

SUPPLEMENTARY INFORMATION

Excited state proton transfer (ESIPT) based molecular probe to sense F⁻ and CN⁻ anions through fluorescence “Turn – On” response

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Figure S12: HRMS spectrum of NTS after interaction with CN⁻ anions.

General

Materials and Chemicals: All the reagents and solvents were purchased from Sigma-Aldrich Chemical Co. Pvt. Ltd. stored in a desiccator under vacuum containing self indicating silica, and used without any further purification. Solvents were purified prior to use. UV-vis absorption spectra were recorded on a Perkin Elmer Lambda-35 UV-vis spectrophotometer using a quartz cuvette (path length = 1cm). Infrared (IR) spectra were recorded in potassium bromide (KBr) on Varian-3100 FT-IR spectrometer. ^1H NMR spectra (chemical shifts in δ ppm) were recorded on a JEOL AL 300 FT-NMR (300 MHz) spectrometer, using tetramethylsilane (TMS) as internal standard. Fluorescence spectra were recorded on Varian eclipse Carry spectrofluorometer using a quartz cuvette (path length = 1 cm) at 500 PMT voltage and slit width 5nm/5nm. All the spectroscopic experiments were carried out at room temperature. High-resolution mass spectra (HRMS) were recorded on Bruker daltonics Data Analysis 3.4 (micrOTOF-Q) and Agilent Q-TOF instrument.

Preparation of Stock solutions and titration experiments:

The stock solution of NTS ($c = 1 \times 10^{-3} \text{ mol L}^{-1}$) were prepared in DMSO. For each absorption and fluorescence measurements 30 μl of stock solution was taken and diluted to 3.0 mL to make the concentration of probe 10 μM in DMSO/ H_2O (9:1 v/v). The stock solutions of different anions ($c = 1 \times 10^{-1} \text{ mol L}^{-1}$) were prepared by dissolving their tetra-n-butylammonium salts in MeCN. The anion interaction studies were performed by the addition of $1 \times 10^{-1} \text{ mol L}^{-1}$ of different anions. For absorption and emission titration experiment $1 \times 10^{-2} \text{ mol L}^{-1}$ stock solution of tetra-n-butylammonium cyanide (TBACN) and tetra-n-butylammonium fluoride (TBAF) was prepared. The absorption and fluorescence titration experiment were performed by the gradual addition of increasing concentration of TBACN ($c = 1 \times 10^{-2} \text{ mol L}^{-1}$) and TBAF ($c = 1 \times 10^{-2} \text{ mol L}^{-1}$). ^1H NMR titration studies were performed in DMSO- d_6 by addition of increasing concentration of TBACN and TBAF to a solution of NTS ($c = 2.1 \times 10^{-2} \text{ mol L}^{-1}$ in DMSO- d_6), respectively.

Estimation of Quantum Yields: The quantum yields were estimated with respect to the quinine sulfate ($\Phi = 0.54$) as standard in 0.1M H_2SO_4 solution, using equation (1) by secondary methods [14].

$$Q = Q_R \cdot I/I_R \cdot OD_R/OD \cdot n^2/n_R^2 \quad (1)$$

Where Q is the quantum yield, I is the integrated intensity, OD is the optical density, and n is the refractive index. The subscript R refers to the reference fluorophore of known quantum yield.

Estimation of Binding Constant: The absorption and fluorescence experimental data were utilized to calculate association constants by Benesi-Hildebrand method [15] (B-H method) employing equations (2) for a 1:1 stoichiometry.

$$1/(I - I_o) = 1/(I - I_f) + 1/K(I - I_f)[M] \quad (2)$$

Where K is the association constant, I is the absorbance/fluorescence intensity of the free probe **NTS**, I_o is the observed absorbance/fluorescence intensity of the **NTS-F⁻** complex, and I_f is the absorbance/fluorescence intensity at saturation level.

Estimation of Limit of detection:

Method

The detection limit of probe for analyte (metal ions/anions) was estimated from the respective fluorescence titration data based on a reported method [16]. According to the result of titration experiment, change in the fluorescence intensity of probe with analyte was normalized between the minimum intensity and the maximum intensity. A linear regression curve was obtained from the plot of these normalized fluorescence intensity of probe with analyte verses $\text{Log} [\text{analyte}]$ and detection limit was calculated by using equation (3).

