TD-DFT investigation on anion recognition mechanism of anthraldehyde-based fluorescent thiosemicarbazone derivatives

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Received: 4 April 2022 / Accepted: 14 July 2022 / Published online: 27 July 2022
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Abstract
The mechanism of host–guest interaction of receptors towards fluoride ion has been investigated using computational methods. To distinguish the effect of aromaticity in host–guest interaction, we investigated unsubstituted (ATSC) and phenyl-substituted (APTSC) anthracene thiosemicarbazones towards different ions. In the ground state of receptor-fluoride complex, the added fluoride ion made hydrogen bond through N−H…F…H−N, whereas the intramolecular hydrogen bonding was through F−H…N in the excited state of receptor-fluoride complex. Experimental absorption and emission spectra were well reproduced by the calculated vertical excitation energies. The transition state (TS) calculations were performed to understand the thermodynamic features and mechanism of host–guest interaction. The natural bond orbital analyses show that the second perturbation energy for donor–acceptor interaction of F− with hydrogen is more than 300 kcal/mol−1 at the excited state of receptor-fluoride complex, which indicates the strong single bond between fluoride and hydrogen atom. The PES scan confirms that deprotonation took place at the excited state of receptor-fluoride complex. The results indicate the excited-state proton transfer (ESPT) process from N–H group nearby the anthracene moiety. The APTSC is a better chemosensor than ATSC. This infers that the aromaticity will increase the efficiency of fluorescence receptor towards fluoride ion.

Keywords TDDFT · TS · NBO · PES · ESPT

Introduction
In view of the fact that ions play a major role in many chemical and biological process, designing ion selective molecular sensors is a challenging entity in supramolecular chemistry [1, 2]. Fluoride ion is a necessary trace element in the human body, which has vital role in a broad range of chemical, biological and environmental processes [3–5]. The excessive absorption of fluoride ion can cause fluorosis of bone, immune system disruption, urolithiasis, kidney damage and cancer [6]. It has one of the most perplexing ion recognition, due to its high electronegativity and hydration enthalpy [7]. The detection of fluoride ion can prevent and cure dental problems and osteoporosis [8]. There are many experimental reports as molecular optical sensors, whilst very few reports of selective fluorescence fluoride sensor are seen, due to the surface charge density and similar basicity of fluoride ion with other ions [9–12].

The theoretical characteristic and the detailed investigation of host–guest mechanism is perilous for fluorescent chemosensor. Based on the experimental results, researchers have proposed several categories of signalling mechanisms for fluoride chemosensor, such as photo-induced electron transfer (PET), intramolecular charge transfer (ICT), excimer and exciplex formation, metal ligand charge transfer (MLCT) and excited-state intramolecular proton transfer. [13–16]. Amongst these, the ESPT performs dynamic role in determining the photophysical and photo-chemical properties of organic molecules, which usually shows dual fluorescence behaviour [17, 18]. The PET mechanism was used to describe the hydrogen bonding, in which enhancing or quenching corresponds to red or blue shifts in the absorption spectra [19–21]. Iverson and others demonstrated that charge transfer and π-π stacking interactions between a colourless...
guest and electron-rich aromatic rings produce coloured donor–acceptor complexes [22].

Amongst the chemosensors, fluorescent chemosensors have many advantages such as ease of detection, low cost, high sensitivity and biologically appropriate diagnostic tools. Recently, Udayakumari et al. reported APTSC as selective chemosensor for fluoride ion over other anions [23]. Taking this system as an example, herein we investigated the sensing mechanism of fluoride ion theoretically. The sensing mechanism of ATSC receptor was also investigated to evaluate the effect of aromatic group in sensing process. By using computational methods, we investigated the host–guest interaction of fluorescent thiosemicarbazones with anthraldehyde as receptors, which contain electron-rich aromatic rings. Furthermore, by comparing the results, we suggested that the aromaticity of the receptor will enhance the chemosensing behaviour.

