

Electronic Supplementary Material

A dual-channel chemosensor could successively detect CN^- and HSO_4^-
in aqueous solution and act as a keypad lock

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1. General Methods

1.1. Materials

All reagents were purchased from commercial supplies and used without further purification. Solvents and twice-distilled water were purified by standard methods. Fresh double distilled water was used throughout the experiment. Tetrabutylammonium salt of anions (F^- , Cl^- , Br^- , I^- , AcO^- , $H_2PO_4^-$, HSO_4^- and ClO_4^-) and sodium salt of anions (CN^- and SCN^-), which were purchased from Alfa–Aesar Chemical, and stored in a vacuum desiccator.

1.2. Instruments

Melting points were measured on X-4 digital melting-point apparatus and were uncorrected. The infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer. 1H NMR and ^{13}C NMR spectra were recorded on an Agilent DD2 at 600 MHz spectra. Electrospray ionization mass spectra (ESI-MS) were measured on an Agilent 1100 LC-MSD-Trap-VL system. UV-vis spectra were recorded on a Shimadzu UV-2550 spectrometer. Fluorescence spectra were recorded on a Shimadzu RF-5301 fluorescence spectrometer.

1.3. General procedure for UV-vis experiments

The solution of sensor **T** (2.0×10^{-4} M) in DMSO was prepared and stored in dry atmosphere. The solution was used for all spectroscopic studies after appropriate dilution. The pure water solutions of each anion (0.01 M) were prepared, via tetrabutylammonium salt of anions (F^- , Cl^- , Br^- , I^- , AcO^- , $H_2PO_4^-$, HSO_4^- and ClO_4^-) and sodium salt of anions (CN^- and SCN^-). All the UV-vis experiments were carried out in DMSO/ H_2O (7/3, v/v) on a Shimadzu UV-2550 spectrometer. Any changes in the UV-vis spectra of the synthesized compounds were recorded on addition of salts while keeping the ligand concentration constant (2.0×10^{-5} M) in all experiments.

1.4. General procedure for Fluorescence spectra experiments

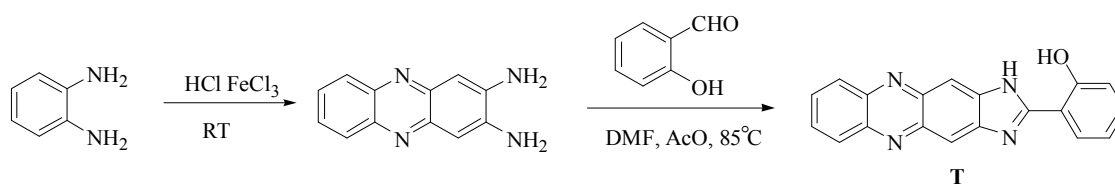
The solution of sensor **T** (2.0×10^{-4} M) in DMSO was prepared and stored in dry atmosphere. The solution was used for all spectroscopic studies after appropriate dilution. The pure water solutions of each anion (0.01M) were prepared, via tetrabutylammonium salt of anions (F^- , Cl^- , Br^- , I^- , AcO^- , $H_2PO_4^-$, HSO_4^- and ClO_4^-) and sodium salt of anions (CN^- and SCN^-). All the fluorescence spectra experiments were carried out in DMSO/ H_2O (7/3, v/v) solutions on a Shimadzu RF-5301 spectrometer. The fluorescence spectra were obtained by excitation at 430

nm. Any changes in the fluorescence spectra of the synthesized compounds were recorded upon the addition of salts while keeping the ligand concentration constant (2.0×10^{-5} M) in all experiments.

1.5. General procedure for ^1H NMR experiments

For ^1H NMR titrations, two stock solutions were prepared in $\text{DMSO-}d_6$, one containing the sensor only and the second containing an appropriate concentration of the metal. Aliquots of the two solutions were mixed directly in NMR tube.

2. Synthesis of **T**



Scheme S1 Structure and synthesis of the sensor **T**

Synthesis of 2, 3-diamino-phenazine was synthesized according to the reported procedure¹⁻².