$$10^{-[\text{Slope} / \text{Intercept}]} \quad (3)$$

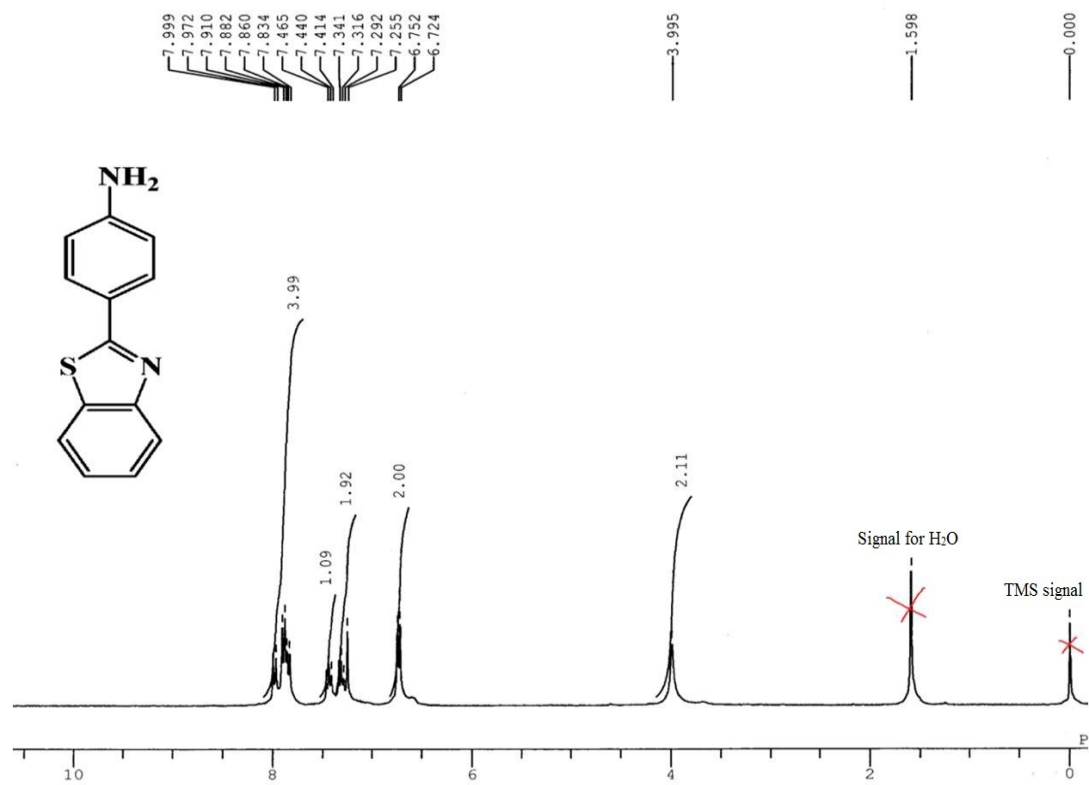


Figure S1: ¹H NMR spectrum of **1** in CDCl₃.

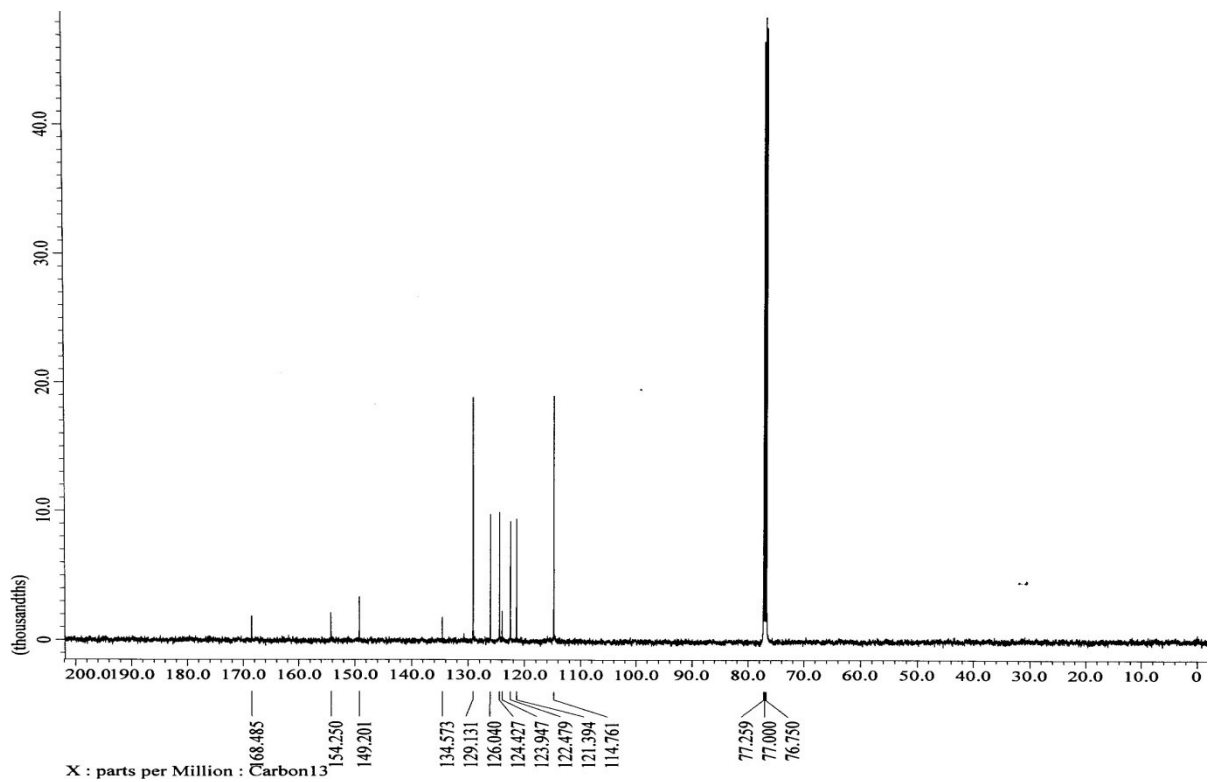


Figure S2: ¹³C NMR spectrum of **1** in CDCl₃.