**Computational methods**

The hybrid density functional theory (DFT) and Time Dependent DFT (TD-DFT) calculations were performed using Gaussian 09 programme. Optimizations have been carried out without symmetry constraints. The ground state of the receptors, receptor-fluoride complexes and deprotonated receptors were optimised using the hybrid B3LYP functional with 6-31G(d,p) basis set, whereas the optimization of excited state geometries were calculated using Handy and co-workers long-range modified version of B3LYP casted as Coulomb-attenuating method (CAM) hybrid function with long-range corrections (CAM-B3LYP) [24]. The vertical state excitation calculations were employed for the calculation of excitation state. The Polarised Continuum Model (PCM) with dimethyl sulfoxide solvent (dielectric constant = 46.826) calculation was implemented throughout the steps to include the solvent effect. To verify the ground state and excited state, optimised geometries are in local minima, and the vibrational frequency calculations were run for all the optimised structures. In order to understand and verify the nature of transition state and intermediate structures, the transition state (TS) and intrinsic reaction coordinate (IRC) calculations were carried out. The natural bond orbital (NBO) analyses were carried out at ground state and excited state structures of receptor-fluoride complexes to understand the charge distribution and energy of bonding and anti-bonding orbitals. The second order Fock matrix calculations were carried out to estimate the host–guest interactions [25, 26]. The ESPT mechanism was confirmed with potential energy surface (PES) analysis [27].

**Results and discussion**

**Geometric studies**

To examine the sensing process for fluoride anion, the ground state and excited state geometries of the chemosensors (APTSC and ATSC), receptor-fluoride complex has been investigated in detail. The optimised geometric structures of APTSC and ATSC receptors and receptor-fluoride complexes (APTSC − F and ATSC − F) at the ground state and excited state are as shown in Figs. 1 and 2. The important structural parameters of ATSC and APTSC are listed in Tables 1 and 2. The vibrational frequency of the ground state structures was positive; hence, all the structures are in local minima. The ground state energies of ATSC and APTSC are −43.34 and −51.824 eV kcal/mol⁻¹, respectively,
Table 1 The dominant structure parameters of APTSC and APTSC-F complex in the optimised geometries

| Bond parameter | APTSC | APTSC* | APTSC-F | APTSC-F* |
|----------------|-------|--------|---------|---------|
| N1-H1          | 1.01  | 1.01   | 1.08    | 1.02    |
| N2-H2          | 1.02  | 1.02   | 1.07    | 1.51    |
| C3=N3          | 1.28  | 1.28   | 1.29    | 1.32    |
| N3-N2          | 1.34  | 1.34   | 1.33    | 1.29    |
| C1-N1-C2       | 130.90| 130.05 | 133.58  | 134.05  |
| C4-C3=N3       | 128.13| 130.72 | 129.08  | 128.10  |
| N2-N3-C3       | 122.31| 122.86 | 121.42  | 119.07  |
| C5-C4-C3-N3    | 115.99| 139.63 | 121.30  | 159.81  |
| C5-C4-N3-N2    | 34.39 | 10.19  | 2.530   | 32.06   |
| S-C2-N2-N3     | 0.16  | 5.22   | 1.19    | 2.55    |
| F-H2           | —     | —      | 1.50    | 0.99    |
| F-H1           | —     | —      | 1.46    | 1.91    |
| F-H2-N         | —     | —      | 153.85  | 163.42  |

Table 2 The dominant structure parameters of ATSC and ATSC-F complex in the optimised geometries

| Bond parameter | ATSC | ATSC* | ATSC-F | ATSC-F* |
|----------------|------|-------|--------|---------|
| N1-H1          | 1.01 | 1.01  | 1.01   | 1.01    |
| N2-H2          | 1.02 | 1.01  | 1.40   | 1.43    |
| C2=N3          | 1.28 | 1.30  | 1.29   | 1.32    |
| N3             | 1.35 | 1.33  | 1.34   | 1.30    |
| C1-C2-N3       | 127.83| 130.88| 129.795| 127.623 |
| N2-N3-C2       | 120.884| 121.043| 117.114| 119.735 |
| C4-C3-C2-N3    | 66.059| 141.483| 120.043| 156.869 |
| C3-C2-N3-N2    | 1.248| 8.725 | 1.837  | 28.680  |
| N1-C1-N2-N3    | 2.242| 1.673 | 179.21 | 179.60  |
| S-C1-N2-N3     | 177.96| 178.91| 1.037  | 1.099   |
| F-H2           | —     | —      | 1.05   | 0.99    |
| F-H1           | —     | —      | 1.97   | 1.98    |
| F-H2-N         | —     | —      | 165.99 | 163.56  |

