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# Multistate luminescent probe: ICT-driven dual ESIPT-AIE for selective fluoride and cyanide ion recognition†

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A highly selective and sensitive fluorescent chemosensor, **HNBZT**, has been designed and developed for the detection of F<sup>-</sup> and CN<sup>-</sup> ions. **HNBZT** exhibits excited-state intramolecular proton transfer (ESIPT), intramolecular charge transfer (ICT), and aggregation-induced emission (AIE) phenomena on a single molecular platform. Its photophysical and sensing behaviour has been evaluated using absorption and fluorescence spectroscopy. Notably, **HNBZT** displays a ratiometric fluorescence “turn-on” response to both anions in a CH<sub>3</sub>CN solvent system. The binding of F<sup>-</sup> and CN<sup>-</sup> ions to **HNBZT** results in distinct absorption and emission colour changes, attributed to the unique electronic and structural perturbations induced by their respective interactions, facilitating visual detection. The lowest detection limits for F<sup>-</sup> and CN<sup>-</sup> ions are 7.6 × 10<sup>-8</sup> M and 1.1 × 10<sup>-7</sup> M, respectively. The coherence between the DLS and FESEM results underscores the consistency and reliability of the observed aggregation behaviour of **HNBZT**. <sup>1</sup>H NMR titrations of **HNBZT** with F<sup>-</sup> and CN<sup>-</sup> ions reveal distinct binding mechanisms, with F<sup>-</sup> ions forming hydrogen bonds, while CN<sup>-</sup> ions induce nucleophilic addition, which is also supported by theoretical studies. The binding stoichiometry of **HNBZT** with F<sup>-</sup> and CN<sup>-</sup> ions is determined to be 1:1 using Job’s plot analysis.

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## 1. Introduction

In the field of molecular design, there is a growing interest in developing compounds with multiple functionalities, capable of exhibiting diverse photophysical phenomena simultaneously. Among these phenomena, excited-state intramolecular proton transfer (ESIPT), intramolecular charge transfer (ICT), and aggregation-induced emission (AIE) stand out as key areas of exploration, offering flexible platforms for various applications ranging from sensing to optoelectronic devices.<sup>1–6</sup> Integrating these phenomena within a single molecular framework not only enhances their individual capabilities, but also reveals emergent properties to opening up new possibilities for advanced molecular sensing.

ESIPT, ICT, and AIE are three key phenomena shaping the development of fluorescent probes and materials.<sup>7–10</sup> ESIPT facilitates the transfer of a proton between two molecular sites upon photoexcitation, inducing significant structural and

electronic changes in excited states, thereby altering their photophysical properties like emission wavelength and intensity.<sup>11–15</sup> Similarly, ICT involves the redistribution of electron density upon photoexcitation, offering a versatile platform for controlling charge transfer processes within molecules and enabling substantial changes in absorption and emission spectra.<sup>16–19</sup> Furthermore, the AIE phenomenon enhances light emission intensity upon aggregation, diverging from conventional fluorophores that often undergo fluorescence quenching in aggregated states. This transformative property of AIE-active molecules makes them highly attractive for diverse applications including biological imaging, chemical sensing, and optoelectronic devices.<sup>20–25</sup>

The emergence of molecules with double ESIPT, ICT, and AIE properties presents an exciting opportunity to combine these phenomena and unlock novel functionalities. Such molecules hold great promise for applications requiring multifunctionality, including simultaneous detection of ions.<sup>26,27</sup> Detecting different ions is crucial for environmental monitoring, biomedical diagnostics, and industrial safety due to their significance as indicators of water quality, environmental contamination, and chemical toxicity.<sup>28–30</sup>

The selective detection of anions, such as fluoride (F<sup>-</sup>) and cyanide (CN<sup>-</sup>), is of significant interest due to their unique chemical properties and widespread relevance in environmental, biological, and industrial processes.<sup>31–33</sup> For example,

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fluoride ions play a critical role in dental care, such as water fluoridation, and are used in various industrial applications, while cyanide is known for its toxicity, yet it is widely utilized in gold mining and chemical synthesis.<sup>34–36</sup> As a result, the development of sensitive and selective methods for detecting these anions is essential for both environmental monitoring and safety.<sup>37,38</sup>

The challenge lies in designing a sensor that can selectively interact with both anions despite their distinct sizes, geometries, and chemical behaviors. Fluoride is a small, highly electronegative ion, whereas cyanide is larger, less electronegative, and can engage in both hydrogen bonding and covalent interactions. A well-designed chemosensor must not only recognize these differences but also exhibit distinct, measurable responses to each anion.

This study introduces a novel fluorescent chemosensor capable of differential sensing for F<sup>−</sup> and CN<sup>−</sup> ions with exceptional selectivity and sensitivity. **HNBZT** showed ESIPT, ICT, and AIE phenomena within a single molecular framework. Furthermore, **HNBZT** exhibited a ratiometric fluorescence “turn-on” response to both anions when dissolved in CH<sub>3</sub>CN solvent. Moreover, we elucidated **HNBZT**'s stoichiometry in interaction with F<sup>−</sup> and CN<sup>−</sup> ions through Job's plot analysis. This comprehensive investigation illuminates the multifaceted behavior of **HNBZT**.

## 2. Experimental section

### 2.1. Materials and instruments

All chemicals and solvents used in the experimental work were of analytical grade and were procured from Sigma-Aldrich, Spectrochem, and Rankem Ltd, depending on availability. These were used without further purification. The progress of the chemical reactions was monitored using thin layer chromatography (TLC). Melting points were recorded using the open capillary method and were uncorrected. The synthesized compounds were characterized using NMR spectroscopy on a JEOL ECS-400 MHz instrument in DMSO-*d*<sub>6</sub> with TMS as the internal standard. HRMS spectra were obtained using an XEVO G2-XS QTOF of WATERS. Absorption studies were performed with a SHIMADZU UV-2600 spectrophotometer, employing quartz cells with a 1 cm path length. Fluorescence studies were conducted using an Agilent Technologies Cary Eclipse Spectrophotometer, with excitation and emission slit widths set to 5 nm each. Absorption and emission scans were saved as ACS files and subsequently processed in Excel™ to generate the

presented graphs. The stoichiometry of the complexes was analyzed using Job's plot analysis. Time-resolved fluorescence studies were carried out using a DeltaFlex Modular Fluorescence Lifetime Spectrofluorimeter from HORIBA Scientific. The FE-SEM analysis was carried out using a ZEISS MERLIN Compact field emission-scanning electron microscope.

### 2.2. Solutions for absorption and emission studies

The stock solution of **HNBZT** was prepared in CH<sub>3</sub>CN:DMSO (9.5:0.5) at 10<sup>−3</sup> M concentration. Tetrabutyl ammonium salts of F<sup>−</sup>, Cl<sup>−</sup>, CN<sup>−</sup>, Br<sup>−</sup>, I<sup>−</sup>, SCN<sup>−</sup>, AcO<sup>−</sup>, NO<sub>3</sub><sup>−</sup>, P<sub>2</sub>O<sub>7</sub><sup>4−</sup>, H<sub>2</sub>PO<sub>4</sub><sup>−</sup>, and HSO<sub>4</sub><sup>−</sup> were used for anions. The stock solutions of the anions were prepared in acetonitrile at 10<sup>−1</sup> M concentration. As needed, the stock solutions were further diluted to the desired concentration.

### 2.3. Calculation of binding constants and detection limits

The binding constants were calculated using the Benesi–Hildebrand method using eqn (1) where *I*<sub>0</sub>, *I*, and *I*<sub>max</sub> are the absorption/emission intensities of the compound in the absence of analyte, at an intermediate, and at complete titration with the analyte, respectively. *K*<sub>a</sub> is the binding constant; *C* is the concentration of analyte and *n* is the number of analytes bound per molecule.