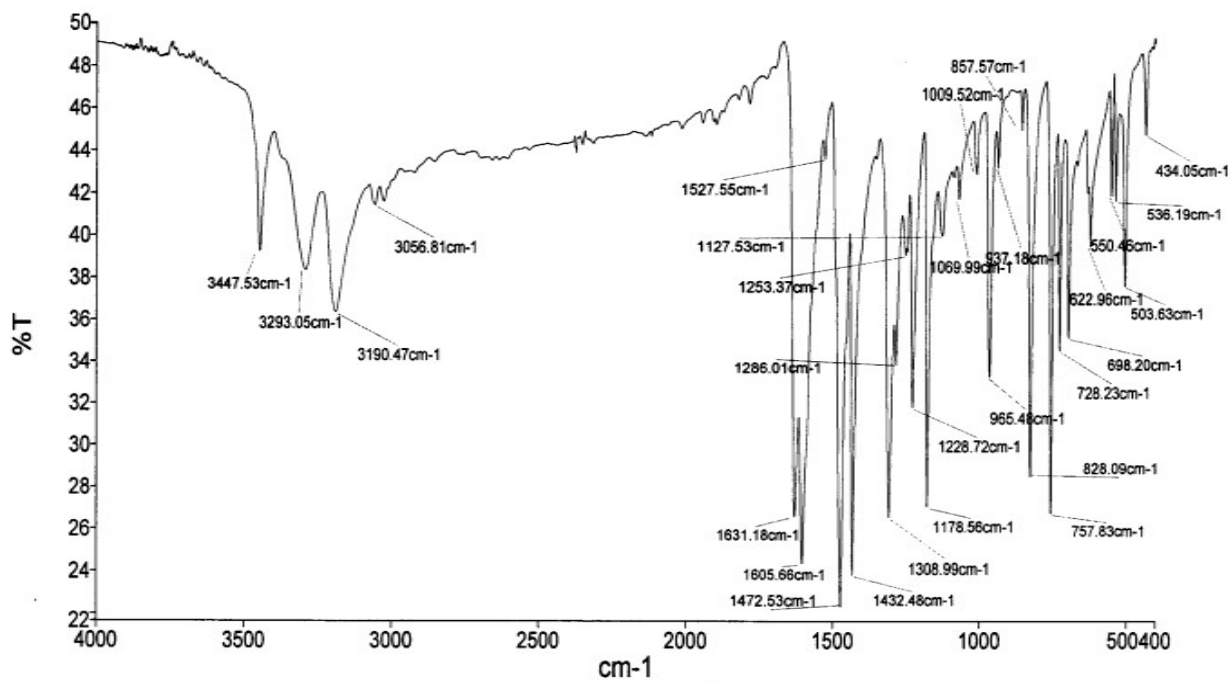


Figure S3: FT-IR spectrum of 1.

