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# Journal of Fluorine Chemistry



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# Experimental and theoretical studies of novel hydroxynaphthalene based chemosensor, and construction of molecular logic gates $\stackrel{\ensuremath{\sim}}{\sim}$



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#### ARTICLE INFO

Article history: Received 24 June 2016 Received in revised form 4 October 2016 Accepted 5 October 2016 Available online 5 October 2016

Keywords: Chemosensing Single crystal XRD TDDFT Molecular logic gate

#### ABSTRACT

2-Hydroxynaphthalenyl-N(4)-cyclohexyl thiosemicarbazone (CHNT) was synthesized and characterized for selective sensing of fluoride, cyanide and copper ions. The interaction between CHNT with fluoride, cyanide and copper ions have been investigated through their absorption, fluorescence and electrochemical behavior, and binding constants of corresponding ions have been calculated, which is in order of  $Cu^{2+} < CN^- < F^-$ . The <sup>1</sup>H NMR titration study strongly support the deprotonation was takes place from the N<sub>2</sub>–H<sub>8</sub> proton which is near to the naphthalene group. The fluoride and copper sensing mechanism of CHNT has been investigated by DFT and TDDFT methods. The theoretical results indicate that the proton of the N<sub>2</sub>–H in thiosemicarbazone group is captured by the added fluoride ion and then deprotonated in excited state. The excited state proton transition mechanism was further confirmed with NBO and PES analysis. The CHNT found good reversibility character with the alternative addition of  $Ca^{2+}$  and  $F^-$ . The multi ion detection of CHNT was used to construct the NOR, XNOR and NAND molecular logic gates.

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# 1. Introduction

Cations and anions play a vital role in chemical and biological processes [1-3]. The effective and selective detection of these metal ions and anions are done by the chemosensors which has grabbed the attention over a period [4,5]. The fluoride, cyanide ions have major activity in human health, where one such example of fluorine is used in the treatment of Osteoporosis<sup>5</sup> and toxic when its content (<1.5 mg/l) more in human body [6]. Due to small size and highly electronegativity of the fluorine, it can form H-bonding easily [7,8]. The fluoride chemosensors are mainly based on via hydrogen bonding interaction, Lewis acid-base or selective chemical reactions [9,10]. Based on these modes the fluorescent probes were designed to sense the fluoride anion. Cyanide has a wide spread importance in the industrial level, such as raw material in many organic chemical production and in polymer synthesis such as nitrils, nylon, and acrylic plastics [11–13]. As it

interacts strongly with the heme group and causes cellular respiration problem. There by affect the vascular, cardiac, visual and metabolic activities [14,15]. The cyanide chemosensor are constructed based on reversible binding and on the bases of reaction [16]. Due to high solvation energy of cyanide in aqueous medium it affects the hydrogen bonding between the receptor and cyanide ion. The fluorescent sensing probes are of great use due to its high sensitivity, image analysis and simple operating method [17]. Copper has its wide spread application among other transition metals and it acts as a catalytic cofactor of metalloenzymes in biological processes [18]. Copper is a required nutrient for human health only trace quantity when the limit exceeds or decreases it causes disorders like Alzheimer's, Menkes and Wilson diseases [19]. The bioavailability of copper concentration inside the cell are strictly regulated by copper homeostasis system [20]. Even though there are only very few reports for the detection of multi ions with a single receptor [21].

Understanding of the theoretical aspect and the detailed study of chemosensing mechanism is critical for fluorescent chemosensor to develop and design better chemosensor for the applications in environmental protection and human health [22,23]. Scientists proposed different mode of chemosensing mechanisms such as photo-induced electron transfer (PET), excimer and exciplex formation, intramolecular charge transfer

<sup>\*</sup> CCDC: 1477652 contains the supplementary crystallographic data for CHNT. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

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http://dx.doi.org/10.1016/j.jfluchem.2016.10.005 0022-1139/© 2016 Elsevier B.V. All rights reserved.

(ICT), metal ligand charge transfer (MLCT), fluorescence resonance energy transfer (FRET) and excited state proton transfer (ESPT) [24–29]. The hydroxyl (O—H) and amine (N—H) group are wellknown proton donor site for strong hydrogen bonding of the anion sites [30]. Now a days, the developments in supramolecular chemistry have attracted great attention in the construction of photonic devices that function as molecular level logic gate based on optical signals [31]. The receptor with multiple detection of ions are using to construct the logic gate, which results in the development of molecular logic gates such as AND, OR, NOR, INHIBIT, XOR, NAND [32–34]. Recently, the new area of fluorescent probes for redox change was proposed [51–53].

In this connection we have designed and synthesized a novel ratiometric colorimetric sensor toward fluoride, cyanide and copper ions using photo-induced electron transfer (PES) and internalcharge charge transfer (ICT) as a signaling mechanism for the naked eye detection, and explained the logic gate behavior of the receptor by analyzing the optical signal as input. The chemosensing mechanism was revealed using computational methods. Previously, we have reported the experimental studies on selective anion sensing using the thiocarbohydrazone and thiosemicarbazones based chemosensors [35–37].

#### 2. Experimental section

# 2.1. Synthesis of CHNT

Ethanolic solution of cyclohexyl isothiocyanate (0.706 g, 5 mmol) and hydrazine hydrate (0.25 g, 5 mmol) were mixed and kept in constant stirring for 1 h. The white precipitate N(4)-cyclohexyl thiosemicarbazide was formed, which was then filtered, washed, dried and recrystallized from ethanol. The product (N-(4)-cyclohexylthiosemicarbazide, 0.346 g, 2 mmol) was dissolved in methanol (30 ml) and was added to 2-hydroxyl-1-naphthaldehyde (0.344 g, 2 mmol), which was dissolved in methanol (5 ml). The mixture then refluxed for 4 h after adding a few drops of acetic acid. The reaction mixture was kept aside for slow evaporation at room temperature. After evaporation, the product has been formed was isolated. Further, the product was recrystallized from chloroform and methanol mixture (1:1) and was dried in vacuum (Scheme 1).