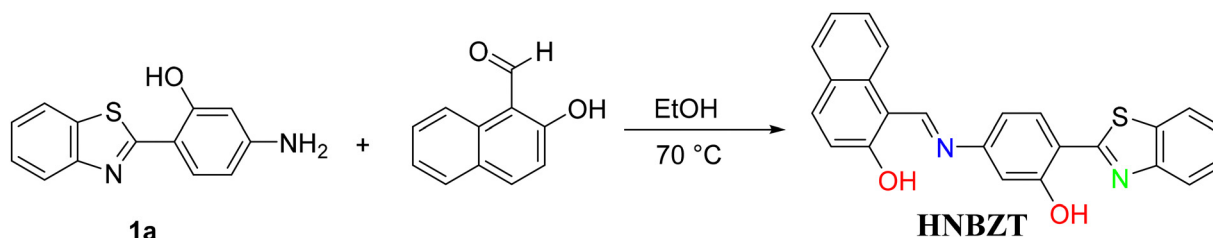
$$\frac{1}{I - I_0} = \frac{1}{K_a(I_{\max} - I_0)[C]^n} + \frac{1}{I_{\max} - I_0} \quad (1)$$

Limit of detection (LOD) was determined from the following equation:

$$DL = \frac{3 \times \text{standard deviation of the blank solution}}{\text{slope of calibration curve}} \quad (2)$$

### 2.4. Synthetic procedure for HNBZT

Compound **1a**<sup>39</sup> (200 mg, 0.8 mmol) and 2-hydroxy-1-naphthaldehyde (156 mg, 0.9 mmol) were stirred at 70 °C in ethanol for 3 h (Scheme 1). On completion, the reaction mixture was cooled at room temperature, and the crude solid was filtered and washed with ethanol to obtain an orange coloured solid of **HNBZT** in 85% yield. M.p. 270–275 °C; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz): δ (ppm) 9.63 (d, 1H, *J* = 8.0 Hz, −CH=N), 8.48 (d, 1H, *J* = 8.0 Hz, ArH), 8.22 (d, 1H, *J* = 7.8 Hz, ArH), 8.13 (d, 1H, *J* = 8.0 Hz, ArH), 8.05 (d, 1H, *J* = 8.0 Hz, ArH), 7.92 (d, 1H, *J* = 12.0 Hz, ArH), 7.76 (dd, 1H, <sup>1</sup>*J* = 3.4 Hz, <sup>2</sup>*J* = 8.0 Hz, ArH), 7.54–7.50 (m, 2H, ArH), 7.44–7.42 (m, 1H, ArH), 7.34–7.30 (m, 2H, ArH), 7.24 (d, 1H, *J* = 4.0 Hz, ArH), 6.95 (d, 1H, *J* = 7.4 Hz, ArH) (Fig. S1, ESI<sup>†</sup>). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz): δ (ppm) 173.1, 165.4, 157.9, 155.4, 151.9, 147.1, 138.4, 134.5, 133.7,



Scheme 1 Synthesis of **HNBZT**.



130.3, 129.6, 128.8, 127.1, 125.6, 124.3, 123.2, 122.5, 121.0, 116.9, 112.5, 109.1, 108.6 (Fig. S2, ESI<sup>†</sup>). HRMS (ESI-TOF): (*m/z*) [*M* + *H*]<sup>+</sup> calcd for C<sub>24</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>S: 397.1007, found: 397.1015 (Fig. S3, ESI<sup>†</sup>). FT-IR (cm<sup>-1</sup>): 3462 ( $\nu_{\text{O-H}}$ ), 3204 ( $\nu_{\text{C-H str.}}$ , aromatic), 2969 ( $\nu_{\text{C-H str.}}$ , aromatic), 1573 ( $\nu_{\text{C=NH}}$ ), 1343 ( $\nu_{\text{C-C}}$ ), (Fig. S4, ESI<sup>†</sup>).

## 2.5. Real sample analysis

For the practical application of **HNBZT** for detecting F<sup>-</sup> and CN<sup>-</sup> ions, water samples were collected from different sources. The qualitative applications of F<sup>-</sup> and CN<sup>-</sup> ions were estimated through a calibration curve. All these samples were further spiked with different concentrations of F<sup>-</sup> and CN<sup>-</sup> ions (20  $\mu\text{M}$  and 40  $\mu\text{M}$ ). **HNBZT** (20  $\mu\text{M}$ ) was added to these solutions (3 mL) having different F<sup>-</sup> and CN<sup>-</sup> ion concentrations. The spiked samples were estimated using the calibration curve.

## 3. Results and discussion

### 3.1. Photophysical properties of HNBZT

The photophysical properties of **HNBZT** were investigated using absorption and emission spectroscopy. The absorption spectrum

of **HNBZT** (20  $\mu\text{M}$ ) in CH<sub>3</sub>CN displayed a high-energy transition band at 400 nm and two low-energy transition bands at 445 nm and 475 nm. Upon excitation at 400 nm, **HNBZT** (20  $\mu\text{M}$ ) exhibited an emission band at 505 nm, corresponding to a Stokes shift of 105 nm. Due to the presence of electron donor and acceptor units, an intramolecular charge transfer (ICT) process is likely enabled in **HNBZT**. To explore the influence of ICT on steady-state absorption and emission spectra, various solvents with differing polarities were employed. In non-polar solvents, the absorption peak was observed at 400 nm. However, as solvent polarity increased, the absorption maximum red-shifted to 475 nm, accompanied by an enhancement of a shoulder band at 535 nm (Fig. 1a). This red shift in absorption maxima is attributed to the ICT process, involving electron transfer from the hydroxy naphthalene unit to the benzothiazole moiety. Similarly, while the emission maxima were predominantly at 505 nm in most solvents, they shifted to 535 nm in CH<sub>3</sub>OH and 560 nm in H<sub>2</sub>O as the solvent polarity increased (Fig. 1b, Table 1). These shifts in emission maxima further support the presence of ICT in the excited state. Additionally, **HNBZT** exhibited noticeable color changes from light yellow to orange with increasing solvent polarity (Fig. 1c), providing a visual indication of the ICT process.

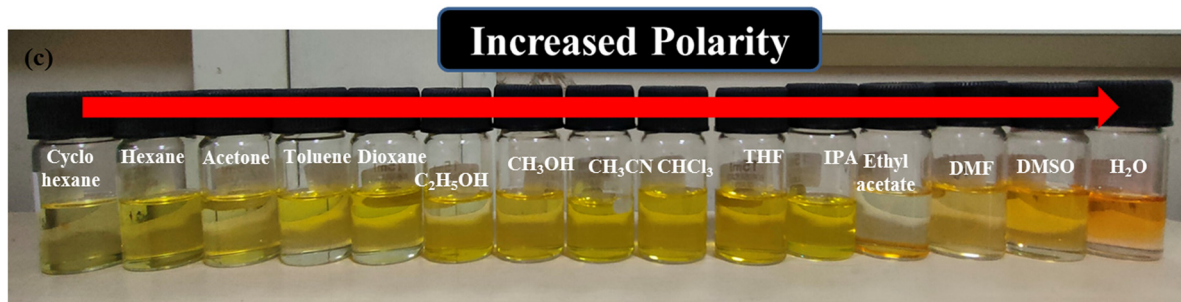
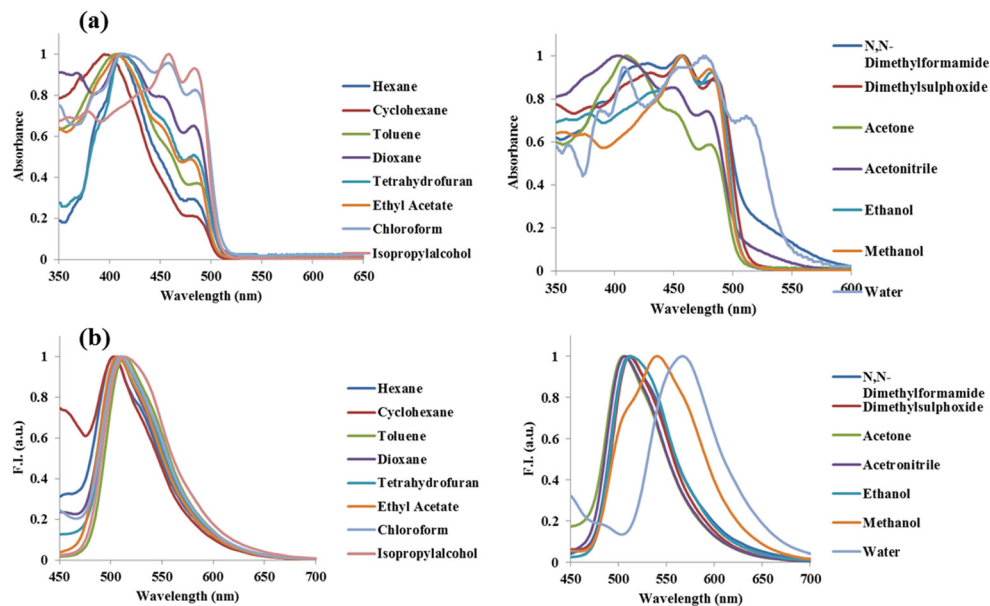


Fig. 1 (a) Absorption and (b) emission spectra of **HNBZT** (20  $\mu\text{M}$ ) in solvents of different polarity, and (c) colorimetric response of **HNBZT** (20  $\mu\text{M}$ ) upon increasing polarity of the solvents.