3-Diamino-phenazine (0.42 g, 2.0 mmol), 2-hydroxyl-1-benzaldehyde (0.27 g, 2.2 mmol) and catalytic amount of acetic acid (AcOH) were combined in hot absolute DMF (10 mL). The solution was stirred under reflux conditions for 8 h, after cooling to room temperature, the brown precipitate was filtrated, washed with hot absolute ethanol three times, then recrystallized with DMF-H₂O to get brown powdery product **T**. The other compound **T** was prepared by similar procedures.

T: yield: 75%; m.p. > 300 C; ¹H NMR (DMSO-d₆, 400 MHz) d 13.45 (1H, NH), d 12.95 (1H, OH), d 8.43-8.24 (2H, ArH) 7.91-7.89 (2H, ArH) 7.56-7.53 (1H, ArH) 7.17-7.11 (2H, ArH). ¹³C NMR (DMSO-d₆, 150 MHz) d 172.52, 160.23, 141.83, 140.44, 129.47, 129.28, 128.55, 119.32, 117.75. IR (KBr, cm⁻¹) v: 3310.70 (O-H), 3047.32 (N-H), 1661.20 (C=N), 1613.04 (Ar, C=C), 1528.76 (Ar, C=C), 1488.12 (Ar, C=C). ESI-MS m/z: (M+H)⁺ Calcd for C₁₉H₁₂N₄O 313.2; Found 313.3; Anal. Calcd. For C₁₉H₁₂N₄O: C 73.07, H 3.87, N 17.94; Found C 73.04, H 3.84, N 17.90.

3. Determination of association constant

The association constants (K) were calculated based on the fluorescent titration curve of the probes with ions. Association constants were determined by a nonlinear least squares fit of the data with the following equation as referenced elsewhere.

I is the observed the fluorescence intensity of **T** at the fixed concentrations of CN^- . I_{max} and I_{min} are the corresponding maximum and minimum, respectively.

$$\log \frac{I - I_{min}}{I_{max} - I} = \log K + 2 \log [CN^-]$$

$$K = 1.24 \times 10^{10} M^{-2}$$

I is the observed the fluorescence intensity of **T-CN⁻** at the fixed concentrations of HSO_4^- . I_{max} and I_{min} are the corresponding maximum and minimum, respectively.

$$\log \frac{I - I_{min}}{I_{max} - I} = \log K + \log [HSO_4^-]$$

$$K = 1.70 \times 10^4 M^{-2}$$

4. UV-vis and fluorescence responses of T, T + CN⁻ and T + CN⁻ with HSO₄⁻

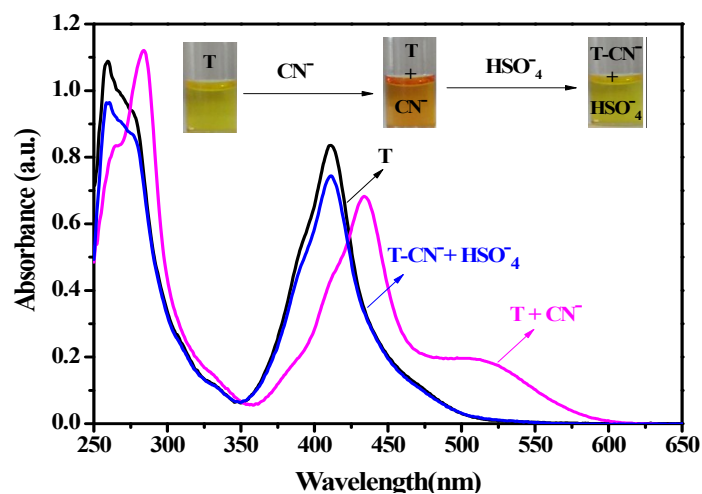


Figure S1 UV-vis absorbance spectra of T (2.0×10^{-4} M) in the presence of CN⁻ (50 equiv.) and HSO₄⁻ (50 equiv.) in DMSO/H₂O (7: 3, v/v) solution. Inset: photograph from left to right shows the color changes of only T, T + CN⁻ and T + CN⁻ plus HSO₄⁻ in DMSO/H₂O (7: 3, v/v) solution