**CHNT** (pale green), Yield: 88%, M.P: 202–204 °C, Chemical Formula:  $C_{18}H_{21}N_3OS$ , Anal Calcd: C 66.02, H 4.96, N 19.52, S 11.06; Found: C 66.05, H 4.92, N 19.49, S 11.09; **IR Data** (cm<sup>-1</sup>): 1537 (s, v (C=N)), 1224 (s, v(C=S)), 3381 (br, v(O–H)), 3130 (s, v(N–H)), <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 10.76 (s, 1H), 10.19 (s, 1H), 9.06 (s, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.82 (dd, *J* = 16.0, 8.5 Hz, 2H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 8.9 Hz, 1H), 6.62 (d, *J* = 13.4 Hz, 2H), 1.66 (d, *J* = 12.9 Hz, 1H), 1.46 (dd, *J* = 24.5, 11.9 Hz, 2H), 1.38–1.20 (m, 3H). <sup>13</sup>**C NMR** (125 MHz, CDCl<sub>3</sub>,  $\delta$  ppm) 175.2 (C12 = S), 157.7 (C1 – O), 143.9 (C11 = N), 133.6, 132.1, 129.2, 128.5, 128.0, 124.0, 120.3, 118.5, 108.1 (aromatic carbons, C2-C10), 53.4 (Cyclohexyl carbon (C13)), 32.7, 25.4, 24.7 (cyclohexyl carbons, C14-C18); **ESI MASS**: 350.15 (Na+m).

#### 2.2. Single crystal X-ray diffraction studies

A BRUKER Venture X-ray (kappa geometry) diffractometer was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the APEX3 software suite. The sample was optically centered with the aid of a video camera such that no translations were observed as the crystal was rotated through all positions. The X-ray radiation employed was generated from a Cu-I $\mu$ s X-ray tube (K<sub>a</sub> = 1.5418 Å with a potential of 50 kV and a current of 1.0 mA). The crystal mounted on a nylon loop was then placed in a cold nitrogen stream (Oxford) maintained at 100 K. The unit cell was verified by examination of the hkl overlays on several frames of data. No super-cell or erroneous reflections were observed. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX3. The integration method employed a three dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects. Finally the data was merged and scaled to produce a suitable data set. The absorption correction program SADABS was employed to correct the data for absorption effects. A solution was obtained readily using XT/XS in APEX3, which was confirmed using PLATON (ADDSYM). The structure was refined (weighted least squares refinement on  $F^2$ ) to convergence [38]. Olex2 was employed for the final data presentation and structure plots. The crystallographic data along with details of structure solution refinements are given in Table 1.

#### Table 1

Crystal data and structure refinement for CHNT.

Compound	CHNT
Empirical formula	C <sub>18</sub> H <sub>21</sub> N <sub>3</sub> OS
Formula weight	327.44
Temperature	100.0 K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P 1 21/c 1
Unit cell dimensions (Å)	a = 14.5894(3), b = 5.79900(10),
	c = 19.1169(4)
Volume	1617.36(6) Å3
Z	4
Density (calculated)	1.345 Mg/m3
Absorption coefficient	1.836 mm-1
F(000)	696
Crystal size	$0.216\times0.047\times0.045mm3$
Theta range for data collection	3.029 to 70.137°.
Index ranges	-17 < =h < =17, -6 < =k < =6, -23 < =l < =23
Reflections collected	28474
Independent reflections	3058 [R(int)=0.0699]
Completeness to theta = $67.679^{\circ}$	99.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7533 and 0.5640
Refinement method	Full-matrix least-squares on F2
Data/restraints/parameters	3058/0/209
Goodness-of-fit on F2	1.087
Final R indices [I>2sigma(I)]	R1 = 0.0411, wR2 = 0.0907
R indices (all data)	R1 = 0.0511, wR2 = 0.0967
Extinction coefficient	n/a
Largest diff. peak and hole	0.335 and –0.292 e.Å-3



Scheme 1. Synthesis of thiosemicarbazone compound (CHNT).

#### 2.3. Computational method

All calculations were performed using Gaussian 09 program. The hybrid density functional theory (DFT) and time dependent DFT (TDDFT) calculations were run to deal with the electronic spectra and electronic excited state. The geometry optimizations for the ground state were run using hybrid exchange-correlation function B3LYP and 6-31G(d,p) basis set, which is moderate and suitable for such large organic compounds. Considering that the experiments were conducted in DMSO solvent, all computational calculations were included polarizable continuum model (PCM) with dielectric constant of DMSO ( $\varepsilon$  = 46.826). The TDDFT analysis was carried out using CAM- B3LYP/6-31G(d,p) level, which is [50]. The B3LYP/LanL2DZ level used for CHNT-Cu complex. The transition state (TS) and intrinsic reaction coordinate (IRC) calculations were carried out to figure out the mechanism of the sensing [39]. The local minima in the ground state, transition state, intermediate and excited state were confirmed with the vibrational frequency analysis [40]. The charge distribution, occupancy and the energy of the bonding orbitals were calculated using natural bond orbital (NBO) analysis at the same theoretical level as ground state and excited state geometry optimized structure of CHNT-F and CHNT-Cu complexes. The second order perturbation energy of the CHNT-F and CHNT-Cu were calculated to evaluate the donor-acceptor interaction [41]. The potential surface curve (PES) calculations were carried to confirm the sensing mechanism (Table 2).

# 3. Result and discussion

# 3.1. Characterization of CHNT

The CHNT was synthesized by schiff's base condensation of 2hydroxylnapthaldehyde and cyclohexyl thiosemicarbazide, which is given in the scheme. It was well characterized by FT-IR, <sup>1</sup>H, <sup>13</sup>C NMR and MASS spectra before using in application. The elemental analysis data where good agreement with calculated values. In the FT-IR spectroscopy we get the information about the presence of functional group in the compound such as CH=N, N-NH, O-H, etc. by the absorption peak which arise due to the stretching vibrations of the bond in the group. Sharp peaks observed at 1537 and  $1224 \text{ cm}^{-1}$  which attributes the presence of v(C=N) and v(C=S) groups respectively in the CHNT. The O-H and N-H groups have its vibration frequency at a range of 3381 and 3130 cm<sup>-1</sup>. The NMR spectroscopy is one of the principle techniques which gives the structural information about molecules. The <sup>1</sup>H NMR of CHNT gives a singlet around  $\delta$  12.7 and 11.67 ppm corresponding to the N<sub>2</sub>-H and N<sub>3</sub>-H protons respectively. The protons of the aromatic ring has its doublets and triplets at around  $\delta$  6.9–7.3 ppm. The sharp singlet found at  $\delta$ 9.06 ppm confirms the presence of N=C-H proton. The lower field multiplet peaks at  $\delta$  2.13 and 1.5 ppm correspond to the presence of

Table 2

Selected	l bond	lengths	(A),	bond	l angle	es (°)	and	torsio	n angl	les (	°) of	the	CHNT.	
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Cy–C–H and cyclohexyl protons. The <sup>13</sup>C NMR spectrum has well defined peaks at 175.35, 157.98 and 144.30 ppm assign to thionyl carbon (C=S), hydroxyl group attached aromatic carbon (C=C–OH) and azomethine (C=N) groups respectively. The aromatic carbons in naphthalene group were found at  $\delta$  110–120 ppm. The cyclohexyl carbon attached to nitrogen was found at  $\delta$  53.05 ppm. The peaks at 32.7, 25.4 and 24.7 ppm corresponds to the cyclohexyl carbons.