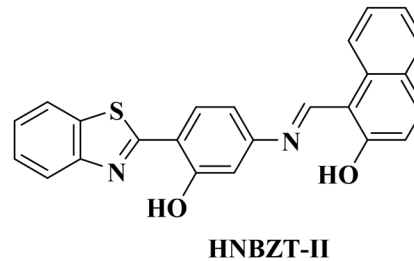
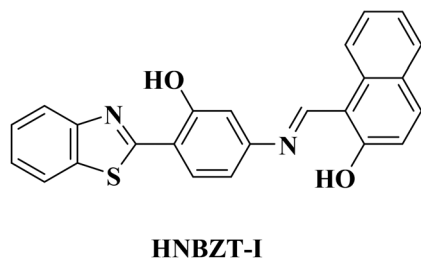


Table 1 Photophysical properties of **HNBZT**

S. no.	Solvent	$\lambda_{\max}$ (nm)	Molar absorptivity $\epsilon$ ( $M^{-1} \text{ cm}^{-1}$ )	$\lambda_{\text{em}}$ (nm)	Stokes shift $\Delta\nu$ ( $\text{cm}^{-1}$ )	Quantum yield ( $\Phi$ )
1	Hexane	405	6050	505	4890	0.49
2	Cyclohexane	405	16 300	505	4890	0.45
3	Toluene	405	19 500	509	4890	0.51
4	Chloroform	405	14 900	509	4890	0.59
5	Tetrahydrofuran	405	5300	510	4890	0.53
6	Acetone	405	15 550	507	4890	0.55
7	Dioxane	405	15 700	508	4890	0.55
8	Ethyl acetate	405	19 550	511	4890	0.56
9	Dimethylsulphoxide	455	17 550	513	2180	0.48
10	<i>N,N</i> -Dimethylformamide	455	15 300	515	2180	0.54
11	Acetonitrile	405	16 900	506	4890	0.72
12	Isopropylalcohol	475	15 400	507	1250	0.75
13	Ethanol	455	18 350	515	2180	0.58
14	Methanol	475	16 100	535	2360	0.65
15	Water	475	5300	560	3190	0.69

Stokes shift =  $1/(\lambda_{\text{em}} - \lambda_{\text{max}})$ , reference for quantum yield is quinine sulphate.

**HNBZT** exhibited torsional flexibility concerning single bonds, specifically C—N rotation at the imine center connection and C—C rotation at the benzothiazole unit connection, which resulted in different conformations. The theoretical calculations indicate that the plausible configurations, which were optimized at the  $S_0$  state, have a significant population of 55% and 45%, respectively, and are relatively stable due to the formation of strong intramolecular hydrogen bonding in the **HNBZT-I** and **HNBZT-II** conformers. In the  $S_0$  state with no imaginary frequency, **HNBZT**'s geometry was slightly twisted in both of these configurations.



Three low-lying excitations of **HNBZT-I** and **HNBZT-II** were calculated in accordance with  $S_0$  geometry in order to investigate the photoexcitation process. Table 2 contains a tabulation of the computed excitations. With an oscillation strength of 1.2213 at 419 nm for  $S_0 \rightarrow S_1$  excitation, the TDDFT calculation for **HNBZT-I** showed an orbital transition contribution of 98.5% from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO),

which is close to the experimental absorption peak at 405 nm. In contrast,  $S_0 \rightarrow S_1$  excitation for **HNBZT-II** was calculated at 416 nm, with an orbital contribution of 98.5% from the HOMO to LUMO transition and oscillation strength of 1.2079. We have only taken into consideration the  $S_0 \rightarrow S_1$  excitation for further analysis because the calculated  $S_0 \rightarrow S_2$  and  $S_0 \rightarrow S_3$  excitations have low oscillation strengths for both configurations.

Furthermore, both qualitative and quantitative assessments were made for the change in electronic distribution. For both configurations, **HNBZT-I** and **HNBZT-II**, the involved molecular

orbitals showed a shift in electron density from the benzothiazole unit (in the HOMO) to the Schiff base unit (in the LUMO) (Fig. 2). The ensuing hole–electron analysis revealed a large distance of electron/hole centroid ( $D = 7.953 \text{ \AA}$  for **HNBZT-I** and  $7.863 \text{ \AA}$  for **HNBZT-II**) and a low overlap integral ( $S_r = 0.42174$  for **HNBZT-I** and  $S_r = 0.42741$  for **HNBZT-II**) of hole/electron distribution, establishing an intramolecular charge transfer process in **HNBZT** for both configurations.

Table 2 Summary of excitation spectra of **HNBZT-I** and **HNBZT-II**

<b>HNBZT-I</b>			<b>HNBZT-II</b>		
Excitation	$\lambda$ (nm)	MO	Excitation	$\lambda$ (nm)	MO
$S_0 \rightarrow S_1$	419.72 ( $f = 1.2213$ )	H $\rightarrow$ L (98.5%)	$S_0 \rightarrow S_1$	416.66 ( $f = 1.2079$ )	H $\rightarrow$ L (98.5%)
$S_0 \rightarrow S_2$	363.29 ( $f = 0.0216$ )	H-1 $\rightarrow$ L (95%)	$S_0 \rightarrow S_2$	360.66 ( $f = 0.0261$ )	H-1 $\rightarrow$ L (96%)
$S_0 \rightarrow S_3$	332.23 ( $f = 0.0757$ )	H-2 $\rightarrow$ L (89.6%)	$S_0 \rightarrow S_3$	333.26 ( $f = 0.0760$ )	H-2 $\rightarrow$ L (59%), H-4 $\rightarrow$ L (15%), H $\rightarrow$ L + 1 (14%)

$\lambda$  = calculated excitation wavelength (nm); MO = molecular orbitals contributing to excitations; H = HOMO; L = LUMO.



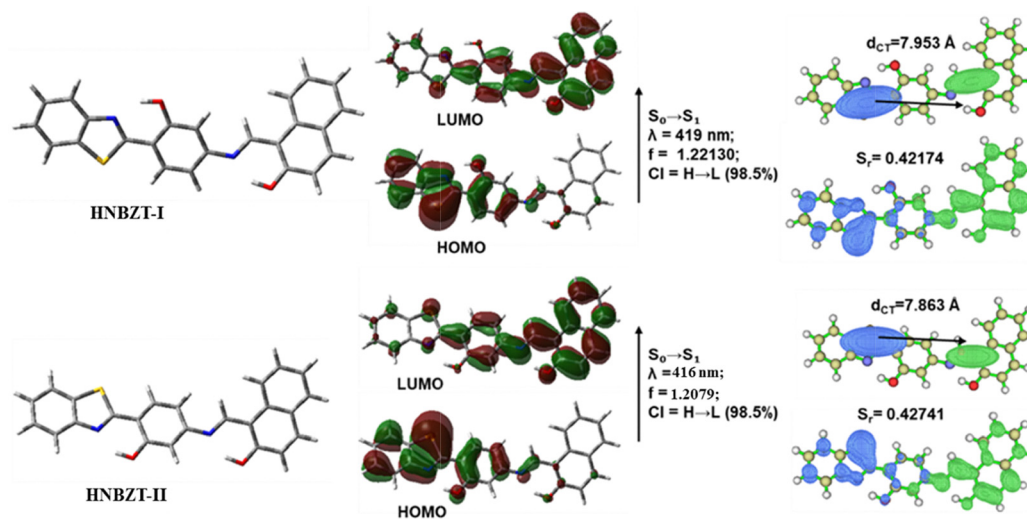


Fig. 2 Optimized structures of HNBZT along with their frontier molecular orbitals.

