-enol, the hydrogen bond is strengthened in the excited state. In order to analyze the hydrogen bonding effect on the whole electronic structure and to predict the possible electrophilic and nucleophilic reaction sites, the intramolecular electrostatic potential (MEP) was calculated. At the TD-B3LYP/TZVP level, the electrostatic potential isosurfaces on the excited state of DFAN and DFAH are plotted, as shown in Fig. 7. Different colors on the surface of the electrostatic potential mean different values. The positive electrostatic potential is represented in the red region, and the negative electrostatic potential is represented in the blue area. The H2 atom is in the hydrogen bond donor position, which represents the positive electrostatic potential. The negative potential on the O1 and O3 atoms indicate that they are the obvious hydrogen-bond acceptor sites.

3.4 Frontier molecular orbital (FMO) analysis and sensing mechanism

In general, the transition of electrons from one orbital to another after photo excitation accounts for induced charge redistribution. The calculated wavelengths, corresponding oscillator strength (f), compositions, and experimental values

| Compound | Electronic transition | Energy (nm eV−1) | Experimental absorption (nm eV−1) | f           | Composition     | CI     |
|----------|-----------------------|------------------|----------------------------------|-------------|-----------------|--------|
| DFAN     | S0–S1                | 382/3.25         | 350/3.54                         | 0.0062      | HOMO → LUMO     | 89.6%  |
|          | S0–S2                | 369/3.36         |                                  | 0.0156      | HOMO → LUMO+1   | 8.5%   |
|          | S0–S3                | 362/3.43         |                                  | 1.5257      | HOMO → LUMO+2   | 95.6%  |
| DFAH(N)  | S0–S1                | 362/3.43         | 405/3.06                         | 1.2227      | HOMO → LUMO     | 96.6%  |

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are listed in Tables 3 and 4, while the molecular orbitals are shown in Fig. 8. As shown in Table 3, the dominant transition of DFAN is the S0 → S1 transition, with the oscillator strength of 0.0062 lying at 350 nm, which is mainly assigned to the HOMO → LUMO (89.6%) transition with smaller components of HOMO → LUMO+1. The transition for HOMO → LUMO+2 is the local transition of ππ*-type between the cyanogroup cyan-appended benzyne unit and the carbonyl benzene unit, and the other two transitions are from the cyanogroup cyan-appended benzyne unit and the carbonyl benzene unit to the 2,4-dinitrophenyl ether group, respectively, with complete charge separation, as shown in Fig. 8. In particular, the energy of LUMO and LUMO+1 orbitals for the 2,4-dinitrophenyl ether group is located between HOMO and LUMO+2 orbitals for the cyanogroup cyan-appended benzyne unit and carbonyl benzene unit. Briefly, the complete charge separation from the cyanogroup cyan-appended benzyne unit and the carbonyl benzene unit to the 2,4-dinitrophenyl ether group in the relaxation process fits perfectly with the definition of the PET mechanism, which well-explains the fluorescence quenching effect. It can also be seen from Table 3 that the S0 → S1 transition for DFAH-enol is predicted at about 362 nm with an oscillator strength of 1.2292, and the process from HOMO to LUMO is assigned as a dominant ππ*-type transition. As shown in Fig. 8, the distribution of MO is non-localized on the DFAH conjugated system, indicating that the S1 state is the local excited state. Thus, the enol type of DFAH exhibits fluorescence emission.

As shown in Table 4, the S1 state for DFAN is a dark state, and its oscillator strength is 0.0072. On the contrary, the S3 → S0 transition for DFAH (99.3%) transition with smaller components of HOMO → LUMO+1. The transition for HOMO → LUMO+2 is the local transition of ππ*-type between the cyanogroup cyan-appended benzyne unit and the carbonyl benzene unit, and the other two transitions are from the cyanogroup cyan-appended benzyne unit and the carbonyl benzene unit to the 2,4-dinitrophenyl ether group, respectively, with complete charge separation, as shown in Fig. 8. In particular, the energy of LUMO and LUMO+1 orbitals for the 2,4-dinitrophenyl ether group is located between HOMO and LUMO+2 orbitals for the cyanogroup cyan-appended benzyne unit and carbonyl benzene unit. Briefly, the complete charge separation from the cyanogroup cyan-appended benzyne unit and the carbonyl benzene unit to the 2,4-dinitrophenyl ether group in the relaxation process fits perfectly with the definition of the PET mechanism, which well-explains the fluorescence quenching effect. It can also be seen from Table 3 that the S0 → S1 transition for DFAH-enol is predicted at about 362 nm with an oscillator strength of 1.2292, and the process from HOMO to LUMO is assigned as a dominant ππ*-type transition. As shown in Fig. 8, the distribution of MO is non-localized on the DFAH conjugated system, indicating that the S1 state is the local excited state. Thus, the enol type of DFAH exhibits fluorescence emission.