#### 3.2. Single crystal X-ray crystallography

The molecular structure of CHNT with the atom numbering and molecular packing are shown in Fig. 1 and Fig. 2, and the important bond parameters were listed in Tables 2 and 2a. The suitable colorless needle with very well defined faces with dimensions (max, intermediate, and min)  $0.216 \times 0.047 \times 0.045 \text{ mm}^3$  from a representative sample of crystals of the same habit. CHNT crystallizes monoclinic  $P12_1/c1$  in the space group with Z=4. The crystal structures of the compound showed the existence of an intramolecular hydrogen bonding interaction between hydroxide proton and imine nitrogen. The sulfur atom S(1) and the hydrazone nitrogen N(3) are in the *E* position with respect to the C(12)-N(2)bond. The N(1)–N(2)(1.373(2)Å) and N(2)–C(12)(1.354(2)Å) bond distances in CHNT are intermediate between ideal values of corresponding single [N—N, 1.45 Å; C—N, 1.47 Å] and double bonds [N=N, 1.25 Å; C=N, 1.28 Å], giving evidence for an extended  $\pi$ -delocalization along the thiosemicarbazone chain [42].

#### 3.3. Colourimetric analysis and UV-vis spectroscopy

The interaction of the CHNT with various anions (such as F<sup>-</sup>, CN<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, H<sub>3</sub>PO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, OH<sup>-</sup> and AcO<sup>-</sup>) and cations (such as  $(Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+})$ were investigated in DMSO solution through colourimetric analysis. Noticeable and appreciable colour change was observed with the addition of fluoride, cyanide and copper ions, imparting a red, light red and deep yellow colour respectively. Addition of other anions and cations didn't show any visible colour changes. The UVvis spectra were recorded in DMSO solvent at room temperature. The CHNT shows a broad peak at 258 nm which is the result of  $\pi{\rightarrow}\pi^*$  transition. While a second absorption peak with two shoulder peak at 321 and 332 nm attributes the CHNT is a conjugated compound. There is also  $n \rightarrow \pi^*$  transition which is confirmed by the peak at 370 nm. As Fig. 3 shows, the addition of anions and cations to the CHNT didn't show any spectral change, except fluoride, cyanide and copper ions.

Upon the addition of fluoride ion to the CHNT results bathochromic shift at a difference nearly 66 nm, new broad peaks were found at 416 and 483 nm, simultaneously the peak at 370 nm which is the result of intramolecular charge transfer of the compound shows gradual hypsochromic shift. The formation of new broad peaks attributes the presence of CHNT–F complex and

Bond lengths (Å)		Bond angles (°)		Torsion angles (°)	
S(1) -C(12)	1.693(2)	C(1)-O(1)-H(1)	109.5	O(1)-C(1)-C(2)-C(3)	178.66(16)
O(1) - H(1)	0.8400	C(11)-N(1)-N(2)	114.86(16)	O(1)-C(1)-C(2)-C(11)	-3.2(3)
O(1) - C(1)	1.352(2)	N(1)-N(2)-H(2)	119.1	O(1)-C(1)-C(6)-C(5)	178.28(17)
N(1) - N(2)	1.373(2)	C(12)-N(2)-N(1)	121.83(16)	N(1)-N(2)-C(12)-S(1)	173.85(13)
N(1) - C(11)	1.294(2)	C(12)-N(2)-H(2)	119.1	N(1)-N(2)-C(12)-N(3)	-6.8(3)
N(2) - H(2)	0.8800	C(12)-N(3)-H(3)	118.1	N(2)-N(1)-C(11)-C(2)	178.90(16)
N(2) - C(12)	1.354(2)	C(12)-N(3)-C(13)	123.88(16)	N(3)-C(13)-C(14)-C(15)	-178.35(15)
N(3) —H(3)	0.8800	C(13)-N(3)-H(3)	118.1	N(3)-C(13)-C(18)-C(17)	179.83(16)
N(3) - C(12)	1.335(2)	O(1)-C(1)-C(6)	115.91(17)	C(1)-C(2)-C(11)-N(1)	0.9(3)
N(3) -C(13)	1.467	N(1)-C(11)-C(2)	123.02(17)	C(11)-N(1)-N(2)-C(12)	-179.27(17)



Fig. 1. Structure of AntCy with labelling of selected atoms. Anisotropic displacement ellipsoids Exhibit 30% probability levels. Hydrogen atoms are drawn as circles with small radii.



Fig. 2. Molecular packing viewed down c axis showing intermolecular interactions in CHNT.

#### Table 2a

Hydrogen bonds for CHNT [Å and °]\_.

D–H ···· A	d(D-H)	$d(H \cdots A)$	$d(D \cdots A)$	<(D-H-A)
$O(1) - H(1) \cdots N(1)$	0.84	1.91	2.65	145.8
$N(2) - H(2) \cdots S(1)$	0.88	2.52	3.37	164.1

Symmetry transformation used to generate equivalent atoms:. #1-X+1, y+2, -z+1.

hydrogen bond in between host-guest molecules. The newly formed band in visible region shows the hyperchromic shift along with the addition of fluoride ion. Very clear isobistic points where observed at 397, 338 and 322 nm, which attributes the presence of multi-compounds such as CHNT–F, deprotonated CHNT, etc in the solution. While the presence of cyanide ion, a new broad peak at 450 nm, which is gradually increasing with increasing the concentration of cyanide ion. Up on the addition of the Cu<sup>2+</sup> to the CHNT, new absorption band at 417 nm with a shoulder peak at 435 nm were observed which is due to the charge transfer from ligand to metal. There are two isobistic points at 394 and 348 nm, which implies the presence of multi complexes in the solution. The change in the absorption band and the colour when CN<sup>-</sup> and F<sup>-</sup> are added to the CHNT is may be due to the formation of hydrogen bond, and the deprotonation of CHNT. The bathochromic shift at  $n \rightarrow \pi^*$  is also the result of hydrogen bonding interaction between the ion and CHNT. The spectral profile for fluoride, cyanide and copper along with CHNT is shown in Fig. 4.