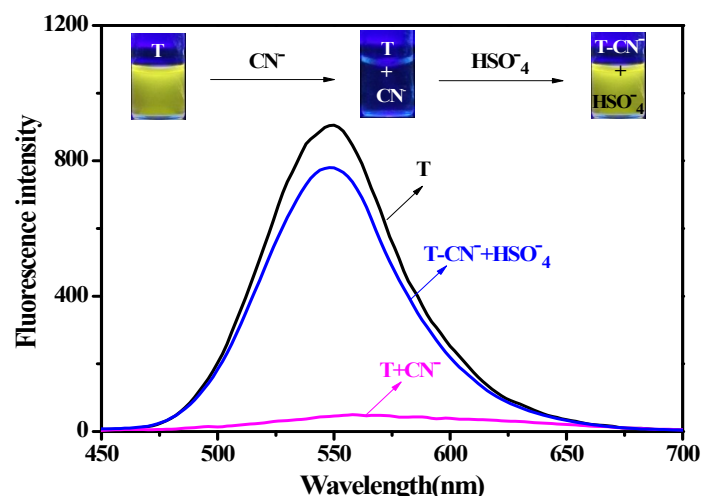


Figure S2 Fluorescence emission ($\lambda_{\text{ex}} = 430$ nm) spectra of T (2.0×10^{-4} M) in the presence of CN⁻ (50 equiv.) and HSO₄⁻ (50 equiv.) in DMSO/H₂O (7: 3, v/v) solution. Inset: photograph from left to right shows the change in the fluorescence of only T, T + CN⁻ and T + CN⁻ plus HSO₄⁻ in DMSO/H₂O (7: 3, v/v) solution under irradiation at 365 nm.

5. UV-vis and fluorescence responses of T, T + CN⁻ and T + CN⁻ with HSO₄⁻, HCl, HNO₃, H₂PO₄, and HClO₄

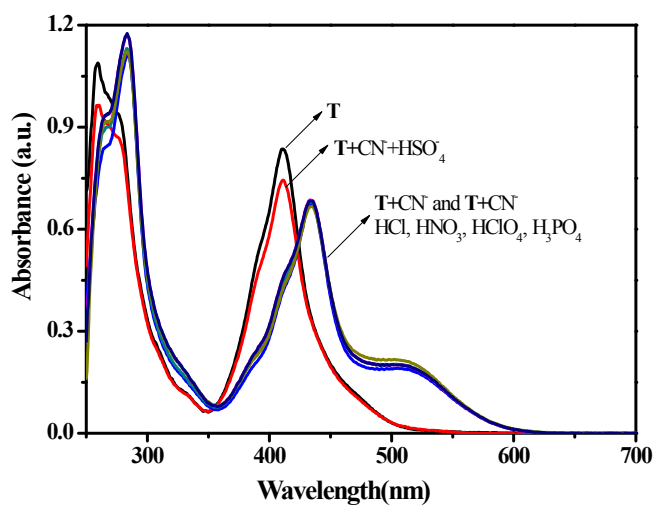


Figure S3 UV-vis absorbance spectra of T (2.0×10^{-4} M), T + CN⁻, T + CN⁻ with HSO₄⁻, HCl, HNO₃, H₂PO₄, and HClO₄ (50 equiv.) in DMSO/H₂O (7: 3, v/v) solution.

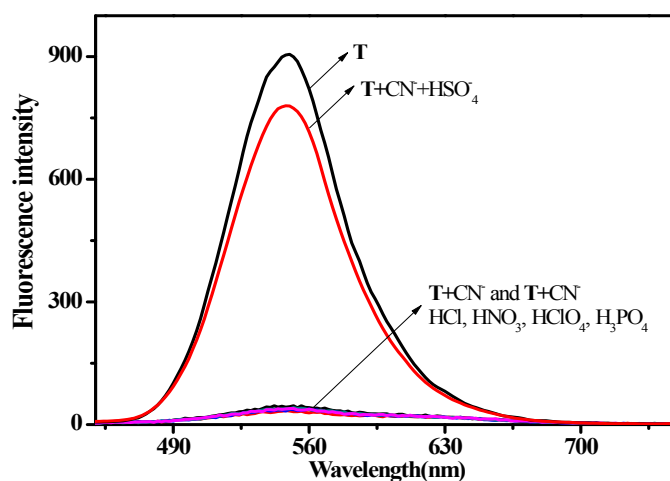


Figure S4 Fluorescence emission ($\lambda_{\text{ex}} = 430$ nm) spectra of T (2.0×10^{-4} M), T + CN⁻, T + CN⁻ with HSO₄⁻, HCl, HNO₃, H₂PO₄, and HClO₄ (50 equiv.) in DMSO/H₂O (7: 3, v/v) solution.