Absorption and molecular orbital analysis

The absorption spectral studies were carried out for receptors and receptor-fluoride complexes to understand the change in optical behaviour in the host–guest process. The molecular orbitals involved in the major electronic transitions with the largest oscillator strength are shown in Figs. 3 and 4. Theoretical calculations predict six absorption transitions for each compound, and the dominant absorption transition of APTSC, APTSC-F complex, ATC and ATSC-F complex are given in Tables 3 and 4. The intense absorption transition for APTSC is calculated at 367.48 nm, with large oscillating strength 0.2957, which is assigned as π→π* transition from the highest occupied molecular orbital (HOMO, H) to the lowest unoccupied molecular orbital (LUMO, L). In HOMO, the electron delocalized over anthracene moiety and imine group, whereas in LUMO, the electron cloud only delocalized at anthracene moiety. The second dominant absorption peak was at 310 nm, which corresponds to HOMO, third lowest unoccupied molecular orbital (LUMO + 2, L + 2), where the electron delocalized throughout the anthracene moiety. Whilst in APTSC-F complex, the absorption peak at 367 nm decreases and accompanies with the formation of a new band at 374 nm. The high oscillating strength and percentage π→π* transition were between HOMO to...
LUMO. In the HOMO of APTSC-F complex, the electron was delocalized only on imine group, whereas the electron was delocalized on anthracene moiety in LUMO.

In the case of ATSC, the high oscillated frequency wavelength at 411 nm with 3.0136 eV energy. The high percentage orbital transition was in between HOMO-1 and LUMO. The second major absorption transition was at HOMO to LUMO orbitals. In HOMO, the electrons delocalized in anthracene moiety and thiosemicarbazide group, whilst the HOMO-1 and HOMO-2 orbitals had electron cloud only on imine group, not in anthracene moiety, whereas in LUMO, LUMO + 1 and LUMO + 2 orbitals, the electron clouded only at anthracene moiety. The resulting electron cloud rearrangement is cause for the changes in the photophysical properties of receptor in the host–guest interaction. Figure 5 displays the calculated orbital energies of APTSC and APTSC-F complex. The energy gap between HOMO and LUMO orbitals in emission profile is higher than that of absorption profile. The complete charge separation from thiosemicarbazone group to anthracene in the relaxation process is in good accordance with the definition of PET. The absorption profiles are calculated using the Gaussian models and compared with the experimental results.

Emission spectral analysis

To confirm the ESPT mechanism in chemosensing, the geometries at the ground state and excited states of both receptors (ATSC and APTSC) and receptor-F complexes were optimised. The fluorescence spectral analysis was performed in detail using six step vertical excited energy calculations. The emission spectra of APSTC and APSTC-F complex are shown in Fig. 6. The ground state energies of ATSC and APTSC are $-739,686.293$ and $-884,475.883$ kcal/mol$^{-1}$, respectively, whereas the energies are very much higher in excited state, which are found to be $-802,369.249$ and $-947,168.814$ kcal/mol$^{-1}$ for ATSC-F and APTSC-F complexes, respectively. It exhibits in S7 that the receptor-fluoride complexes have less oscillator strength than corresponding receptors. The experimental emission peak of APTSC and APTSC-F complex was observed at 475 and 495 nm, whereas the calculated fluorescence peak was observed at 461 and 478 nm, respectively. The receptors ATSC and APTSC show low energy emission peak at 455 and 461 nm, respectively, which assign to $\pi-\pi^*$ transition of anthracene moiety, whereas the corresponding fluoride complexes, such as ATSC-F and APTSC-F, exhibit very intense emission peaks at 464 and 478 nm, respectively. The red shift in the fluorescence peaks after the addition of fluoride ion confirms sensing behaviour of the receptors. The intense red shift in the fluorescence spectra infers that the presence of fluoride ion extends the conjugation behaviour of receptors. For both receptors (ATSC and APTSC), the intense
emission transitions are from LUMO to HOMO, where the electron density delocalized over anthracene moiety, and consequently the strong fluorescence emits.