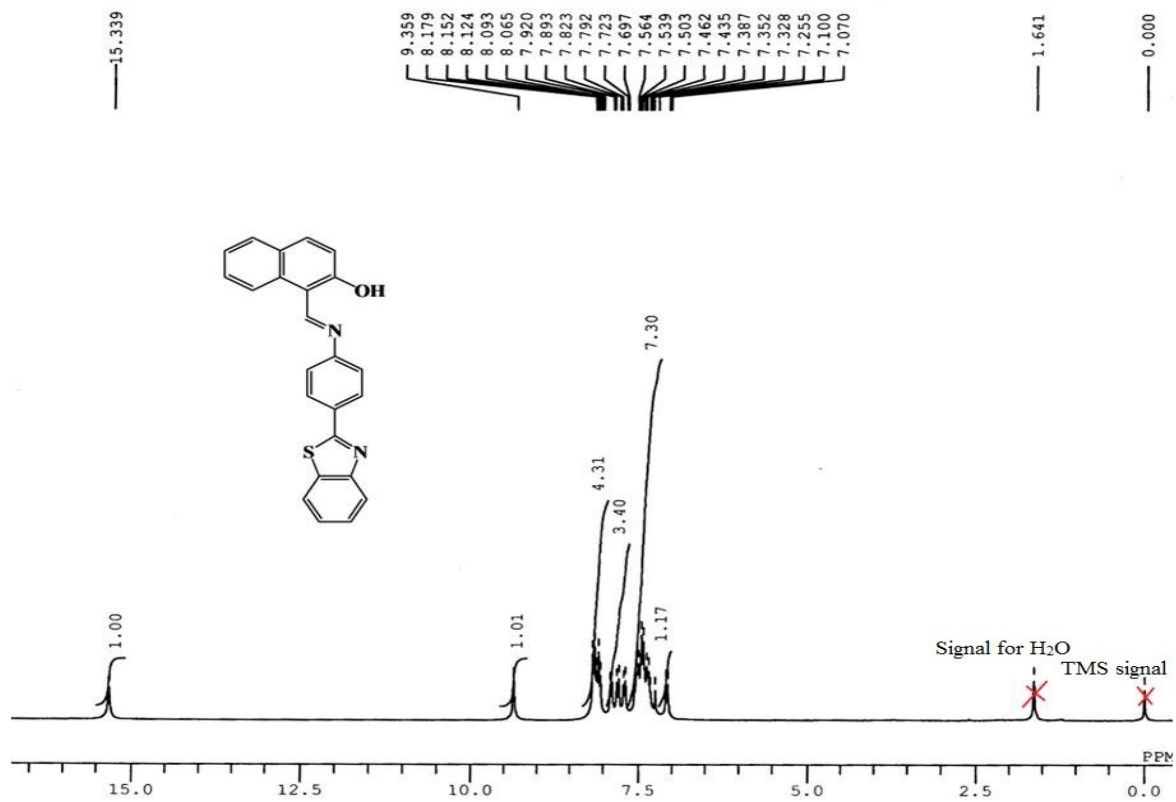


Figure S4: ¹H NMR spectrum of NTS in CDCl₃.

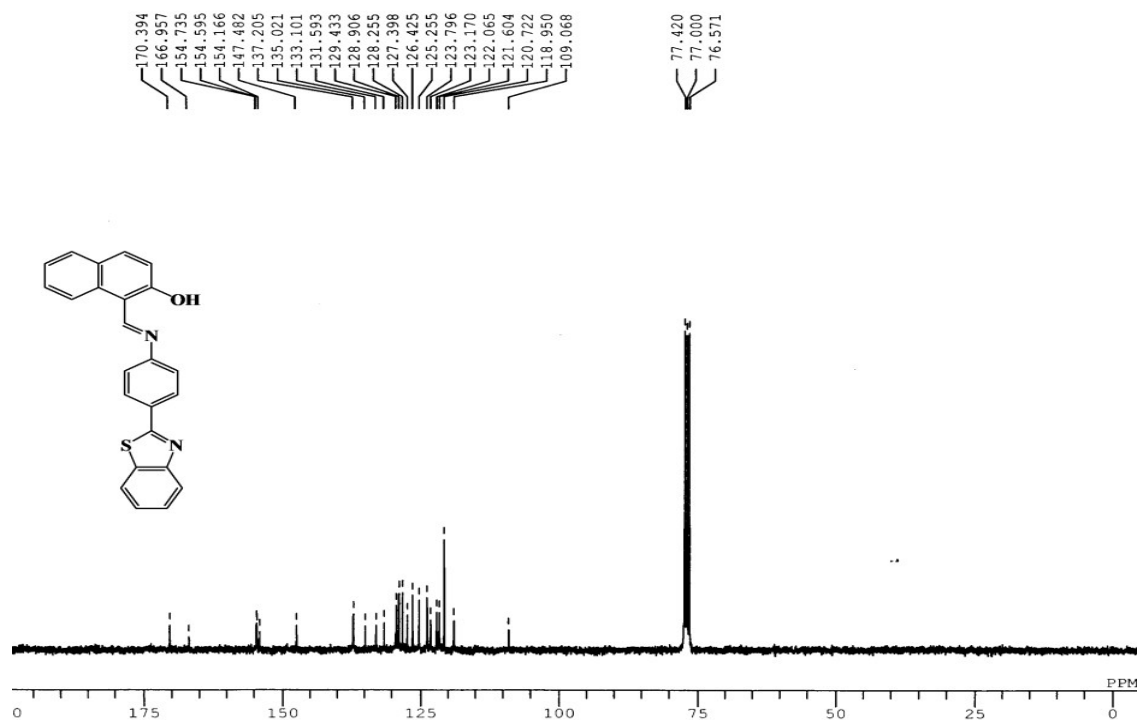


Figure S5: ¹³C NMR spectrum of NTS in CDCl₃.