6. ^1H -NMR titration of compound T

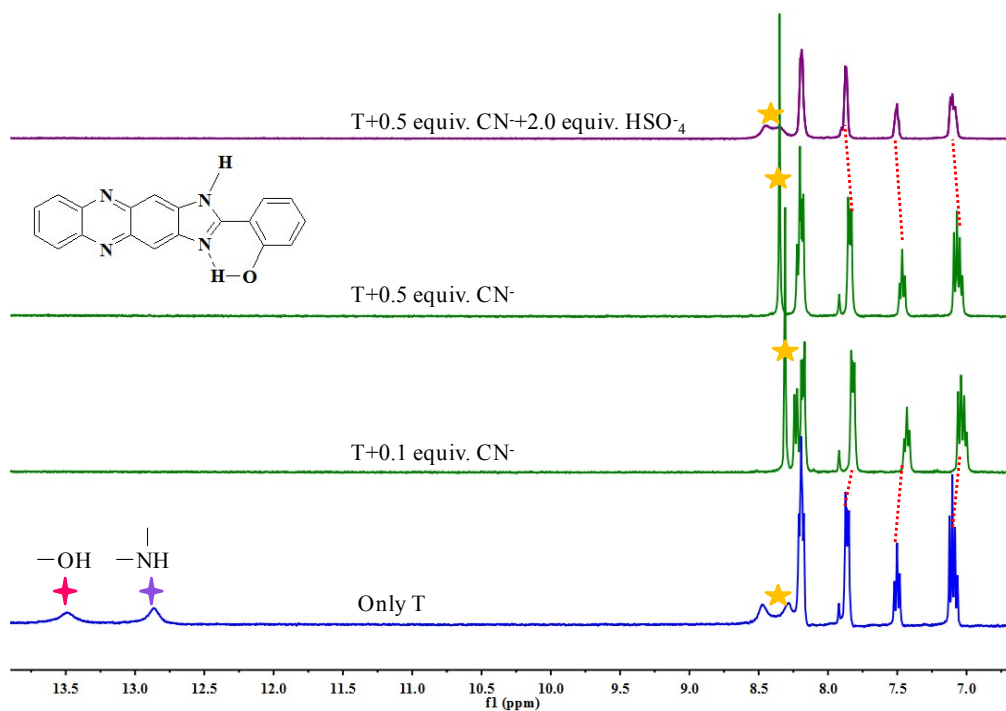


Figure S5 ^1H NMR spectra (600 MHz, DMSO-d_6) of free T and in the presence of CN^- and HSO_4^- , respectively.

7. UV-vis spectroscopy and fluorescence spectroscopy of T, T + CN⁻ and T + OH⁻

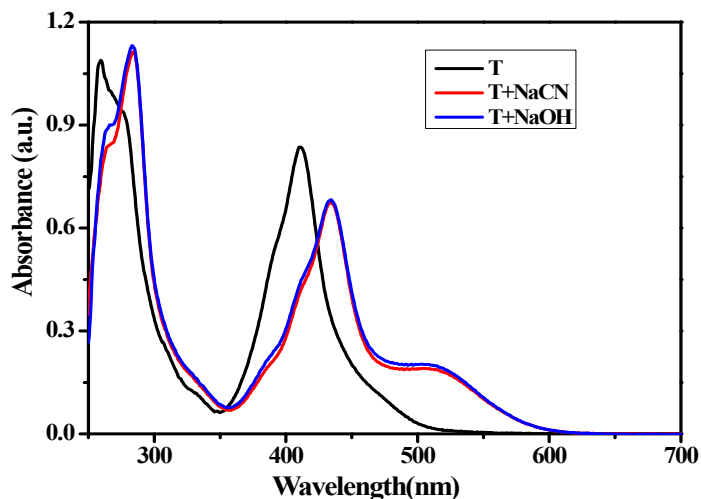


Figure S6 UV-vis absorbance spectra of T (2.0×10^{-4} M), T (2.0×10^{-4} M) in the presence of CN⁻ (50 equiv.) and T (2.0×10^{-4} M) in the presence of OH⁻ (50 equiv.) in DMSO/H₂O (7: 3, v/v) solution.