### 3.2. Geometrical parameters and tautomeric conversion

HNBZT contained two kinds of asymmetrical intramolecular hydrogen bonding (IraHB) labeled as A and B with short interaction distance (less than the sum of van der Waals radii

of hydrogen and nitrogen) and angles. For HNBZT-I, on photoexcitation to  $S_1$  state, the intramolecular distances for A type interaction were decreased from 1.686 Å to 1.635 Å, while the bond angle increased from 146.80° to 149.23°. On the other

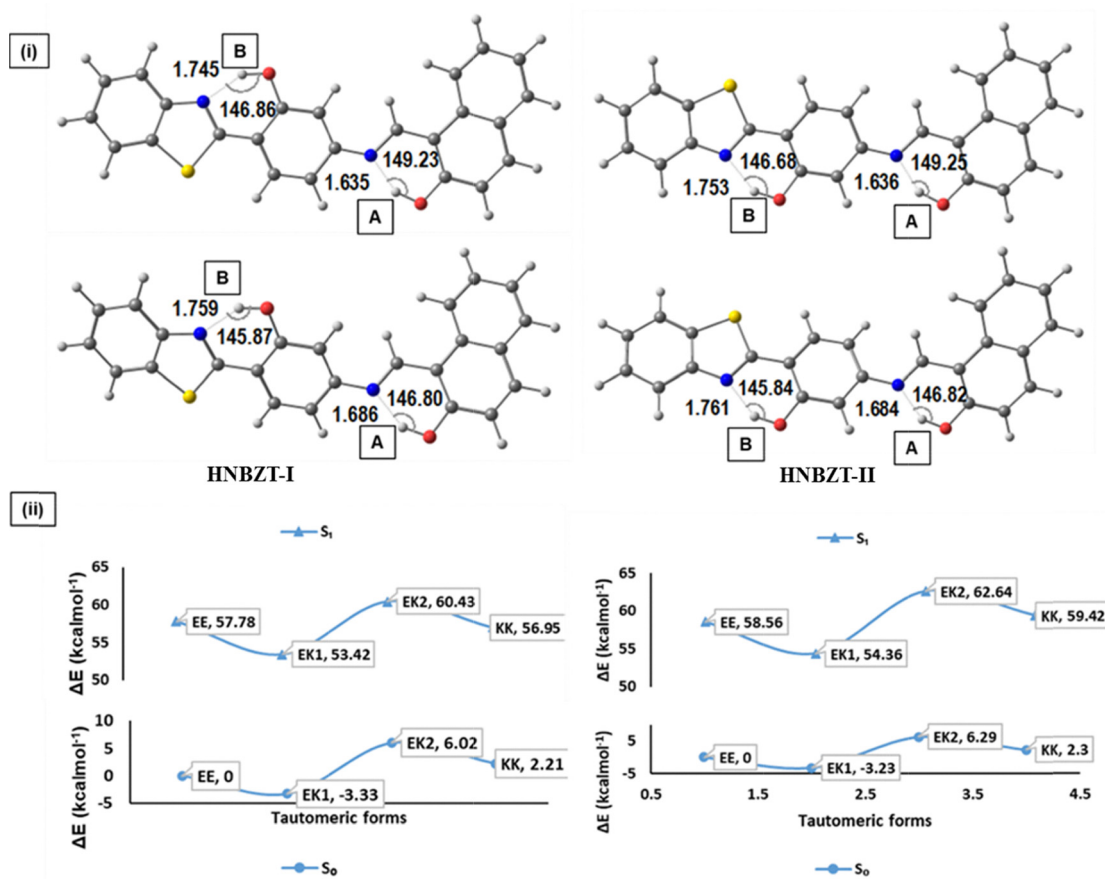


Fig. 3 (i) Optimized structures of HNBZT-I and HNBZT-II along with significant geometrical parameters and (ii) energy profile of the tautomeric forms at  $S_0$  and  $S_1$ .



hand, B type interaction showed a decrease in distance from 1.759 Å to 1.745 Å, while the bond angle increased from 145.87° to 146.86°. A similar trend was observed for the **HNBZT-II** conformer too. It was also noted that a significant molecular planarity was achieved with a decrease of dihedral angle of the Schiff base unit for both conformers in the  $S_1$  state. These alterations in bond distance and angle (on photoexcitation) established strengthening of intramolecular hydrogen bonding, which could prompt the proton transfer process in the excited state (Fig. 3). Therefore, the tautomeric conversion through the proton transfer process in **HNBZT** could result in four different tautomeric forms (EE, EK1, EK2, KK). The relative free energy ( $\Delta G$ ) profile of the tautomeric forms for **HNBZT-I** established a relationship of EE (0 kcal mol<sup>-1</sup>) > EK1 (-3.33 kcal mol<sup>-1</sup>) < EK2 (6.02 kcal mol<sup>-1</sup>) > KK (2.21 kcal mol<sup>-1</sup>) in the  $S_0$  state and EE (57.78 kcal mol<sup>-1</sup>) > EK1 (53.42 kcal mol<sup>-1</sup>) < EK2 (60.43 kcal mol<sup>-1</sup>) > KK (56.95 kcal mol<sup>-1</sup>) in the  $S_1$  state. A similar trend has been observed for **HNBZT-II**.

### 3.3. Aggregation induced emission (AIE) studies

Aggregation-induced emission (AIE) characteristics are commonly observed in organic fluorophores containing rotor structures. We investigated the AIE effect of the naphthalene rotor in **HNBZT**

by conducting experiments in CH<sub>3</sub>CN/H<sub>2</sub>O mixtures with varying H<sub>2</sub>O content. The absorption spectra of **HNBZT** exhibited a blue shift from 400 nm to 355 nm as the H<sub>2</sub>O content increased from 0% to 50%. However, as the H<sub>2</sub>O fraction increased from 60% to 100%, the absorption intensity progressively increased, accompanied by a noticeable red shift from 355 nm to 480 nm and the appearance of a levelling-off tail in the absorption band (Fig. 4a). The bathochromic shift observed is associated with the formation of J-type aggregates. Further variations in the emission spectra of **HNBZT** were observed with changing the H<sub>2</sub>O percentages in the CH<sub>3</sub>CN solutions (0–100%). As the H<sub>2</sub>O fraction increased, the emission intensity also increased significantly (Fig. 4b). This enhancement in emission intensity is attributed to the aggregation-induced emission (AIE) process in **HNBZT**. The visible color change from dark yellow to pale of the **HNBZT** solution upon increasing the H<sub>2</sub>O ratio was observed, which is attributed to Mie scattering and the aggregation of **HNBZT** with increasing H<sub>2</sub>O content (Fig. 4c). Thus, the observed tailing between 450–550 nm in Fig. 4a is characteristic of aggregate formation, and this aggregate-induced emission enhancement is supported by emission spectra, DLS, and FESEM results. Regarding the emission spectra, intermolecular hydrogen bonding with water would typically shift the parent emission of **HNBZT** to a shorter

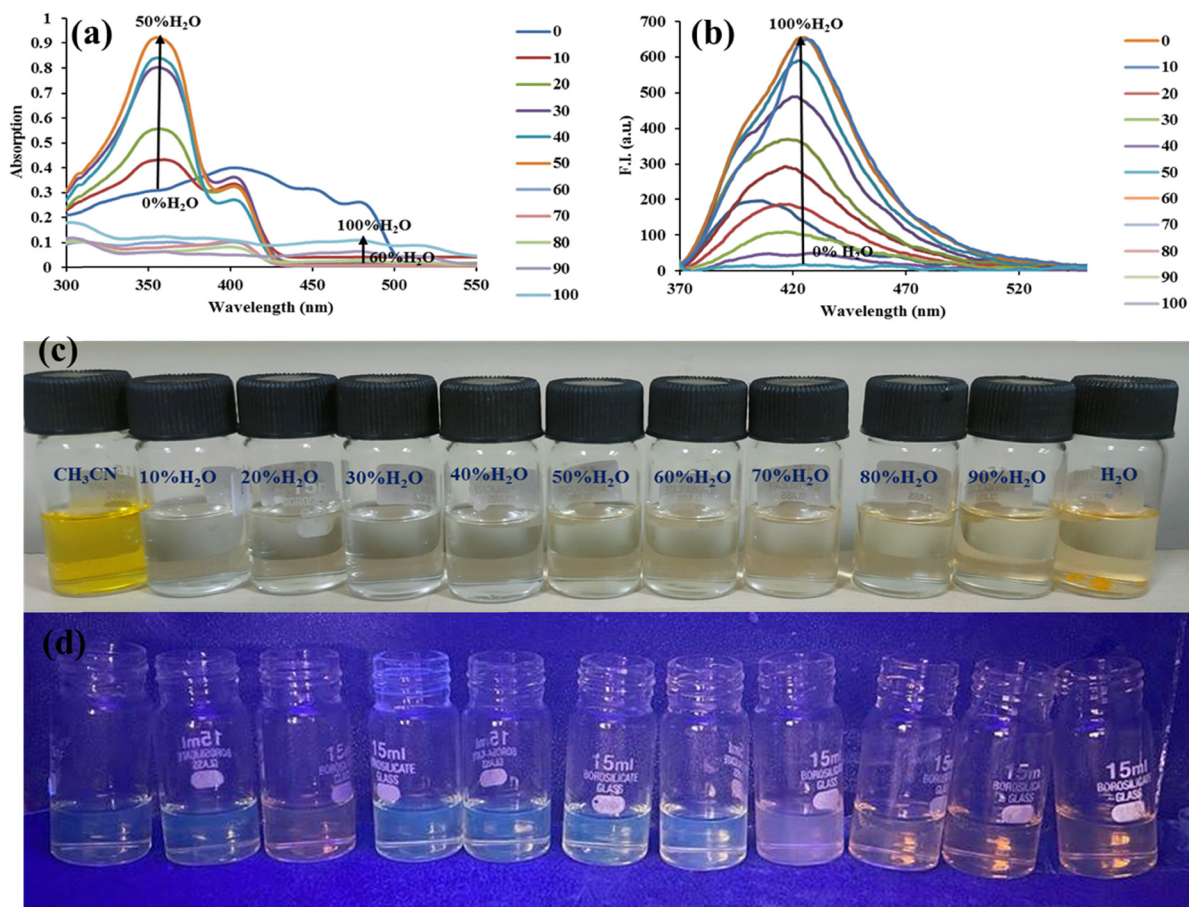


Fig. 4 (a) Absorption and (b) emission spectra of **HNBZT** with increasing H<sub>2</sub>O ratio in CH<sub>3</sub>CN. (c) Colorimetric and (d) emission response of **HNBZT** upon increasing H<sub>2</sub>O content in CH<sub>3</sub>CN.