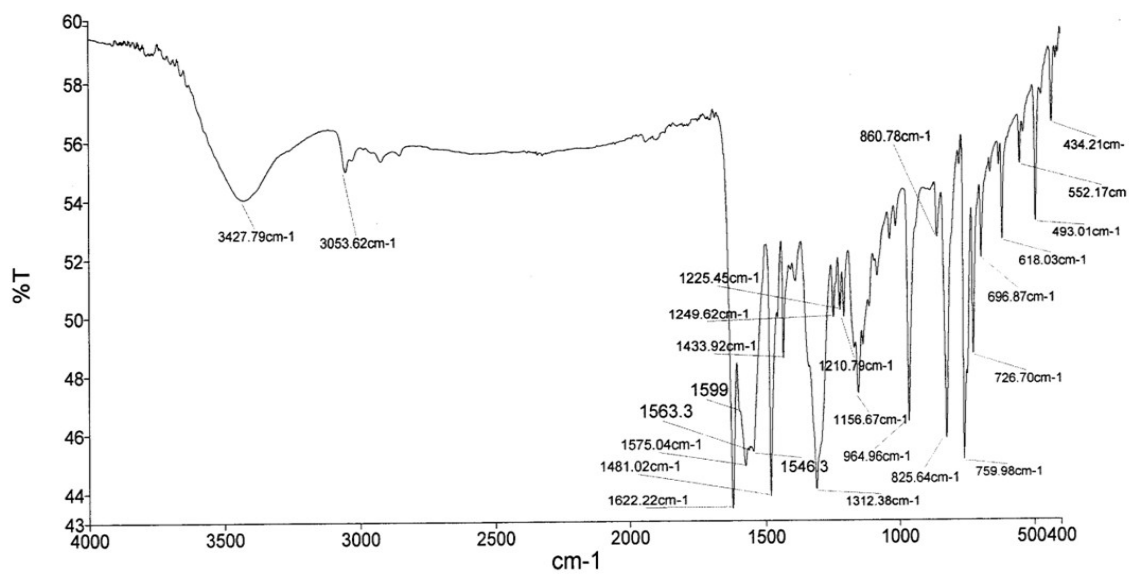


Figure S6: FT-IR spectrum of NTS.

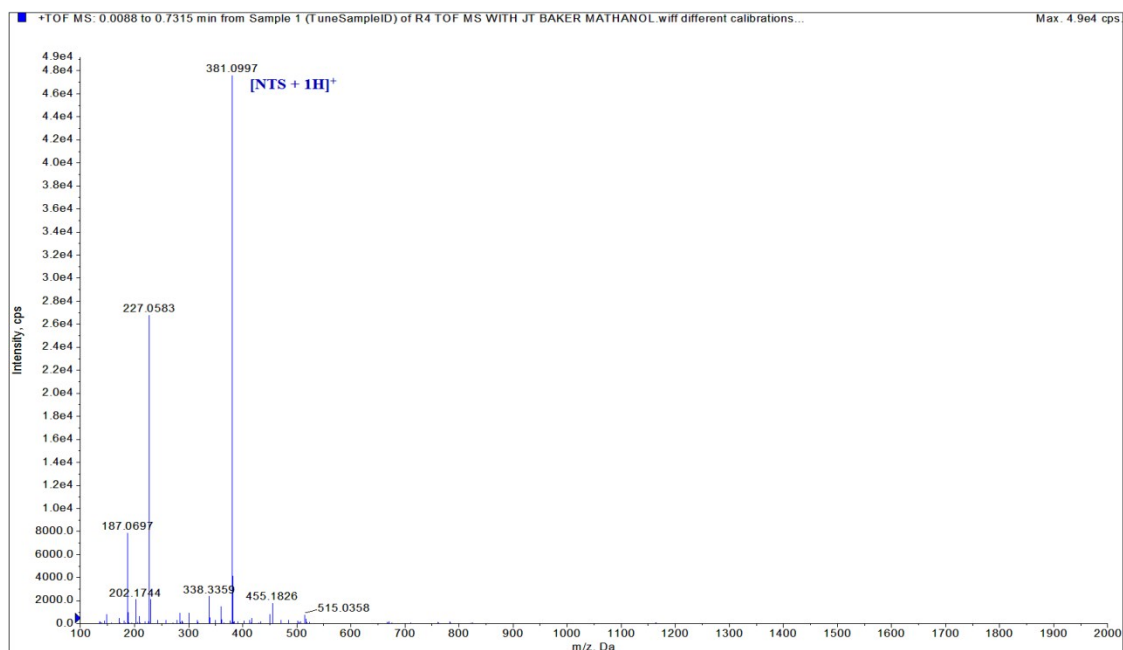


Figure S7: HRMS spectrum of NTS.

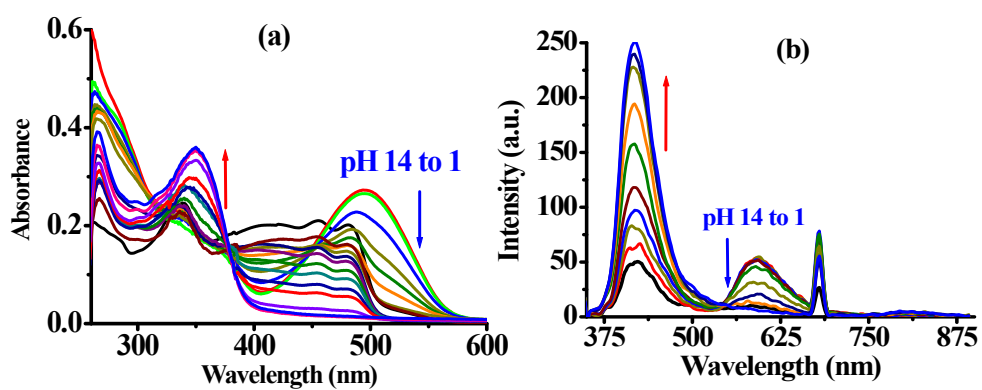


Figure ESI 1: Change in (a) absorption and (b) emission spectra ($\lambda_{\text{ex}}=340$ nm) of NTS (10 mM) at different pHs in HEPES buffer.