Job's plot method was carried out to find the stoichiometric ratio with CHNT and ions. As in Fig. 5, the fluoride and cyanide bonded with 2:1 ratio, and copper is for 1:1 ratio with sensor CHNT. The association constant  $K_a$  is calculated in accordance to the Benesi-Hildebrand equation [43], which is as bellow,

$$\frac{1}{A - A_0} = \frac{1}{A_\infty - A_0 K[C]} + \frac{1}{A_\infty - A_0}$$

where 'A, A<sub>0</sub> and A<sub>∞</sub> are the absorbance with a specific ion concentration, absorbance of free compound and absorbance at excess amount of ion respectively. "K" and [C] is the association constant (M<sup>-1</sup>) and the concentration of ion respectively. The binding constant (K) values were calculated from the plot 1/(A-A<sub>0</sub>) vs 1/[C], which shows a linear relationship. The calculated association constant (K<sub>a</sub>) for CHNT with fluoride, cyanide and copper ions are found to be  $3.51 \times 10^5$ ,  $2.07 \times 10^5$  and  $1.09 \times 10^5 \text{ M}^{-1}$  respectively. Thus the sensor CHNT shows binding affinity with ions in order of Cu<sup>2+</sup> < CN<sup>-</sup> < F<sup>-</sup>.

#### 3.4. Fluorescence spectral studies

In order to learn more about the sensing ability of the receptor, fluorescence measurements were carried out similar to that of UV titration. Moreover, compared to absorption spectroscopy, fluorescent emission spectroscopy is a more effective approach for anion sensing. The fluorescent property of CHNT with 369 nm excitation wavelength in the presence of various anions and cations was examined. For CHNT, the emission peak was found at 436 nm. While adding the fluoride and cyanide ion to the CHNT, the fluorescence quenching was happened with appearance of new



Fig. 3. UV-vis spectra of CHNT with (a) different anions and (b) cations.

peak at 435 nm, and simultaneously a new fluorescence enhanced peak was formed at 495 nm. The presence of fluoride and cyanide ions with CHNT leads to fluoresce enhancement, which attributes the PET process in the relaxation of excited state. The fluorescence enhancement can also due to the presence of strong intramolecular hydrogen bond of  $O \cdots H \cdots$  ion and  $N \cdots H \cdots$  ion. Among the cations, the selective sensing towards  $Cu^{2+}$  was shown by CHNT. As in Fig. 2, the addition of copper ion to the CHNT, fluoresce quenching happened at 435 nm, which is due the strong interaction of copper ion with CHNT. The addition of other anions (such as  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $ClO_4^-$ ,  $H_2PO_4^-$ ,  $NO_3^-$ ,  $HSO_4^-$ ,  $OH^-$  and  $AcO^-$ ) and cations (such as  $(Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}$  and  $Zn^{2+}$ ) in CHNT didn't give any change in fluorescence spectra (see Fig. 6).

The binding constant was determined using modified Benesi-Hildebrand equation [44] which is as follows,

$$\frac{1}{(F_x - F_0)} = \frac{1}{(F_\infty - F_0)} + \frac{1}{K[C](F_\infty - F_0)}$$

where  $F_0$  and  $F_x$  are corresponding emission intensity of CHNT alone and CHNT with addition of ions respectively. 'K' is the association constant and 'C' is the concentration of added ions. The association constants were calculated from the plot of  $1/(F_x-F_0)$  vs 1/[C]. The binding constant of CHNT towards  $F^-$ ,  $CN^-$  and  $Cu^{2+}$  were determined from the ratio of intercept/slope, and which found to be  $5.05\times10^5$ ,  $0.74\times10^5$  and  $1.38\times10^5\,M^{-1}$  respectively. From the binding constant values, it is clear that the  $F^-$  has higher fluorescence binding affinity towards CHNT, which is confirming the UV–vis calculation results.

#### 3.5. Electrochemical studies

CHNT shows the reversible reduction potential ( $E_{pc}$ ) at -0.46 V, which is due to greater  $\pi$ -conjugation caused by the electron negative nitrogen atom. Up on the addition of Cu<sup>2+</sup> ion in CHNT, a new reduction peak was observed at -0.87 V, and the 'l<sub>p</sub>' value at that point keep on increasing with increasing the concentration of copper ion. The newly formed cathodic peak indicate the formation of CHNT–Cu complex. But the equimolar addition of copper ion to CHNT effect the disappearance of receptor's reduction peak, and further addition of copper ion results the formation of two cathodic peaks at -0.47 and 0.13 V, which attributes the formation of Cu<sup>2+</sup>/Cu<sup>+</sup> and Cu<sup>+</sup>/Cu respectively [45].

The higher current value at the 0.0.137 V shows the formation of strong Cu-CHNT bond. As in Fig. 7, there is no change observed when other cations (such as  $Cr^{3+}$ ,  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Fe^{3+}$ ,  $Fe^{2+}$ ,  $Ni^{2+}$  and  $Zn^{2+}$ ) and the anions (such as  $F^-$ ,  $Cl^-$ ,  $I^-$ ,  $Br^-$ ,  $OH^-$ ,  $AcO^-$ ,  $CN^-$ ,  $NO_3^-$ ,  $ClO_4^-$ , HSO<sub>4</sub><sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>) added to the CHNT. But, adding equal mixture of different cations in the presence of copper ion gives an extra cathodic peak at -0.46 V, which show the selective electrochemical sensing of chemosensor towards copper ion. The binding constants of the receptors with copper ion were calculated using modified Bensesi-Hildebrand equation, which is as below

$$I^{2} = \frac{1}{K_{b}[C]}(I_{p0}^{2} - I_{p}^{2}) + I_{p\infty}^{2} - [C]$$

where  $l_{p}^2$ ,  $l_{p0}^2$  and  $l_{\infty}^2$  are the reduction current of receptor, after the addition of copper ion and excess addition of copper ion respectively. The 'K<sub>b</sub>' values of CHNT towards Cu<sup>2+</sup> ion was calculated from the reciprocal of slope, which is found to be  $6.25 \times 10^5 \, \text{M}^{-1}$  (see Fig. 8). The binding constant value matches with the previously calculated binding constants from UV–vis and fluorescence spectral studies.

# 3.6. <sup>1</sup>H NMR Titration

For the better understanding of sensing mechanism, <sup>1</sup>H NMR titration were carried out for CHNT in the presence and absence of TBAF in CDCl<sub>3</sub>. In the case of neat CHNT, single peak at 10.75, 10.18 and 9.06 ppm which are correspond to the protons of ' $N_2$ -H', 'N<sub>3</sub>-H', and N=C-H respectively. As in Fig. 9, the addition of 1 equivalent of fluoride ion, the singlet peak of the N<sub>2</sub>–H proton disappears completely and the peak corresponding to the N<sub>3</sub>-H proton is shifted downfield with a broadening of the signal. Whereas, there is no noticeable change for the peak at 9.06 ppm, which infer that the N=C-H proton has no involvement in the sensing process. The peak broadening at 10.18 ppm attributes the hydrogen bonding formation between fluoride anion and N<sub>3</sub>-H proton  $(N_3-H\cdots F)$  [46]. The consequence addition of  $F^-$  to the CHNT results the complete peak disappearance at 10.18 ppm, which attributes the deprotonation takes place from the N<sub>3</sub>-H. Simultaneously, the peak intensity at the 8.01 ppm decreased along with the broadening of the peak. The changes in the <sup>1</sup>H NMR



Fig. 4. UV-vis spectra of CHNT with different concentration of (a) fluoride, (b) cyanide and (c) copper ions. Fluoresence spectra of CHNT with different concentration of (d) fluoride, (e) cyanide and (f) copper ions.