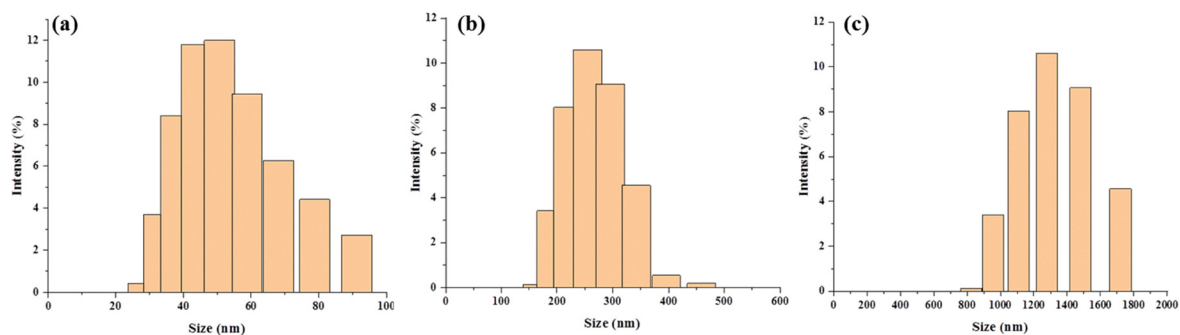


Fig. 5 DLS of HNBZT in (a)  $\text{CH}_3\text{CN}$ , (b) 50%  $\text{CH}_3\text{CN}:\text{H}_2\text{O}$  and (c)  $\text{H}_2\text{O}$ .

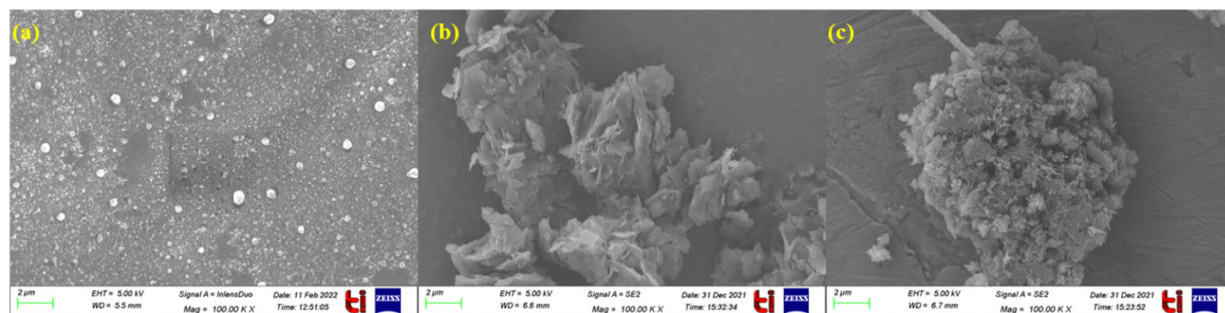


Fig. 6 FESEM images of HNBZT in (a)  $\text{CH}_3\text{CN}$ , (b) 50%  $\text{CH}_3\text{CN}:\text{H}_2\text{O}$  and (c)  $\text{H}_2\text{O}$ .

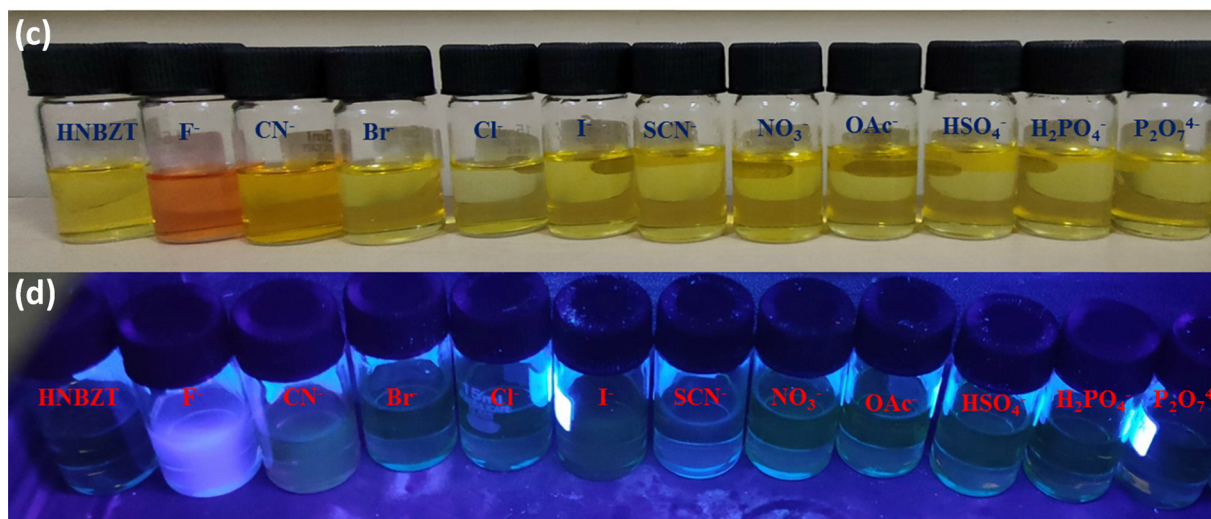
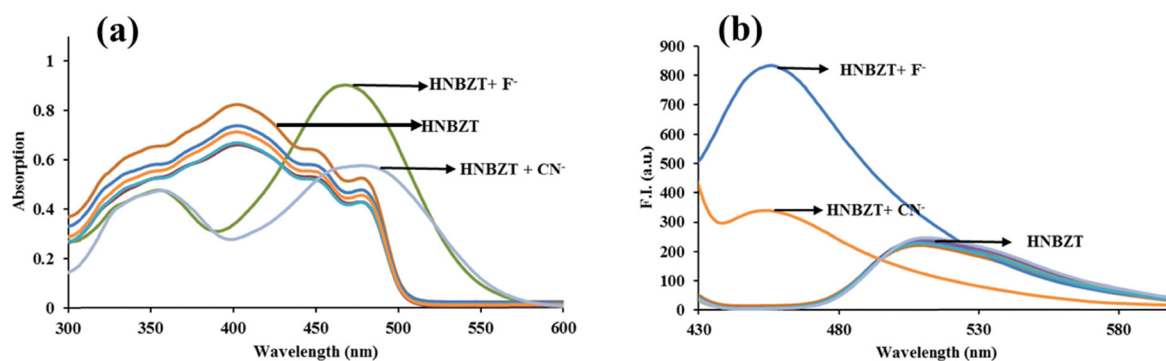


Fig. 7 (a) Absorption and (b) emission spectra of HNBZT (20  $\mu\text{M}$ ) upon interaction of different anions (1000  $\mu\text{M}$ ) in  $\text{CH}_3\text{CN}$ . (c) Colorimetric and (d) fluorogenic responses of HNBZT (20  $\mu\text{M}$ ) upon interaction with different anions in  $\text{CH}_3\text{CN}$ .