**Transition state calculations**

In order to capture the dynamic features of the sensing process, we evaluated the Gibbs free energy profile in DMSO medium. The transition state and intermediate structures were calculated, which are as shown in Figs. 7 and 8. In the transition state and intermediate structures, the fluoride ion interacts with receptor via hydrogen boning. The relaxation of the transition state toward the intermediate and the products by IRC calculations did not detect any intermediates, which revealed that the host–guest process is SN2 type of reaction. The sensing process of ATSC and APTSC with fluoride ion had the free energy (ΔG) of 177.17 and 186.22 kcal/mol. The more negative value of ΔG was the reason for quick response of APTSC than ATSC towards fluoride ion. In the transition state, the bond distance between

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**Table 3** The low-lying absorption energies for APTSC

| Energy (eV) | Wavelength (nm) | Oscillation frequency $f$ | Percentage | Composition |
|-------------|-----------------|---------------------------|------------|-------------|
| APTSC       |                 |                           |            |             |
| 3.3739      | 367.48          | 0.2957                    | 100.00     | H $\rightarrow$ L |
| 3.7167      | 333.59          | 0.0014                    | 41.67      | H-1 $\rightarrow$ L+1 |
| 3.9941      | 310.42          | 0.0067                    | 53.45      | H $\rightarrow$ L+2 |
| 4.5069      | 275.10          | 0.1666                    | 37.48      | H-1 $\rightarrow$ L |
| 4.6459      | 266.87          | 0.2275                    | 38.84      | H-2 $\rightarrow$ L+1 |
| 4.6696      | 265.51          | 0.0297                    | 35.07      | H $\rightarrow$ L+1 |

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**Table 4** The low-lying absorption energies for APTSC-F complex

| Energy (eV) | Wavelength (nm) | Oscillation frequency $f$ | Percentage | Composition |
|-------------|-----------------|---------------------------|------------|-------------|
| APTSC-F     |                 |                           |            |             |
| 3.3150      | 374.01          | 0.2795                    | 85.78      | H $\rightarrow$ L |
| 3.7551      | 330.18          | 0.0034                    | 35.64      | H-1 $\rightarrow$ L+1 |
| 3.9613      | 312.99          | 0.0315                    | 27.16      | H $\rightarrow$ L+2 |
| 4.0145      | 308.84          | 0.0701                    | 31.68      | H-2 $\rightarrow$ L |
| 4.4086      | 281.23          | 0.2229                    | 27.54      | H-2 $\rightarrow$ L+1 |
| 4.4764      | 276.97          | 0.0011                    | 31.03      | H-1 $\rightarrow$ L |

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**Fig. 5** The energy gap between HOMO and LUMO orbitals of ATSC, ground state ATSC-F and excited state ATSC-F complex

**Fig. 6** Emission spectra of APSTC and APSTC-F complex
fluoride ion and N2-H2 and F-H2 was about 1.45 and 1.02 Å, which revealed the fluoride ion has higher hydrogen bond with hydrogen atom than in ground state and results the transition state in higher energy state. The binding constant \( (K_a) \) of the receptor (APTSC and ATSC) with fluoride ion was calculated (In \( K_a = \frac{-\Delta G}{RT} \) where, \( R \), \( T \) and \( K_a \) are the universal gas constant, temperature and the binding constant, respectively). The binding constant of APTSC and ATSC towards fluoride ion was found to be 0.930 and 0.927 M\(^{-1}\), respectively.