Fig. 5. Benezi-Hilderbrand diagram for CHNT with (a) fluoride, (b) cyanide and (c) copper ions. The Jobs plot diagram was given in incert.



Fig. 6. Fluorescence spectra of CHNT with different (a) anions and (b) cations.



Fig. 7. CV responds of CHNT with (a) different cations, and (b) various equivalents of copper ion.



Fig. 8. Modified Benesi-Hildebrand plot of CHNT towards copper ion using CV data.

spectrum indicates that the formation of hydrogen bonding between ' $N_3$ -H  $\cdots$  F' in the excess amount of fluoride.

# 3.7. COMPUTATIONAL METHODS

#### 3.7.1. Geometric study

To reveal the sensing mechanism of the CHNT, the ground state, excited state and deprotonated geometries were optimized with and without the presence of ions, which are shown in Fig. 10. The energy of CHNT in cis and trans form in the ground state is  $-35.08 \times 10^5$  and  $-35.09 \times 10^5$  Kcal/mol respectively. In the ground state, the dihedral angle between naphthalene moiety and thiosemicarbazone group is  $137.17^{0}$ , which shows the structure is not a coplanar. And the dihedral angle between boat shaped cyclohexyl group and thiosemicarbazone group is  $135.56^{0}$ ,

and it increased to 148.08<sup>0</sup> at the excited state of CHNT. After the bonding with fluoride ion, the dihedral angle twisted to 51.19<sup>0</sup>. The ground state optimized energy of the CHNT–F complex is less than that of CHNT. After the formation of fluoride complex, the dihedral angles between cyclohexyl group-thiosemicarbazone and naphthalene moiety-thiosemicarbazone found same. In the ground state of CHNT, the  $O-H, N_1-H_1$  and C=N bond distances were found to be 0.96, 1.02 and 1.29 Å respectively, which were increased in the CHNT-F complex. The bond length elongation attributes the formation of single bond between C-N. While the  $N_2-H_2$  and C=S bond distances found same in CHNT, the ground state and the excited state CHNT-F complex. In the excited state of CHNT-F complex (CHNT-F\*), the calculated dihedral angle between naphthalene moiety and thiosemicarbazone group is 158.39<sup>0</sup>, which much higher than in the ground state structure of CHNT and CHNT-F complex. The calculated bond length of C-O show 1.30 Å for CHNT–F\*, which is closer to double bond C=O. It demonstrated that the CHNT-F and CHNT-F\* are better conjugated than CHNT. In the CHNT-F\*, the bond distance between  $F-H_{21},\,F-H_8$  and  $F-H_7$  found as 1.49, 1.53 and 1.93 Å respectively. The F-H<sub>21</sub> and F-H<sub>7</sub> are higher with comparing with the ground state structure of CHNT-F complex, which indicate the excited state proton transfer (ESPT) process. With considering two fluoride ion attach to CHNT, the CHNT-F<sub>2</sub> complex structure also optimized. In CHNT-F<sub>2</sub>, the O-H and N-H bond distance found higher that of CHNT and CHNT-F, which features the deprotonation occurs from 'O1' and 'N2'. With comparing CHNT, the C–S and C=N bonds have no noticeable change in CHNT-F<sub>2</sub>. The calculated bond distance of F-H<sub>21</sub> and F-H<sub>8</sub> were found 1.02 and 1.40 Å respectively, which are close to the single bond formation between the atoms. The dihedral angle between naphthalene moiety and thiosemicarbazone group are twisted to 20.88<sup>0</sup>, which gives higher planarity and conjugation than CHNT and CHNT-F complex. In the fluoride complex, the negative charge on the fluoride ion might be delocalized over other conjugated system. Therefore the photophysical properties of CHNT-F and CHNT-F<sub>2</sub> are different from the CHNT.



Fig. 9. <sup>1</sup>H NMR titration of CHNT with different equivalents of fluoride ion.



Fig. 10. Optimized structure of CHNT (A), trans CHNT(A-trans), ground state CHNT–F (AF), ground state trans CHNT–F complex (AF-trans), excited state CHNT (AF\*), excited state trans CHNT (AF-trans\*) and deprotonated CHNT (A-de1 and A-de2).

In the CHNT–Cu complex, the C–S bond distance found to be 1.83 Å, which is higher than CHNT, and closer to single bond distance. The C–N bond distance found elongated to 1.32 Å, which attributes the single bond between C–N. The calculated dihedral angle between N–N–C–S found 0.56<sup>0</sup>, which is 13.43<sup>0</sup> in CHNT. The Cu–O, Cu–N<sub>1</sub> and Cu–S bond distances were found as 1.84, 1.95 and 2.28 Å respectively, which attributes the CHNT act ass tridentate ligand to form CHNT–Cu complex. The dihedral angle between naphthalene moiety and thiosemicarbazone group are 0.74<sup>0</sup>, which attributes the naphthalene moiety and thiosemicarbazone group is twisted to 89.70<sup>0</sup>. The dominant structural parameters in the optimized structures of CHNT, CHNT–F, CHNT–F<sup>\*</sup> and CHNT–Cu complexs are given in Table 3.

#### 3.7.2. UV-vis spectra and molecular orbital analysis

In order to investigate the absorption behavior of the CHNT in the sensing process according to their optimized ground state geometry, molecular excitation study were carried out at TDDFT/ CAM-B3LYP/6-31G(d,p) level [47]. The molecular orbitals involved in the main transition with the largest oscillator strength have been shown in Fig. 11. And the major absorption transition of CHNT, CHNT-F and CHNT-Cu complexes are given in Table 4. CHNT shows an intense absorption band at 303 nm with 0.4325 oscillating strength as dominant  $\pi$ - $\pi$ <sup>\*</sup> transition, which is from highest molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). In the HOMO, the electron delocalized through thione moiety and carbazonyl group. But in LUMO, the electron delocalized mainly in naphthalene moiety. The second dominant transition is at 254 nm with 4.51 eV energy gap, which is corresponds to the experimental absorption band at 259 nm. This transition is between HOMO-2 to LUMO, where in HOMO-2 orbital. the electrons are delocalized through thionyl group and naphthalene moiety. Whereas the CHNT-F<sub>2</sub> complex, the bathochromic shift was occurred and the peak shifted to 362 nm with 0.5827 oscillating strength. The major transition occurs between HOMO and LUMO, which is assign as  $\pi \rightarrow \pi^*$  type transition. In HOMO and LUMO, the electron delocalized though naphthalene moiety and thiosemicarbazone group. The second major transition is between

Table 3			
The dominant struc	ture parameters i	in the optimized	geometries.