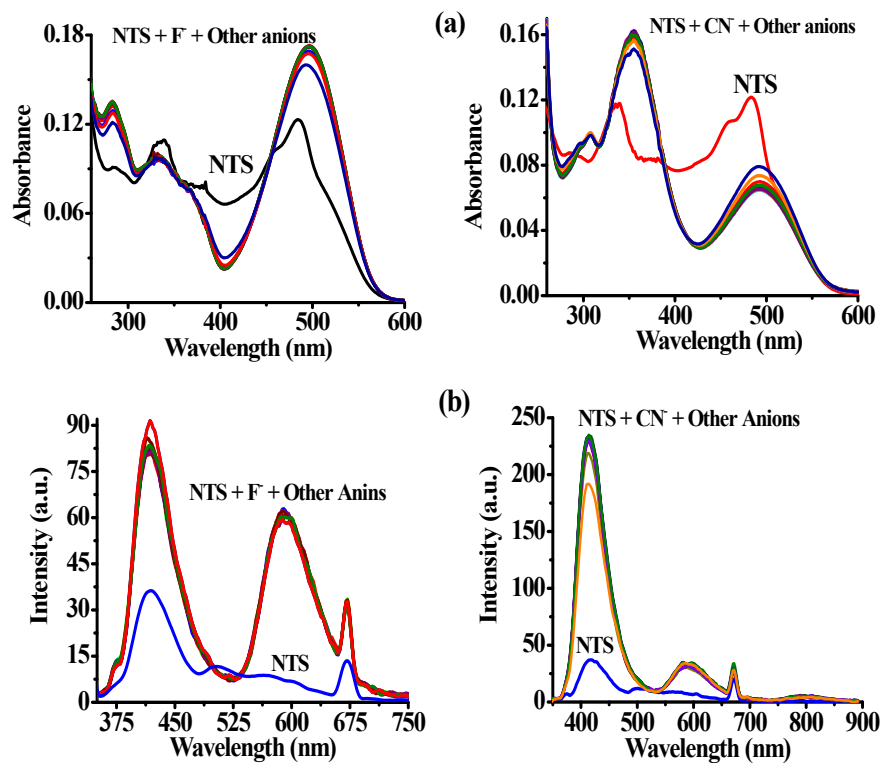


Figure S8: (a) Absorption and (b) emission of interference of different anions (15.0 equiv.) to a solution of NTS+F⁻ and NTS+CN⁻.

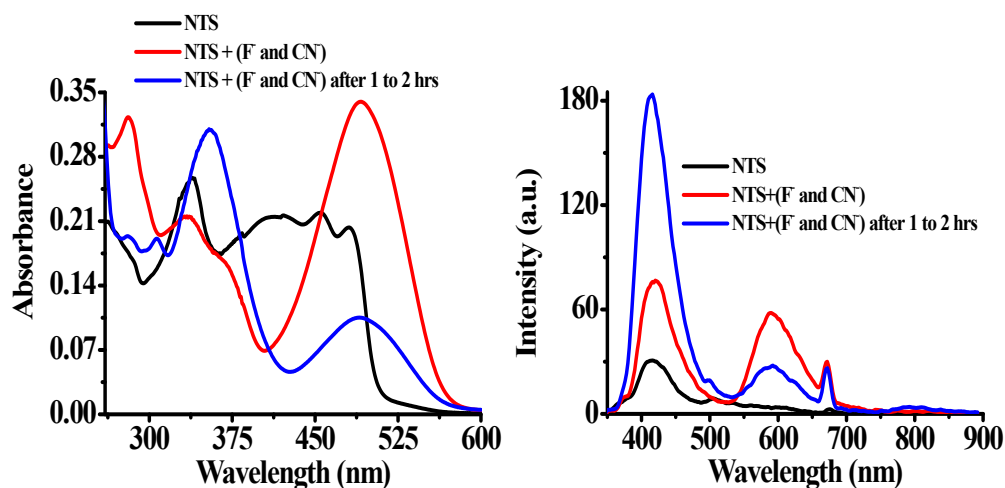


Figure ...: (a) Absorption and (b) emission spectra of NTS (10 μM) upon addition 15.0 equiv. of (F⁻ and CN⁻ ions), with the progress of time in DMSO/H₂O (9:1, v/v).