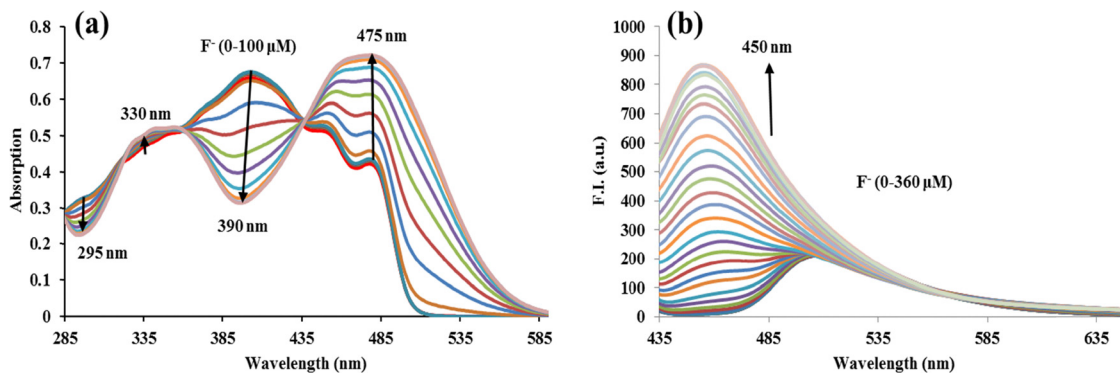


Fig. 8 (a) Absorption spectra of **HNBZT** upon incremental addition of 0–100  $\mu\text{M}$  of  $\text{F}^-$  ions and (b) emission spectra of **HNBZT** upon incremental addition of 0–360  $\mu\text{M}$  of  $\text{F}^-$  ions.

wavelength, as seen in its interactions with  $\text{F}^-$  and  $\text{CN}^-$  ions. The characteristic keto emission at 515 nm arises from intact intramolecular hydrogen bonding in **HNBZT**, whereas disruption of this bonding results in enol-type emission around 450 nm. This behaviour is further supported by theoretical calculations.

To investigate the aggregation behaviour of **HNBZT**, dynamic light scattering (DLS) experiments were conducted. The results confirmed the aggregation behaviour of **HNBZT** and provided insights into the size of aggregates under varying  $\text{CH}_3\text{CN}:\text{H}_2\text{O}$  ratios. In pure  $\text{CH}_3\text{CN}$ , the aggregate size ranged from 20–100 nm, with an average size of 50 nm and a polydispersity index (PDI) of 0.3. In a 50%  $\text{CH}_3\text{CN}:\text{H}_2\text{O}$  mixture, the aggregate size increased to 100–500 nm, with an average size of 250 nm and a PDI of 0.6. This hydrodynamic diameter further increased significantly to 1250 nm in pure  $\text{H}_2\text{O}$ , with a PDI value of 0.8 (Fig. 5). Field emission scanning electron microscopy (FESEM) analysis supported these findings, showing particle sizes of 20 nm in pure  $\text{CH}_3\text{CN}$ , 150 nm in 50%  $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ , and 993 nm in pure  $\text{H}_2\text{O}$  (Fig. 6). The coherence between the DLS and FESEM results underscores the consistency and reliability of the observed aggregation behaviour of **HNBZT**.

### 3.4. Anion binding behavior of **HNBZT**

The binding behavior of **HNBZT** (20  $\mu\text{M}$ ) toward various anions was investigated in  $\text{CH}_3\text{CN}$ . As previously discussed, **HNBZT** exhibited a high-energy transition band at 400 nm and two low-energy transition bands at 445 nm and 475 nm in the absorption spectrum. A weak emission band was observed at 505 nm

Table 3 Binding constants and detection limits of **HNBZT** for  $\text{F}^-$  and  $\text{CN}^-$  ions

	Binding constant	LOD
<b>HNBZT</b> + $\text{F}^-$	$2.9 \times 10^5 \text{ M}^{-1}$	$7.6 \times 10^{-8} \text{ M}$
<b>HNBZT</b> + $\text{CN}^-$	$7.5 \times 10^3 \text{ M}^{-1}$	$1.1 \times 10^{-7} \text{ M}$

upon excitation at 400 nm. The anion-binding affinity of **HNBZT** was examined in the presence of different anions, including  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{AcO}^-$ ,  $\text{HSO}_4^-$ ,  $\text{P}_2\text{O}_7^{4-}$ ,  $\text{CN}^-$ , and  $\text{SCN}^-$  using absorption and emission spectroscopy where **HNBZT** demonstrated a strong binding affinity for  $\text{F}^-$  and  $\text{CN}^-$  anions. For both  $\text{F}^-$  and  $\text{CN}^-$ , the absorption band at 475 nm intensified with a quantum yield of 0.81 and 0.79, respectively, while the bands at 400 nm and 445 nm disappeared (Fig. 7a). In the fluorescence spectra, the emission maximum of **HNBZT** at 505 nm underwent a blue shift to 450 nm upon interaction with  $\text{F}^-$  and  $\text{CN}^-$  anions (Fig. 7b). Additionally, **HNBZT** exhibited a notable colorimetric response, changing from light yellow to orange with  $\text{F}^-$  and to dark yellow with a  $\text{CN}^-$  anion (Fig. 7c) while **HNBZT** under UV light showed emission colour change from mild green fluorescence to purplish blue fluorescence in the presence of  $\text{F}^-$  ions (Fig. 7d). These results highlighted the strong binding and distinct optical responses of **HNBZT** to  $\text{F}^-$  and  $\text{CN}^-$  anions.

Titration assays were presented to investigate the binding affinities of **HNBZT** for  $\text{F}^-$  and  $\text{CN}^-$  ions. In the absorption

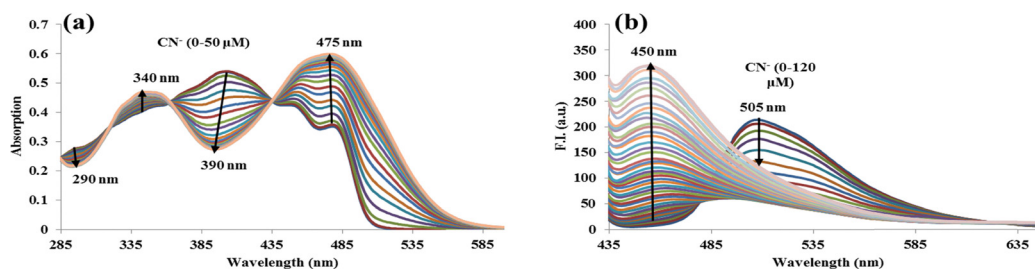


Fig. 9 (a) Absorption spectra of **HNBZT** upon incremental addition of 0–50  $\mu\text{M}$  of  $\text{CN}^-$  ions and (b) emission spectra of **HNBZT** upon sequential addition of 0–120  $\mu\text{M}$  of  $\text{CN}^-$  ions.



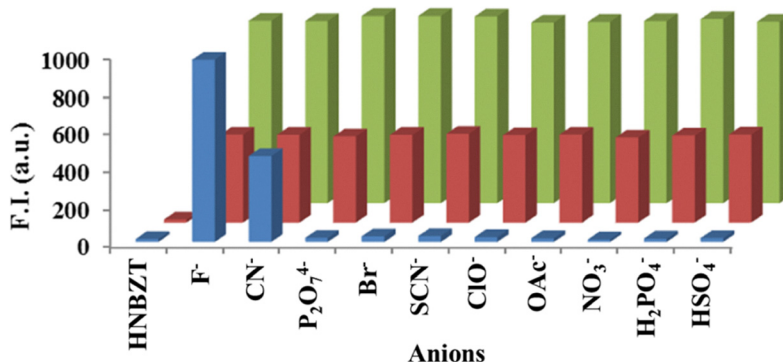


Fig. 10 Relative emission intensity of **HNBZT** (20  $\mu\text{M}$ ) in  $\text{CH}_3\text{CN}$  ( $\lambda_{\text{ex}} = 390 \text{ nm}$ ) with different competing anions in the absence and presence of  $\text{F}^-$  and  $\text{CN}^-$  ions at  $\lambda_{\text{em}} = 450 \text{ nm}$ , where blue bars represent the emission intensity change of **HNBZT** with different anions (1000  $\mu\text{M}$ ), red bars represent **HNBZT** +  $\text{CN}^-$  in the presence of different relevant competing anions (1000  $\mu\text{M}$ ) and green bars represent **HNBZT** +  $\text{F}^-$ .

spectra, the band centered at 405 nm decreased with a slight blue shift to 390 nm, while the band at 475 nm intensified upon incremental addition of  $\text{F}^-$  (0–100  $\mu\text{M}$ ). Additionally, the absorption band at 330 nm showed a slight increase in intensity, whereas the band at 295 nm decreased. The formation of two isosbestic points at 435 nm and 355 nm indicated the equilibrium between multiple species (Fig. 8a). Similarly, emission titration experiments with sequential addition of  $\text{F}^-$  ions (0–360  $\mu\text{M}$ ) revealed an enhancement of the emission band at 450 nm, while the band at 515 nm disappeared (Fig. 8b). To determine the reaction stoichiometry between **HNBZT** and  $\text{F}^-$  ions, emission spectra were analyzed at different mole fractions of  $\text{F}^-$ . The emission maximum observed at a mole fraction of 0.5 indicated a 1 : 1 stoichiometry, determined with Job's plot analysis (Fig. S5a, ESI<sup>†</sup>).