	· · · · · · · · · · · · · · · · · · ·										
	$0 - H_{21}$	$N_2 - H_8$	$N_3 - H_7$	C–S	$N_1 N_2 C_{10} S$	$F-H_{21}$	F-H <sub>8</sub>	F-H <sub>7</sub>	$C_8 C_7 C_1 C_9$	$C_{13}C_{11}N_3C_{10}$	O1-H21-F
CHNT	0.96	1.02	1.01	1.70	13.43	-	-	-	47.71	135.5	
CHNT*	0.96	1.02	1.01	1.68	0.052				21.25	88.41	
CHNT-F	1.06	1.03	1.03	1.71	15.01	1.34	1.7	1.66	51.19	138.2	164.9
CHNT-F*	1.05	1.07	1.03	1.71	30.31	1.49	1.53	1.93	158.3	90.09	176.9
CHNT-F <sub>2</sub>	1.37	1.10	1.04	1.73	0.712	1.02	1.40	1.63	20.88	138.8	177
d-CHNT	-	-	-	1.82	2.24	-	-	-	10.69	85.54	-
	OCuN	COCu				CuO	CuS	CuN			CSCu
CHNT-Cu	95.9	128.0	1.01	1.83	0.565	1.84	2.28	1.95	0.741	89.70	91.4



Fig. 11. The energy gap between HOMO and LUMO orbitals of CHNT, CHNT-trans, CHNT-F, CHNT-F trans and excited state CHNT-F complexes.

Table 4

Dominant absorption energies and the fluorescence emissions for the chemosensor for CHNT, CHNT-F, CHNT-F2 and CHNT-Cu.

$\Delta {\rm E}~{\rm eV}$	λ	f	%	Transition	$\Delta { m E}~{ m eV}$	λ	f	%	Transition		
Absorption Er	Absorption Energies										
CHNT		-1335.6153	2105 AU.		CHNT-F		-1435.5915	2269 AU.			
4.0837	303.61	0.4325	75.30	$H \longrightarrow L$	4.0810	303.80	0.4113	100	$H \longrightarrow L$		
4.5186	274.39	0.1821	42.16	$H3 \rightarrow L$	4.5305	273.67	0.1950	35.53	$H3 \rightarrow L$		
4.8684	254.67	0.1176	24.95	$H-2 \rightarrow L$	4.9077	252.63	0.2207	27.00	$H \longrightarrow L \textbf{+} 1$		
CHNT-Cu	<b>CHNT–Cu</b> –1142.38262722 AU.			CHNT-F2 -1535.54594158			4158 AU.				
1.3655	907.96	0.0001	22.53	$H3 \rightarrow L$	3.4174	362.80	0.5827	100	$H \longrightarrow L$		
1.9193	646.00	0.0006	23.07	$H1 \to L$	4.3280	286.47	0.4533	53.15	$H \longrightarrow L \textbf{+} 1$		
2.2111	560.74	0.0236	17.43	$H4 \to L$	5.1205	242.13	0.4796	30.30	$H{-}2 \to L$		
Fluorescence	Emissions Energi	ies									
CHNT	HNT –1335.63437792 AU.			CHNT-F2		-1535.9561	526 AU.				
3.0063	395.42	0.8812	100	$L\!\!\to H$	4.0810	482.80	0.4113	100	$L \mathop{\longrightarrow} H$		
3.8861	319.04	0.0027	52.51	$L\!\rightarrow\!H\text{-}1$	4.3737	383.48	0.0015	42.40	$L \textbf{+} \textbf{1} \rightarrow H\textbf{-}\textbf{1}$		

HOMO to LUMO+2 orbital, where the electron transition occurs between hydroxyl group to thione group. In the CHNT–Cu complex, the major absorption transition with higher oscillator strength is at 560 nm, which is between HOMO to LUMO. In the HOMO, the electron delocalized through naphthalene moiety, cyclohexyl group and thiosemicarbazone group. But in LUMO, the electron delocalization absent in the cyclohexyl group. An excitedstate proton transfer (ESPT) process, induced by both intermolecular and intramolecular hydrogen-bonding interactions, is proposed to account for the fluorescence sensing mechanism of a fluoride chemosensor [5]. The comparison of experimental and computational spectral wavelength are given in Table 5.

# 3.7.3. Transition state and gibbs free energy calculations

In order to study the dynamic features of the deprotonation process, we calculated the Gibb's free energy of CHNT, CHNT–F complexes in DMSO medium. The ground state and excited state Gibb's free energy of the CHNT was found to be  $-8.38 \times 10^5$  and  $-8.46 \times 10^5$  Kcal/mol respectively. The transition state calculations were run between ground sate and excited state of CHNT–F

Table 5

Comparison of experimental and computational UV-vis and Fluorescence spectral data of CHNT and CHNT-F complex.

Compound	UV-vis spectra	(nm)	Fluorescence Spectra (nm)		
	Experimental Theoretical		Experimental	Theoretical	
CHNT CHNT-F	258 321	254.67 303.61	436 495	425.42 482.80	

complex, the Gibbs energy profile of CHNT with fluoride ion is as in Fig. 12. In the ground state of CHNT–F, the bond distance between fluorine atom and the H<sub>21</sub>, H<sub>8</sub> and H<sub>7</sub> hydrogen are found to be 1.34, 1.76 and 1.66 Å respectively, which attribute a weak hydrogen binding interaction of CHNT with fluoride ion. Whereas, in the excited state of CHNT–F complex, 'H<sub>21</sub>' proton removed from the CHNT, and form  $FH_{21}$  bond with 1.00 Å bond length. The total