### Natural bond orbital (NBO) calculation

Natural bond orbital (NBO) analysis provides the most accurate possible ‘natural Lewis structure’ picture, because all orbital details are mathematically chosen to include the highest possible percentage of the electron density. Further confirming the ESPT process and the deprotonation of H2 from receptor via hydrogen bond, the NBO analysis was carried out at the ground state and excited state of receptor-fluoride complex. The binding energy (\( \Delta E \)) between the binding sites of fluoride ion and the residue for receptor plays an important role in revealing the ability for fluoride anion to attach proton. The binding energies between the two segments separated by H1 – F and H2 – F of receptor-fluoride complexes were calculated. The second-perturbation energy of APTSC with fluoride ion suggested that the formation of intermolecular hydrogen bond between host and guest molecules and the energy details are listed in Table 5. The natural atomic hybrid calculation gave the bond order on each hybrid atoms. The hybridisation with single bond between N25 – H41 and N27 – H42 is listed in S3. In ground state APTSC-F complex, sp3 nitrogen was hybridised to ‘s’ hydrogen, but this bond was not in excited state. Resulting, a strong host–guest interaction between fluoride ion and APTSC occurred, which can be treated by the second-perturbation energy \( E(2) \). The interaction between host and guest can be explained by using second perturbation energy, which has been calculated using the equation, \( E(2) = \Delta E = \frac{q_i^2 F_{ij}}{\epsilon_i - \epsilon_j} \), where \( E(2) \) is the second perturbation energy, \( F_{ij} \) is the off-diagonal element in the NBO Fock matrix, \( q_i \) is the donor orbital occupancy and \( \epsilon_i \) and \( \epsilon_j \) are orbital energies. The NBO characters in ground state and excited state of ATSC-F complex are given in the S4. The \( \sigma-\sigma^* \) and \( n-\sigma^* \) host–guest interactions were seen at the ground state and excited state of ATSC – F and APTSC – F complexes. In the ground state, two modes of interactions were presented via fluoride to N25 – H41 and N27 – H42, whereas the excited state had only one interaction, which was via fluoride ion with H41. In the ground state of

### Table 5 The second-perturbation energy \( E(2) \) (kcal/mol\(^{-1}\)) of host–guest interaction with respect to receptor-fluoride complexes in ground state and excited state

| Donor (i) | Acceptor (j) | Interaction | \( E(2) \) | Donor (i) | Acceptor (j) | Interaction | \( E(2) \) |
|-----------|-------------|-------------|-------------|-----------|-------------|-------------|-------------|
| APTSC-F (ground state) | APTSC-F* (excited state) | | | | | | |
| CR F | BD* N25-H41 | \( \sigma-\sigma^* \) | 2.14 | CR F | LP* H41 | n-\( \sigma^* \) | 11.71 |
| LP F | BD* N27-H42 | n-\( \sigma^* \) | 8.78 | LP F | LP* H41 | n-\( \sigma^* \) | 12.69 |
| LP F | BD* N25-H41 | n-\( \sigma^* \) | 28.52 | LP F | LP* H41 | n-\( \sigma^* \) | 352.76 |
| LP F | BD* N27-H42 | n-\( \sigma^* \) | 44.42 | LP F | LP* H41 | n-\( \sigma^* \) | 3.30 |
receptor-fluoride complex, the second perturbation energies were varying from 0.3 to 44 kcal/mol\(^{-1}\), which revealed that both the receptors make hydrogen bonding with fluoride ion in the ground state. But, the excited state of receptor-fluoride complexes has \(\text{LP}(\text{F}) \rightarrow \text{LP}\* (\text{H41})\) interaction with more than 300 kcal/mol\(^{-1}\) energy, which shows that the fluoride ion makes strong bond with H(41) proton. This interaction generated from lone pair electron (n) of fluoride ion to n* of hydrogen (H41). The interactions were generated from core electron and lone pair electron. More overlap of the electron density confirms the strong donor–acceptor interactions; due to this, the H(41) preferred to interact with fluoride ion rather than H(43).

**Potential energy curve of excited state geometry**

To confirm the ESPT mechanism in host–guest interaction, the potential energy curve investigation of the ground state and excited state receptor-fluoride had been evaluated. The PES curve of APTSC-F complex in ground state and excited state is as shown in Fig. 9. The PES calculations employed with only varying the N–H bond length from 0.90 to 1.80 Å in steps of 0.05 Å, which can provide qualitative energetic pathways for the ESIPT process. In the case of APTSC-F complex, the bond distance between N(25)−H(42) and N(27)−H(43) at ground stat and excited state where N(25) is at nearby anthracene moiety and (N27) is nearby Phenyl group. The less energy was seen for the excited state N(25)−H(42) bond distance at 1.00 Å, and the same at ground state was more stable at 1.10 Å bond distance. These results confirm that the fluoride ion forms an intermolecular hydrogen bond with receptor’s nitrogen (N2), which is the NH proton near by the anthracene moiety. In the host–guest interaction, the fluoride ion was first reacted with receptor and forms hydrogen bond via N–H\(^+\)-F, not in free H\(^+\) ion. Hence, it shows a red shift in the fluorescence emission spectra and UV absorption spectra. This change in fluorescence colour signal can be directly detected with the naked eye. The potential energy curves of ATSC–F complex in ground state and excited state are as shown in S4.