Using the Benesi–Hildebrand equation, the binding constant for **HNBZT** and  $\text{F}^-$  was calculated to be  $2.9 \times 10^5 \text{ M}^{-1}$ . The lowest detection limit for  $\text{F}^-$  ions was determined to be  $7.6 \times 10^{-8} \text{ M}$ , highlighting the high sensitivity of **HNBZT** for  $\text{F}^-$  detection.

Similar results were observed for the  $\text{CN}^-$  ion. During absorption titration, the band at 475 nm was increased, while the band at 405 nm decreased with a slight blue

shift to 390 nm. Moreover, the absorption band at 340 nm revealed a slight increase in intensity, while the band at 290 nm decreased (Fig. 9a). The presence of two isosbestic points indicated an equilibrium between multiple species. In the emission titration, the emission band at 505 nm decreased, accompanied by an increase in emission intensity at 450 nm (Fig. 9b). The binding constant for  $\text{CN}^-$  was calculated to be  $7.5 \times 10^3 \text{ M}^{-1}$ , with the lowest detection limit of  $1.1 \times 10^{-7} \text{ M}$  (Table 3). Job's plot analysis confirmed a 1 : 1 stoichiometry for the interaction between **HNBZT** and  $\text{CN}^-$  ions (Fig. S5b, ESI<sup>†</sup>).

An interference study was also conducted to evaluate the selectivity of **HNBZT** toward  $\text{F}^-$  and  $\text{CN}^-$  ions. No significant changes were observed in the emission spectra of **HNBZT** +  $\text{F}^-$  and **HNBZT** +  $\text{CN}^-$  upon the addition of excess competitive anions (1000  $\mu\text{M}$ ), including  $\text{F}^-$ ,  $\text{CN}^-$ ,  $\text{Br}^-$ ,  $\text{SCN}^-$ ,  $\text{ClO}^-$ ,  $\text{AcO}^-$ ,  $\text{NO}_3^-$ ,  $\text{P}_2\text{O}_7^{4-}$ ,  $\text{H}_2\text{PO}_4^-$ , and  $\text{HSO}_4^-$  (Fig. 10). This demonstrated that **HNBZT** exhibits high selectivity for both  $\text{F}^-$  and  $\text{CN}^-$  anions.

### 3.5. Time-correlated single photon counting (TCSPC) study

The fluorescence enhancement behaviour of **HNBZT** upon binding with  $\text{F}^-$  and  $\text{CN}^-$  ions was further corroborated by time-correlated single photon counting (TCSPC) studies. The fluorescence decay profiles of **HNBZT** and its complexes were best fitted using a three-exponential function (Fig. 11). For **HNBZT**, three lifetime components were observed: 1.12 ns, 6.90 ns, and 0.07 ns, with population percentages of 7.32%, 8.45%, and 84.23%, respectively. The average lifetime of **HNBZT** was calculated to be 0.09 ns. Upon addition of  $\text{F}^-$  ions to **HNBZT**, the fluorescence decay revealed three components with lifetimes of 1.43 ns, 1.53 ns, and 2.44 ns, and corresponding population percentages of 27.85%, 39.02%, and

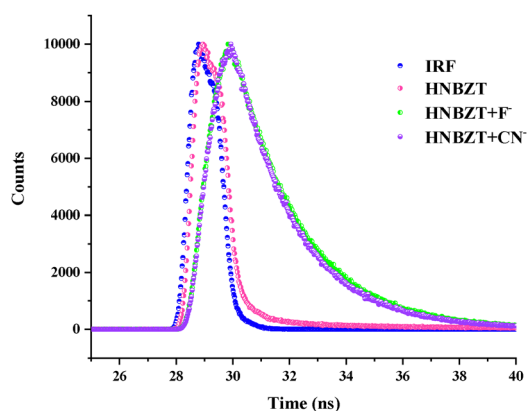


Fig. 11 Time resolved fluorescence decay of **HNBZT** and **HNBZT** with  $\text{F}^-$  and  $\text{CN}^-$  ions.

Table 4 Fluorescence lifetime measurements for **HNBZT** and its complexes with  $\text{F}^-$  and  $\text{CN}^-$  ions in  $\text{CH}_3\text{CN}$

$\text{CH}_3\text{CN}$	$\tau_1$ (ns)	$\tau_2$ (ns)	$\tau_3$ (ns)	$\alpha_1$	$\alpha_2$	$\alpha_3$	$\chi^2$	$\tau_{\text{av}}$ (ns)
<b>HNBZT</b>	1.12	6.90	0.07	7.32	8.45	84.23	1.12	0.09
<b>HNBZT</b> + $\text{F}^-$	1.43	1.53	2.44	27.85	39.02	33.14	1.18	1.71
<b>HNBZT</b> + $\text{CN}^-$	1.76	9.52	2.36	35.42	0.94	63.64	1.07	2.12





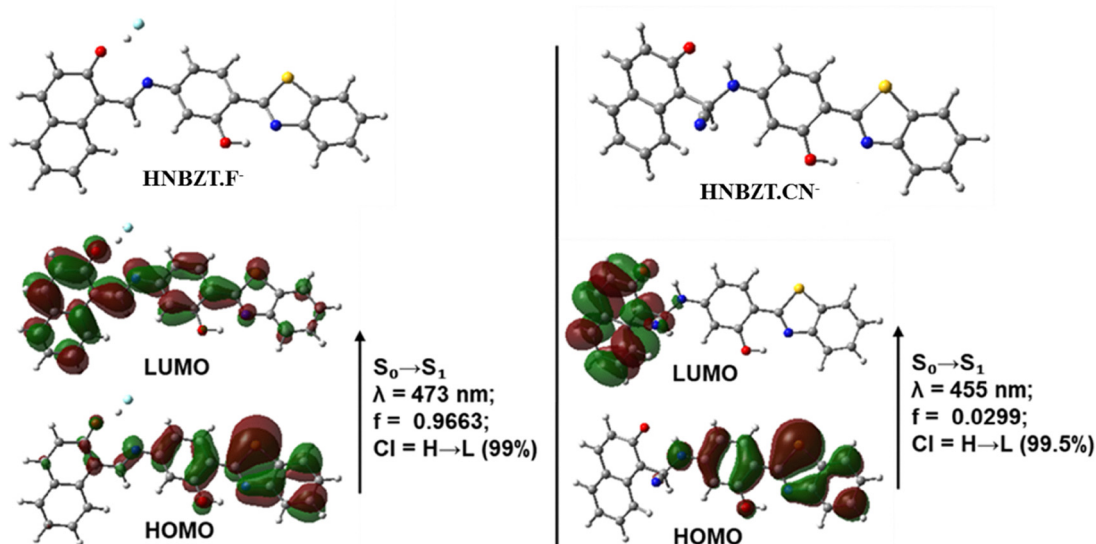


Fig. 14 Optimized structures of **HNBZT.F<sup>-</sup>** and **HNBZT.CN<sup>-</sup>** along with their frontier molecular orbitals.

### 3.6. <sup>1</sup>H NMR of **HNBZT** with **F<sup>-</sup>** and **CN<sup>-</sup>** ions

To investigate the binding mechanisms of **F<sup>-</sup>** and **CN<sup>-</sup>** ions with **HNBZT**, <sup>1</sup>H NMR titrations were conducted in **CD<sub>3</sub>CN-*d*<sub>3</sub>**. In the <sup>1</sup>H NMR spectrum of **HNBZT**, an imine proton was observed at  $\delta$  8.98 ppm. No significant change was detected at this position upon the addition of 1.0 equivalent of **F<sup>-</sup>** ions (Fig. 12). Additionally, the disappearance of the hydroxyl proton indicated hydrogen bonding between the **F<sup>-</sup>** ion and the naphtholic hydrogen. Further changes were observed in the aromatic region upon the addition of **F<sup>-</sup>** ions. The peak corresponding to the **H<sub>a</sub>** proton at  $\delta$  8.28 ppm was shifted, and the peak for the **H<sub>d</sub>** proton at  $\delta$  7.95 ppm shifted to  $\delta$  8.05 ppm. Similarly, the peak at  $\delta$  7.88 ppm due to the **H<sub>e</sub>** proton shifted to  $\delta$  7.95 ppm. These shifts suggested charge delocalization and redistribution within the **HNBZT** molecule after binding with **F<sup>-</sup>** ions, likely as a result of deprotonation. In contrast, the protons in the phenyl ring, appearing at  $\delta$  7.49–7.36 ppm and benzothiazole ring at  $\delta$  8.82 ppm and  $\delta$  8.68 ppm, showed negligible changes, indicating that the phenyl and benzothiazole moieties were not significantly involved in the interaction (Fig. S6, ESI<sup>†</sup>). These findings provided insights into the binding mechanism of **F<sup>-</sup>** ions with **HNBZT** (Scheme 2).