**Fig. 12.** Gibbs free energy profile of the fluoride sensing mechanism. A: CHNT:; A-Tra: CHNT-trans:; de-A: CHNT-de:; AF: CHNT-F:; AF\*: CHNT-F excited state

change in Gibbs free energy ( $\Delta G$ ) in the reaction is 197.01 Kcal/mol. The less  $\Delta G$  value shows the sensing process is reversible, and strongly supporting for the explanation of the sensing mechanism. The calculated entropy change ( $\Delta s = \frac{\Delta H - \Delta G}{T}$ ) in the formation process of the hydrogen bridge involving fluoride ion is -0.0467 KJ/mol, where the negative sign indicate the sensing process is thermodynamically allowed. The binding constant (K<sub>a</sub>) of the CHNT to fluoride ion was calculated from the following equation,

$$\ln K_a = \frac{-\Delta G}{RT}$$

where, R, T and K<sub>a</sub> are the universal gas constant, temperature and the binding constant respectively. The K<sub>a</sub> value was found  $1.08 \times 10^5 \,\text{M}^{-1}$ , which was closer to the result get from the experimental value. To know the binding energy of the sensing process, the energy change ( $\Delta E$ ) and free energy ( $\Delta G$ ) calculated using following equations,

$$\Delta E = (E_{d-CHNT} + E_{HF}) - (E_{CHNT} + E_{F})$$

$$\Delta G = (G_{d-CHNT} + G_{HF}) - (G_{CHNT} + G_{F^-})$$

where,  $E_{CHNT}$ ,  $E_{d-CHNT}$ ,  $G_{CHNT}$  and  $G_{d-CHNT}$  are energy of CHNT, deprotonated CHNT and Gibb's energy of CHNT and deprotonated CHNT respectively. The calculated  $\Delta E$  and  $\Delta G$  are found to be -237.94 and -197.01 Kcal/mol respectively. The negative value of the free energy indicate feasibility of the sensing process in thermodynamic aspect.

#### 3.7.4. Potential energy curve (PES)

To reveal more features of ESPT process in the chemosensing process, the potential energy surface analysis study was carried out both in ground sate and excited state of CHNT–F complex. From the geometrical optimization structure, excited study and transition state calculation indicate the proton transfer was first takes from the hydroxyl group of CHNT. To take this result, PES calculations were carried out with only the variable parameter of OH and F–H bond length separately at the ground state and excited state of CHNT–F complex, where the variable parameter of the bond length from 0.90 to 2.40 Å in the step of 0.05 Å. It is obviously reveal from Fig. 13 that the energy of ground state CHNT–F complex decreases with increasing the bond length between  $F-H_{21}$  and  $F-H_8$ , and it reaches at the lowest energy



**Fig. 14.** The calculated potential energy curve of Cu–O, Cu–S and Cu–N bond length in ground state of CHNT–F complex.

-1436.19 AU, where the F-H<sub>21</sub> and F-H<sub>8</sub> bond length are 1.31 and 1.74 respectively. Where as in the case of O-H bong length calculation, the lowest energy at -1436.19 AU with the bond length 1.06 Å. In the case of CHNT-Cu complex, the Cu-O, Cu-S and Cu-N bond length changes from 1.90 to 2.50 Å with the increment of 0.035 Å. The optimized geometric energy is -2975.47 AU, where the bond distance of Cu-O, Cu-S and Cu-N at stable structure of CHNT-Cu complex was found to be 1.90, 2.24 and 1.90 Å respectively. The detailed PES curves of CHNT-F and CHNT-Cu are as in Figs. 13 and 14.

#### 3.7.5. NBO calculation

To understand the information about interactions in both filled and virtual orbital spaces that could enhance the analysis of intraand inter-molecular interactions, Natural bond orbital (NBO) studies carried out. The change in bond length between  $N_2-H_8$ ,  $O-H_{21}$  and  $H_8-F$  of optimized geometries in the ground state (S<sub>0</sub>), excited state (S<sub>1</sub>) and the emission studies predicts proton from nitrogen and oxygen. In order to support the proton transfer process takes place from  $O-H_{16}$  rather than  $N_3-H_{17}$  proton in the fluoride sensing process, NBO calculation was carried out at ground



Fig. 13. The calculated potential energy curve of  $F-H_7$ ,  $F-H_8$  and O-H bond length in ground state of CHNT-F complex.

 Table 6

 The second-perturbation energy E(2) (kcal/mol) of donor-acceptor interaction with respect to CHNT-F in ground state and excited state states respectively.

Donor (i)	Acceptor (j)	Interaction	E(2) Kcal/mol	ε(j)- ε(i)	F(i,j)						
Ground stat	Ground state										
LP (3) F 45	BD*(1) N 15 - H 22	n-σ*	11.43	0.93	0.092						
LP (3) F 45	BD*(1) N 17 - H 21	n-σ*	24.66	0.93	0.136						
LP (4) F 45	LP*(1) H 44	n-n*	112.07	0.63	0.258						
Excited Stat	e										
LP (3) F 45	BD*(1) N 15 - H 22	n-σ*	12.94	1.06	0.105						
LP (3) F 45	BD*(1) N 17 - H 21	n-σ*	29.02	1.06	0.157						
LP (4) F 45	BD*(1) 0 43 - H 44	n-σ*	94.57	1.01	0.276						

state and excited state of CHNT–F. By comparing the binding energies of F–H<sub>16</sub> and F–H<sub>17</sub> reveals the affinity of fluoride ion to attach the hydrogen atom. The binding energy ( $\Delta E$ ) was calculated from the equation  $\Delta E=E_{AB}-(E_A+E_B)+BSSE$ , where A and B are two fragments. The binding energy of F–H<sub>7</sub>, F–H and F–H<sub>8</sub> are –150.65, –159.64 and –162.59 Kcal/mol respectively. The smallest value of the binding energy for F-H<sub>16</sub> indicate the priority of the binding affinity of fluoride ion towards H<sub>21</sub> than H<sub>8</sub> and H<sub>7</sub>. The strong donor–acceptor interaction between fluoride and the CHNT can be treated by the second–perturbation energy E(2) which has been calculated from the electron donor orbital, acceptor orbital and the interacting stabilization energy in the ground state and excited state and using this we can explain the weak interaction [48]. The second order perturbation equation as below,

$$E(2) = \Delta E = \frac{q_i F_{ij}^2}{\varepsilon_i - \varepsilon_i}$$

where E(2) is the second perturbation energy,  $F_{ii}$  is the off-diagonal element in the NBO Fock matrix, q<sub>i</sub> is the donor orbital occupancy, and  $\varepsilon$ i and  $\varepsilon$ j are orbital energies. It can be seen from Table 6, that the energies between two segments separated by  $F-H_{21}$ ,  $F-H_8$  and F-H<sub>7</sub> at the ground state are found to be 112.07, 24.66 and 11.43 Kcal/mol respectively. The higher energy value of F-H<sub>21</sub> shows the bonding between F and H<sub>21</sub>. All weak interactions have generated from lone-pair electron (n) of F to excited  $\sigma^*$  of N–H bond, in which the  $N_2-H_8$  pair has larger interaction with fluoride atom than N<sub>3</sub>-H<sub>7</sub>. But, the F-H bond interaction is n-n\*, which attributes the bonding between fluoride atom and hydrogen atom. In the excited state (CHNT-F\*), the calculated bonding energies found as 94.57, 29.02 and 12.94 Kcal/mol for F-H<sub>21</sub>, F-H<sub>8</sub> and F-H<sub>7</sub> respectively. And the  $F-H_{21}$  and  $F-H_7$  bond energy values are closer to the hydrogen bonding, hence in excited state of CHNT-F complex show hydrogen bonding via  $F \cdots H_8 - N_1$  and  $F \cdots H_7 - N_2$ . The large overlap of the electron density for the interaction confirms the