**Host–guest interaction**

The hydrogen bond formation was confirmed in the ground state optimised structures of receptor-fluoride complexes, which has been defined as incipient proton transfer reaction from host to guest molecule. The reported experimental fluorescence quenching behaviour can be interpreted by the PET process when the fluoride anion is coordinated with APTSC. The fluorescence quenching was due to the electron transition from \(\pi\)-orbital of phenyl group to \(\pi\) -orbital of anthracene moiety. The optimised structure of receptor and receptor-fluoride complexes in the ground state and excited state suggested that the deprotonation took place at the excited state of receptor-fluoride complex, along the deprotonation that happened at the N−H proton nearby the anthracene moiety. The results from TS calculations, NBO and PES analyses confirm that the deprotonation takes place from the N–H proton, which is near by the anthracene moiety. The transition state and IRC studies confirmed the intermolecular hydrogen bond interaction between the fluoride ion with receptor. The shifts of the signals in absorption and emission spectra are prompted to enhance the strength of host molecules and result to increase the molecular conjugation when deprotonation happens. The great difference between fluorescent properties of the sensor can be used to recognise fluoride anions. The potential energy curve structure of receptor-fluoride in the ground state and the excited state defined the bond parameter for fluoride-sensing mechanism of receptor ATSC and APTSC. Figure 10 shows the sensing mechanism of receptors towards fluoride ion. The experimental absorption and emission spectra of APTSC receptor were well reproduced using TDDFT and vertical excited energy calculations from the optimised ground state geometries (receptor and receptor-F complex).

**Conclusion**

In summary, we have investigated the fluoride anion sensing mechanism of ATSC and APTSC receptors. The ground state and excited state geometry of receptors and receptor-fluoride complexes have been optimised. The experimental absorption and emission spectra are well reproduced by TDDFT and vertical transition energies computed from the ground state optimised geometries.
Theoretical study showed that there is an intramolecular H-bond in the receptor molecule. The fluoride ion in receptor-fluoride leads to the PET process in the relaxation of the excited states. The electron transitions are attributed from thiosemicarbazone moiety to anthracene moiety, which is the reason for the fluorescence quenching effect of receptor. The APTSC shows more quenching than ATSC, which is due to the more aromatic nature of APTSC than ATSC. The coordination of fluoride ion with N–H proton in ground state shows intermolecular hydrogen bond of N–H…F. However, the N–H proton near by the anthracene moiety attaches to fluoride anion in the excited state and results in ESPT process in the excited state to form hydrogen bond via N–H–F. The transition and intermediate state calculations revealed the mechanism of the host-guest interaction. The excited state proton transition mechanism of receptors towards fluoride ion was confirmed by NBO and PES analyses. The second order perturbation energy value confirms that hydrogen bonding and deprotonation take place at the excited state of receptor-fluoride complex. In other words, ESPT in the recognition process plays an important role in designing new types of fluoride chemosensors. By comparing the results APTSC and ATSC, it is clear that the aromaticity plays key factor in fluorescent sensor for quick and efficient sensing.

Supplementary Information  The online version contains supplementary material available at https://doi.org/10.1007/s00894-022-05235-3.

Acknowledgements  Author SMB is grateful to the RGEMS, VIT-AP University, Andhra Pradesh, India, for the financial support.

Author contribution  Dr. SMB conceived and designed the computational analysis and wrote the paper; however, Dr. RG contributed in data and analysis tools.

Data availability  The xyz coordinates of optimised structure of receptor and receptor-fluoride complexes are given in supplementary information.

Code availability  N/A.

Declarations

Conflict of interest  The authors declare no competing interests.

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