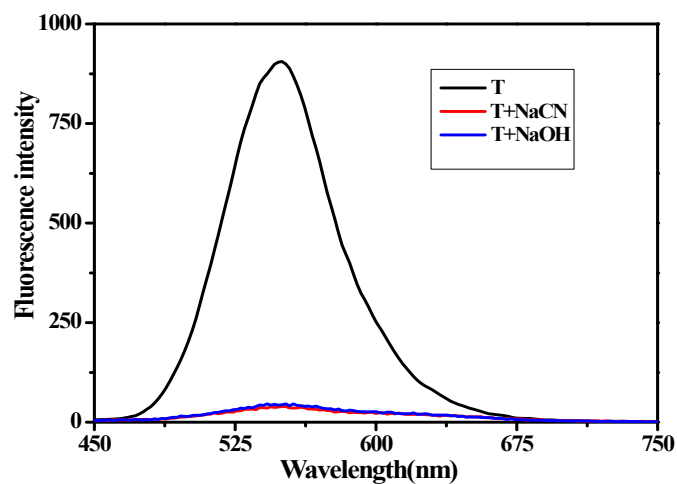
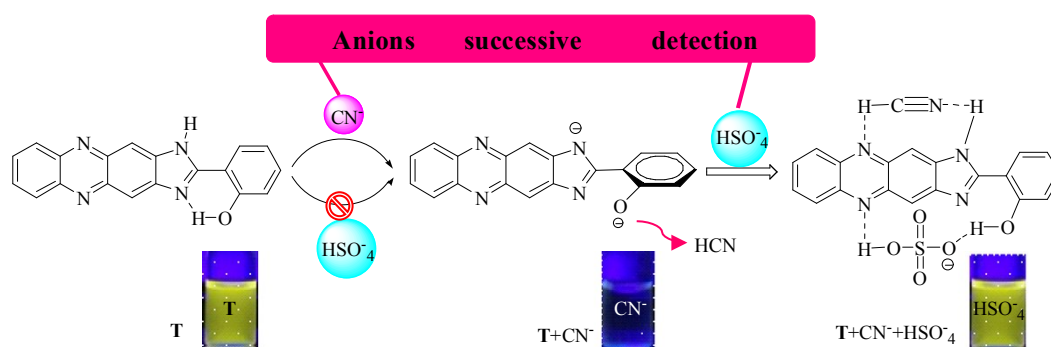


Figure S7 Fluorescence emission ($\lambda_{\text{ex}} = 430$ nm) spectra of T (2.0×10^{-4} M), T (2.0×10^{-4} M) in the presence of CN⁻ (50 equiv.) and T (2.0×10^{-4} M) in the presence of OH⁻ (50 equiv.) in DMSO/H₂O (7: 3, v/v) solution.

8. The proposed mechanism of T for CN^- and T + CN^- for HSO_4^- .



Scheme S2 The proposed mechanism of T for CN^- and T + CN^- for HSO_4^- .