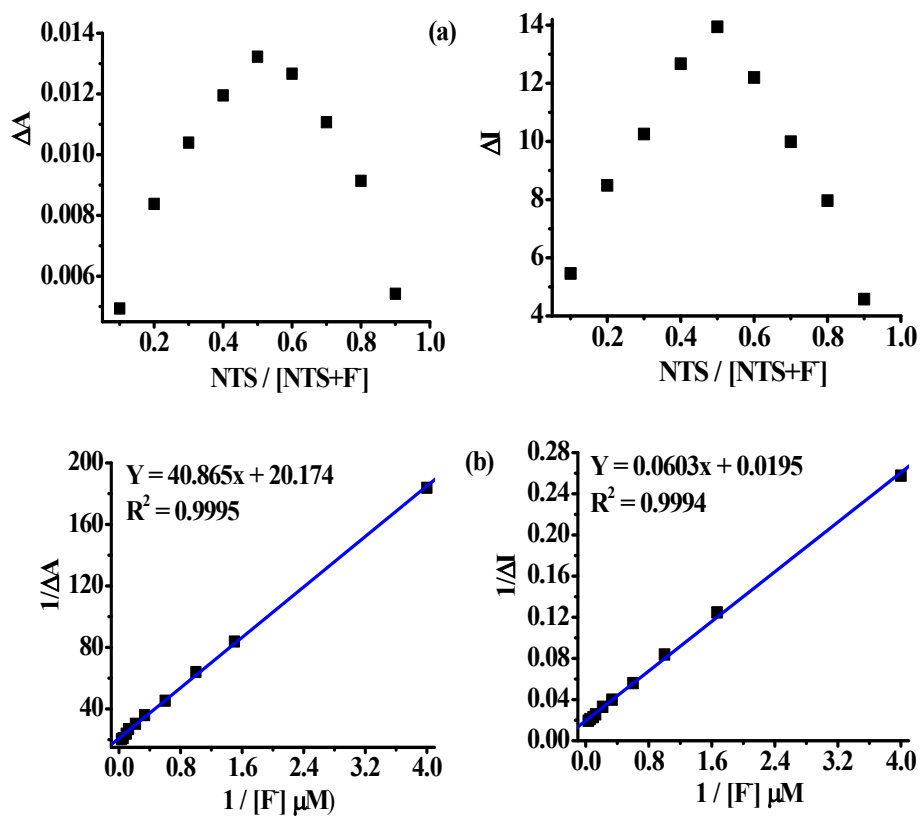
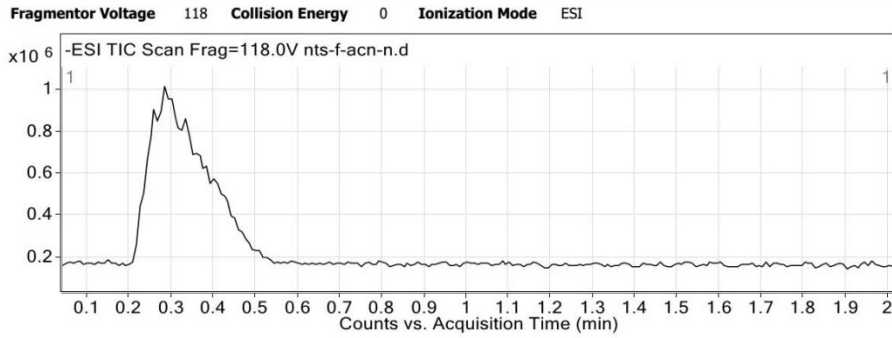


Figure S9: (a) Job's plot and (b) Benesi-Hildebrand plots obtained from absorption and emission spectral data.

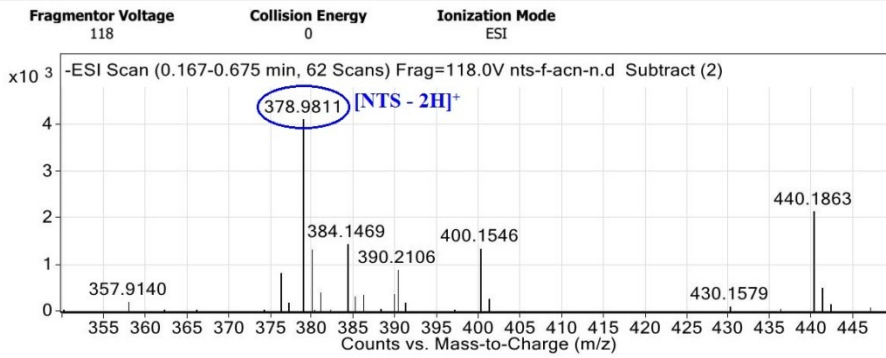
Qualitative Analysis Report

Data Filename	nts-f-acn-n.d	Sample Name	nts-f-acn-n
Sample Type	Sample	Position	Vial 21
Instrument Name	Agilent 6530 Accurate-Mass Q-TOF	User Name	
Acq Method	Direct Mass-2017.m	Acquired Time	22-04-2018 12:51:18
IRM Calibration Status	Success	DA Method	Default.m
Comment			
Sample Group		Info.	
Acquisition SW	6200 series TOF/6500 series		
Version	Q-TOF B.05.00 (B5042.1)		

User Chromatograms



User Spectra



Peak List

m/z	z	Abund
144.8991		2463.59
152.9547	1	27204.04
322.1513	1	7498.5
324.1488	1	2528.19
326.1859	1	3001.8
332.1793	1	199690.31
333.1821	1	38455.8
334.1839	1	5081.33
378.9811	1	4136.79
440.1863	1	2159.05

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Figure S10: HRMS spectrum of NTS after interaction with F⁻ anions.