Fig. 15. (a) The UV-vis and (b) fluorescence spectral changes of CHNT with the addition of individual F<sup>-</sup>, CN<sup>-</sup> and Cu<sup>2+</sup> and its mixture.

strong donor–acceptor interaction, indicating the hydroxyl proton prefer to interact with F atom rather than N–H proton. The proton transfer was undergoes from S<sub>1</sub> state, and which gives excited state proton transfer (ESPT) process. In the case of CHNT–Cu complex, the bonding energy value between Cu–O, Cu–N and Cu–S are found to be 20.36, 15.25 and 9.86 Kcal/mol respectively, where  $n \rightarrow n^*$  interactions were shown between the atoms. The energy values and interactions show the bond between copper towards oxygen, nitrogen and sulfur atoms. In conclusion, the NBO analysis with E(2) further confirms the presence of ESPT process by the excitation of the light for fluoride ion sensing, and the priority of hydroxyl proton and then N<sub>2</sub>–H<sub>8</sub> in attaching to fluoride atom rather than N<sub>3</sub>–H<sub>7</sub> in ESPT process.

#### 3.8. Logic gate behavior

The differential behavior of CHNT toward  $F^-$ ,  $CN^-$  and  $Cu^{2+}$  ions enabled the receptor to elaborate molecular logic gates. Recently, the molecular computing is the subarea of unconventional computing based on chemical reactions that has stimulated interest in the development of molecular logic gates and devices at the molecular level. Molecular logic gates convert input stimulations into output signals with basic protocols [49]. For the analysis of their logic behaviors, the optical values from absorption and emission spectral values are assigned and then logic convention is used for their inputs and outputs signals. It follows that the principles of binary logic can be applied to the signal transduction operated by molecular switches. The absorption maximum at 370 nm of CHNT was reduced with the presence of individual ions ( $F^-$ ,  $CN^-$  and  $Cu^{2+}$ ) and the mixture of ions, which attributes the NOR logic gate.

The addition of fluoride cyanide ions results the formation of new peak at 482 nm. And the presence of copper ion didn't show any change at this wavelength. There is no new peak at 482 nm, when F<sup>-</sup> and/or CN<sup>-</sup> are mix with copper ion. This phenomenon is help to develop the NAND gate. While the presence of copper ion in the CHNT gave new peak at 417 nm, which is retained when the copper ion mix with F<sup>-</sup> and CN<sup>-</sup> ions, which can explained by TRANSFER logic gate. The CHNT show high intense fluorescence spectra at 433 nm. The presence of fluoride and cyanide ions quench the fluorescence intensity of the CHNT, whereas copper ion enhanced the fluorescence intensity. But in the presence of mixture of ions (F<sup>-</sup>, CN<sup>-</sup> and Cu<sup>2+</sup>), the CHNT show fluorescent quenching. This property corresponds to the XNOR logic behavior. However, the presence of fluoride and cyanide ions results red shift along with the formation of new peak at 492 nm. But, which didn't show when the copper ion mix with  $F^-$  and/or  $CN^-$  ion. This behavior can be explained by NAND logic gate. The circuit and the truth table are shown in Figs. 15 and 16.



**Fig. 16. (a)** Changes of absorbance at 370, 483 nm and change in fluorescence intensity at 433 and 492 nm for CHNT with  $F^-/CN^-/Cu^{2+}$ , and their truth table. ('0' and '1' represent the absence and presence of the ion respectively). **(b)** Combinatorial circuit diagram of CHNT with three input ( $F^-$ ,  $CN^-$  and  $Cu^{2+}$  ions).



Fig. 17. proposed sensing mechanism of CHNT with fluoride ion.

### 4. Conclusion

The isobistic points indicates existence of multi compounds in the solution, which indicates the formation of CHNT-ion complex. From the Jobs plot, the stoichiometry between CHNT and anions ( $F^-$  and  $CN^-$ ) are 1:2, which means, the one molecule CHNT binds two molecules of  $F^-$  or  $CN^-$ . The stoichiometric ratio of HCNT and  $Cu^{2+}$  is 1:1, which show one CHNT molecule bind one copper atom. It also indicate the tridentate behavior of the CHNT compound. The presence of  $F^-$  and  $CN^-$  ions gives red colour to the CHNT, and  $Cu^{2+}$ ion gives bright yellow colour. The <sup>1</sup>H NMR titration study strongly support the deprotonation was taken from the hydroxyl proton, then followed by the N–H proton which is near to the naphthalene group. Proposed binding mode of CHNT towards  $F^-/CN^-$  and  $Cu^{2+}$ ions, and their colour changes along with the complex formation is as in Fig. 17 and Fig. 18.

The experimental findings have also been supported by the theoretical (DFT and TD-DFT) calculations. The structural change was calculated by the geometries o CHNT, CHNT–F, de-CHNT and CHNT–Cu complexes. The UV–vis and emission spectra were well reproduced by various transition energies computed from ground state and excited state geometries. The optimized energy values of CHNT and CHNT-trans compounds indicate that the sensing process was takes place in the *trans* form of hydroxyl proton and NH protons in the CHNT. This results can be the explanation of the experimental <sup>1</sup>H titration results. The transition and intermediate state calculations were revealed the mechanism of the F<sup>-</sup> ion sensing by CHNT. The excited state proton transition mechanism was further confirmed with NBO and PES analysis. The second order perturbation energy value confirms the hydrogen bonding and deprotonation was happed in the excited state of CHNT–F



Fig. 18. Proposed binding mode of CHNT towards  $F^{-}/CN^{-}$  and  $Cu^{2+}$  ions, and their colour changes along with the complex formation.

complex. The theoretical results also confirms the deprotonation was first happed from the hydroxyl proton then from the  $N_2-H_8$ proton which is near to the naphthalene moiety.

# Acknowledgments

SMB is thankful for the financial support from the MHRD (India) and Endeavour Research Fellowship (Australia).

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version. at http://dx.doi.org/10.1016/j. jfluchem.2016.10.005.

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