Table 4  Comparison of experimental and calculated emissions at the TD-DFT/B3LYP/TZVP level, including the energy (nm eV⁻¹), oscillator strength (f) and orbital transition (OT) contributions to the electronic exited states (CI)

| Compound | Electronic transition | Energy (nm eV⁻¹) | Experimental emission (nm eV⁻¹) | f    | Composition  | CI  |
|----------|-----------------------|------------------|-------------------------------|------|--------------|-----|
| DFAN     | S1→S0                | 510/2.43         |                               | 0.0072 | LUMO → HOMO | 99.3% |
|          | S2→S0                | 412/3.00         |                               | 0.6382 | LUMO+1 → HOMO | 76.9% |
|          | S3→S0                | 405/3.06         |                               | 1.2562 | LUMO+2 → HOMO | 21.2% |
|          | S4→S0                | 397/3.12         |                               | 0.0016 | LUMO+1 → HOMO | 76.4% |
|          |                      |                  |                               |      | LUMO+1 → HOMO−8 | 21.7% |
| DFAH(N)  | S1→S0                | 437/2.34         | 510/2.43                      | 1.8292 | LUMO → HOMO | 99.2% |

Fig. 6  Mulliken charge distribution of molecule DFAH in S0 and S1 states. The numbers in the parentheses represent the S0 state.

Fig. 7  The electron density isosurface mapped with the molecular electrostatic potential surface (MEPs) for DFAN and DFAH.

Fig. 8  Calculated frontier molecular orbitals involved in the absorption of DFAN and DFAH based on B3LYP/TZVP levels (HOMO, LUMO, LUMO+1 and LUMO+2).
emission with a large oscillator strength of 1.2562 generates a ππ transition character assigned from the 2,4-dinitrophenyl ether group to the cyanogroup cyan-appended benzyne unit and the carbonyl benzene unit, as shown in Fig. 9. The fluorescence quenching effect is demonstrated by complete charge separation; moreover, the accuracy of the previous experimental and theoretical results is verified. Herein, the S1 → S0 transition of DFAH (shown in Fig. 9) corresponding to LUMO → HOMO still presents the local transition of electron density and consequently the strong fluorescence emits.

In general, the details of the sensing mechanism of this probe are as follows: the first and second excited states of DFAN are dark, and the PET process occurs with the complete charge separation between the cyanogroup cyan-appended benzyne unit, carbonyl benzene unit and 2,4-dinitrophenyl ether group, resulting in the disappearance of fluorescence. After the addition of H2S, the sulfur solution reaction of DFAN is triggered by a nucleophilic reaction, the group is eliminated, and DFAH is obtained. The S0 state of DFAH is the LE state, which produces strong fluorescence. The probe of DFAN is sensitive to discern hydrogen sulfide based on changes in the non-fluorescence signals.

4. Conclusions

In this study, the sensing mechanism of probe to H2S is studied via DFT and TDDFT methods. The structure of the S0 state and the S1 state of DFAN and DFAH were optimized, and the variation of the intramolecular hydrogen bond after light excitation was discussed by analyzing the bond length, bond angle, infrared spectrum and RDG isosurfaces, which indicate that DFAH-enol can be strengthened by the intra-HB in the excited state. The potential curve and the transition state show that both PT and ESIPT do not occur and the enol is a more stable configuration. The fluorescence change, which is the basis for the probe to detect H2S, can be explained by the PET sensing mechanism. Furthermore, the PET process caused the fluorescence quenching pathway of DFAN, and the ESIPT process of DFAH is ineffective. It is hoped that the results of our study will have some guiding significance for the design of new fluorescence probes in the future.

Conflicts of interest

There are no conflicts to declare.

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