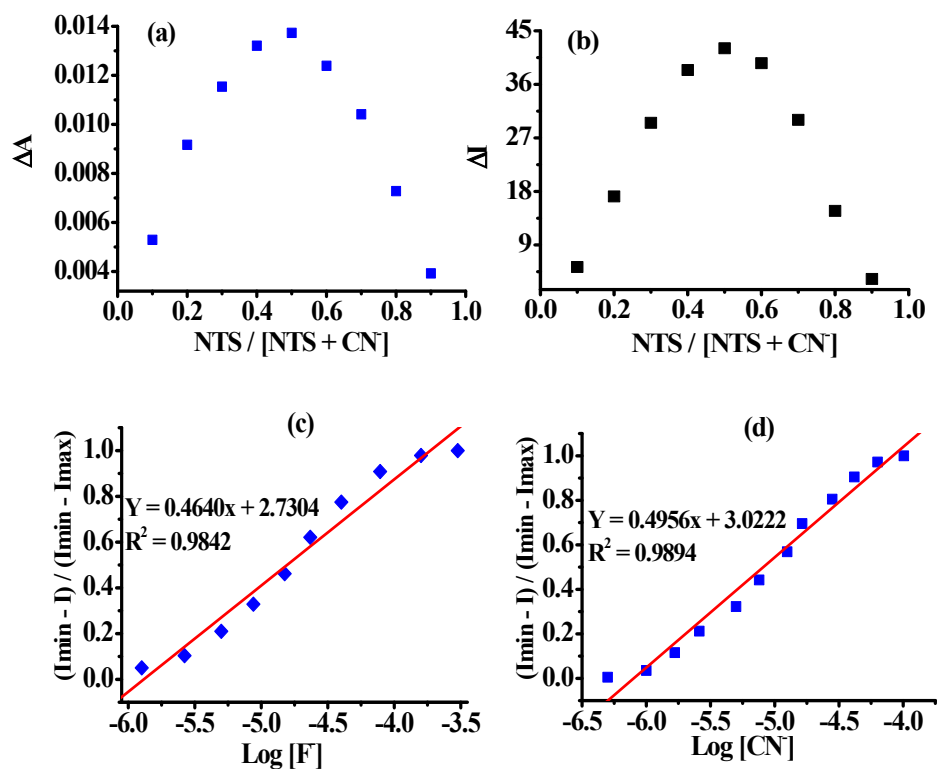
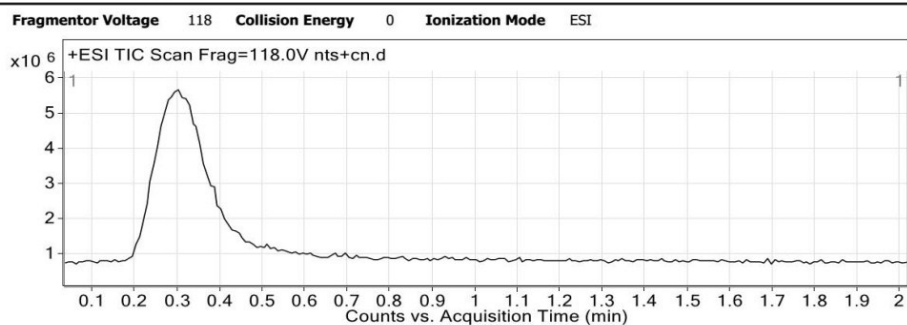


Figure S11: Job's plot obtained from (a) absorption and (b) emission spectral data of NTS with CN⁻. Fluorescence intensity change of NTS (c and d) system (10 μM) upon addition of different concentration of (c) F⁻ and (d) CN⁻ anions.

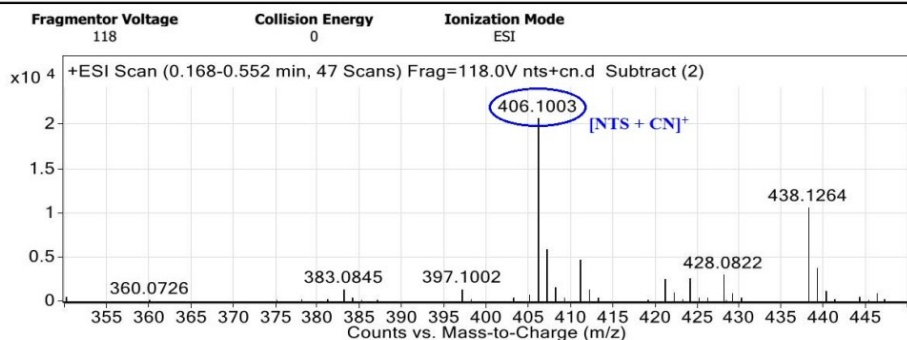
Qualitative Analysis Report

Data Filename	nts+cn.d	Sample Name	nts+cn
Sample Type	Sample	Position	Vial 20
Instrument Name	Agilent 6530 Accurate-Mass Q-TOF	User Name	
Acq Method	Direct Mass-2017.m	Acquired Time	22-04-2018 10:46:09
IRM Calibration Status	Success	DA Method	Default.m
Comment			
Sample Group		Info.	
Acquisition SW Version	6200 series TOF/6500 series Q-TOF B.05.00 (B5042.1)		

User Chromatograms



User Spectra



Peak List

<i>m/z</i>	<i>z</i>	Abund
227.0633	1	43356.93
228.0661	1	6773.53
242.2838	1	1395906.5
242.4248		39362.25
243.2873	1	260329.22
244.2904	1	22073
255.0579	1	13679.42
406.1003	1	20829.69
407.103	1	6019.18
438.1264	1	10714.41

--- End Of Report ---

Figure S12: HRMS spectrum of NTS after interaction with CN⁻ anions.