Similarly, the addition of 1.0 equivalent of **CN<sup>-</sup>** ions to **HNBZT** caused significant changes in the proton signals. The imine proton at  $\delta$  8.98 ppm disappeared completely upon interaction with **CN<sup>-</sup>** ions (Fig. 13). Additionally, the phenyl ring protons at  $\delta$  7.49 and 7.38 ppm were shifted upfield, and the naphthalene ring protons merged, indicating charge propagation across the molecule. In contrast, the protons in the benzothiazole ring, appearing at  $\delta$  8.82 and 8.71, showed negligible changes, thus not involved in the interaction. These observations suggested that the binding mechanism involved nucleophilic addition of **CN<sup>-</sup>** ions to **HNBZT** (Scheme 2). <sup>13</sup>C NMR was also performed to confirm the binding behaviour of **HNBZT** with **CN<sup>-</sup>** ions. With the addition of 1.0 equivalent **CN<sup>-</sup>**

ions, a new peak appeared at 50.40 ppm indicating the nucleophilic addition of **CN<sup>-</sup>** to **HNBZT** (Fig. S7, ESI<sup>†</sup>). The FTIR spectrum of **HNBZT** before and after the addition of **CN<sup>-</sup>** also confirmed the binding mechanism (Fig. S8, ESI<sup>†</sup>).

The binding interactions of **F<sup>-</sup>** and **CN<sup>-</sup>** ions with **HNBZT** were further corroborated through theoretical calculations. The optimized structures of the **HNBZT.F<sup>-</sup>** and **HNBZT.CN<sup>-</sup>** complexes are shown in Fig. 14. The predicted absorption spectra based on these optimized structures were in good agreement with the experimental results. For **HNBZT.F<sup>-</sup>**, three low-lying vertical excitations were identified: the HOMO  $\rightarrow$  LUMO transition (99%;  $f = 0.9663$ ) at 473 nm, the HOMO–1  $\rightarrow$  LUMO transition (77%;  $f = 0.2191$ ) at 396 nm, and the HOMO  $\rightarrow$  LUMO+1 transition (82%;  $f = 0.0373$ ) at 362 nm. Similarly, for **HNBZT.CN<sup>-</sup>**, three low-lying vertical excitations were observed: the HOMO  $\rightarrow$  LUMO transition (99.5%;  $f = 0.0299$ ) at 455 nm, the HOMO  $\rightarrow$  LUMO+1 transition (89%;  $f = 0.2896$ ) at 368 nm, and the HOMO–1  $\rightarrow$  LUMO transition (82%;  $f = 1.0059$ ) at 358 nm. In both complexes, the HOMO  $\rightarrow$  LUMO transitions

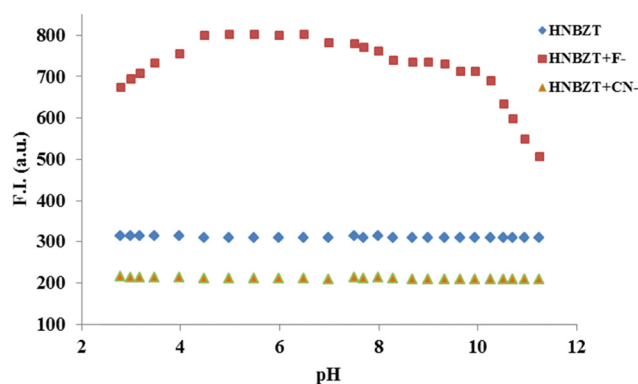


Fig. 15 Effect of pH on emission spectra of **HNBZT** (20  $\mu$ M) and its complexes with ions in **CH<sub>3</sub>CN**.



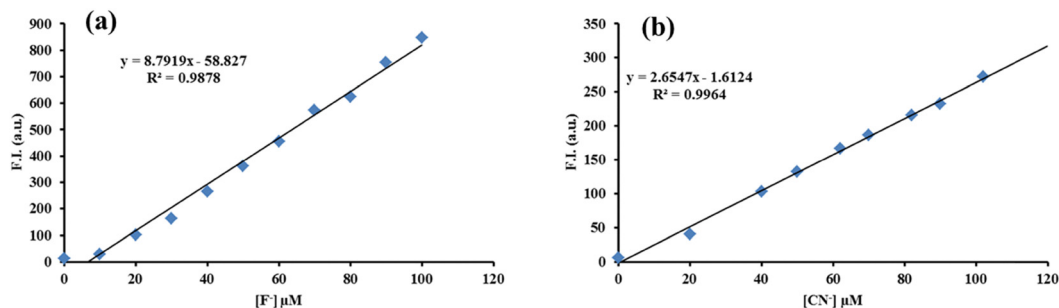


Fig. 16 Emission spectra of **HNBZT** in the presence of different concentrations of spiked (a)  $F^-$  and (b)  $CN^-$  from 0 to 100  $\mu M$ .

exhibited a significant electron density shift from the benzothiazole unit to the Schiff base unit, indicating intramolecular charge transfer (ICT). This ICT is responsible for the observed colour changes in the presence of  $F^-$  and  $CN^-$  ions.

### 3.7. pH titration

We also checked the pH stability of **HNBZT** and its complex with the  $CN^-$  ions. To check the pH stability, we performed acid–base titration. From the acid–base titration, it is clear that our compound was stable in the pH range from 2–12 (Fig. 15). Similarly, the **HNBZT** and  $CN^-$  complex was also stable in the pH range of 2–12. The stability of **HNBZT** and its complex in the pH range 2–12 established its benefit for rapid monitoring in environmental and biological samples. The complex of **HNBZT** and  $F^-$  ions was also stable in the pH range from 4–10, so the detection of these ions using **HNBZT** could be well performed in a given pH range.

### 3.8. Detection of $F^-/CN^-$ ions in real samples

**HNBZT** was used to detect  $F^-$  and  $CN^-$  in real water samples in order to investigate the practical applicability of the chemosensor where satisfactory results were achieved.  $F^-$  and  $CN^-$  sample solutions were prepared using tap water from the laboratory. In this instance, known  $F^-$  and  $CN^-$  ion concentrations were directly spiked into tap water. The emission intensity

was then measured at 450 nm after the samples were subjected to 20  $\mu M$  of **HNBZT** in  $CH_3CN$  (Fig. 16). The favorable recoveries from tap water with varying  $F^-$  and  $CN^-$  ion concentration show practical applicability of **HNBZT** in everyday situations (Table 5). **HNBZT** can detect  $F^-$  and  $CN^-$  ions with high efficiency as compared to the previous reports (Table S1, ESI†). Similarly, good recoveries were obtained from toothpaste samples (Table 6).

## 4. Conclusion

In conclusion, an efficient chemosensor, **HNBZT** was synthesized, and its photophysical properties were thoroughly investigated in various solvent systems. **HNBZT** demonstrated aggregation-induced emission (AIE) behaviour and was successfully employed for the selective and sensitive detection of  $F^-$  and  $CN^-$  ions in a  $CH_3CN$  solvent system. Detection of  $F^-$  and  $CN^-$  ions by **HNBZT** was achievable with the naked eye. The detection limits for  $F^-$  and  $CN^-$  ions were as low as  $7.6 \times 10^{-8}$  M and  $1.1 \times 10^{-7}$  M, respectively.  $^1H$  NMR titration of **HNBZT** with  $F^-$  and  $CN^-$  ions revealed distinct binding mechanisms, with  $F^-$  ions forming hydrogen bonds, while  $CN^-$  ions induced nucleophilic addition which is also supported by theoretical studies. Notably,  $F^-$  and  $CN^-$  ions interacted with **HNBZT** via distinct binding mechanisms.

## Conflicts of interest

There are no conflicts of interest to declare.

## Data availability

The authors confirm that the data supporting the findings of this study are available within the article and/or its ESI.†

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Table 5 Determination of  $F^-$  and  $CN^-$  ions in tap water

Ion	Sample	Ion added ( $\mu M$ )	Ion recovered ( $\mu M$ )	Recovery (%)	RSD
$F^-$	1	20	20.5	102.5	0.31
	2	40	41.1	102.75	0.35
$CN^-$	1	20	18.1	90.5	0.42
	2	40	40.1	100.25	0.55

Table 6 Determination of  $F^-$  ions in toothpaste samples

Sample	$F^-$ found	Added ( $\mu M$ )	Recovered ( $\mu M$ )	Recovery (%)	RSD
Toothpaste 1	1	10	9.5	95	0.71
	2	20	20.2	101	0.80
Toothpaste 2	1	10	9.9	99	0.78
	2	20	19.7	98.5	0.74



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