9. Determination of UV-vis detection limit of CN⁻

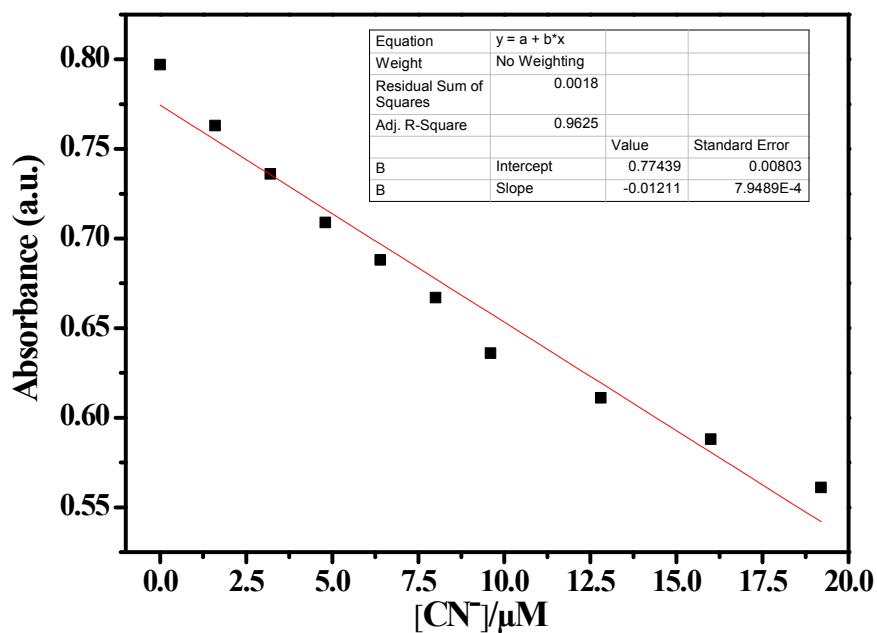


Figure S8 Plot of the absorbance at 410 nm for a mixture of the sensor **T** and CN⁻ in DMSO/H₂O (7: 3, v/v) solution in the range 0 to 18.8 μM.

The result of the analysis as follows:

Linear Equation: $Y = -0.012 \times X + 0.774$ $R^2 = 0.962$

$S = 1.2 \times 10^3$

$$\delta = \sqrt{\frac{\sum (A_0 - \bar{A}_0)^2}{N - 1}} = 0.00333 \quad (N=20) \quad K = 3$$

$LOD = K \times \delta / S = 2.55 \times 10^{-7} \text{ M}$

10. Determination of fluorescence detection limit of CN⁻

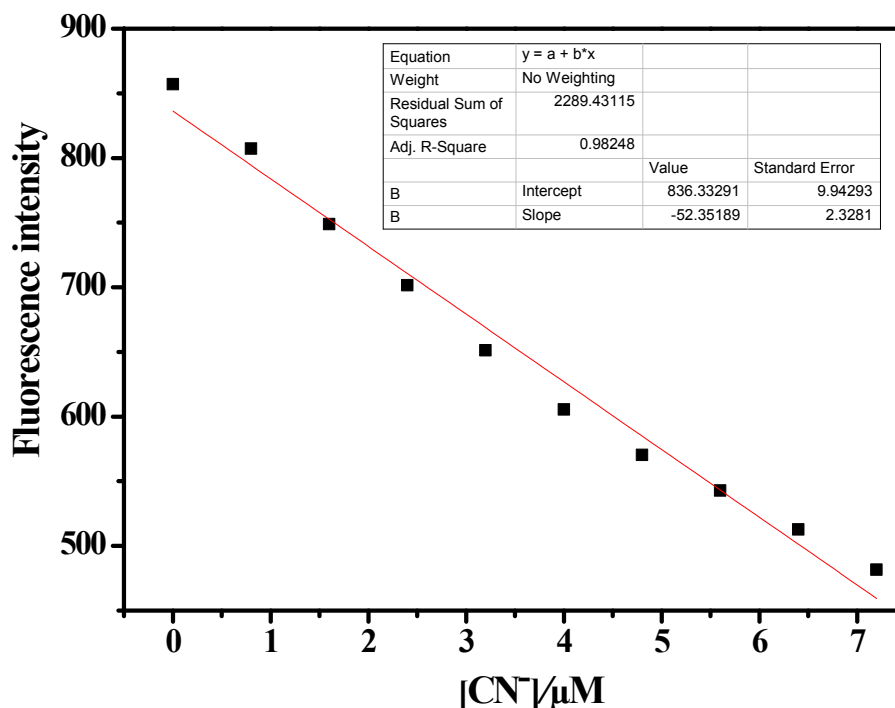


Figure S9 Plot of the intensity at 550 nm for a mixture of the sensor **T** and CN⁻ in DMSO/H₂O (7: 3, v/v) solution in the range 0.00 to 7.23 μM ($\lambda_{\text{ex}}=430\text{nm}$).

The result of the analysis as follows:

$$\text{Linear Equation: } Y = -52.35 \times X + 836.33 \quad R^2 = 0.982$$

$$S = 5.23 \times 10^7$$

$$\delta = \sqrt{\frac{\sum (F_0 - \bar{F}_0)^2}{N - 1}} = 1.5534 \quad (N=20) \quad K = 3$$

$$\text{LOD} = K \times \delta / S = 8.90 \times 10^{-8} \text{ M}$$

11. Determination of UV-vis detection limit of HSO₄⁻

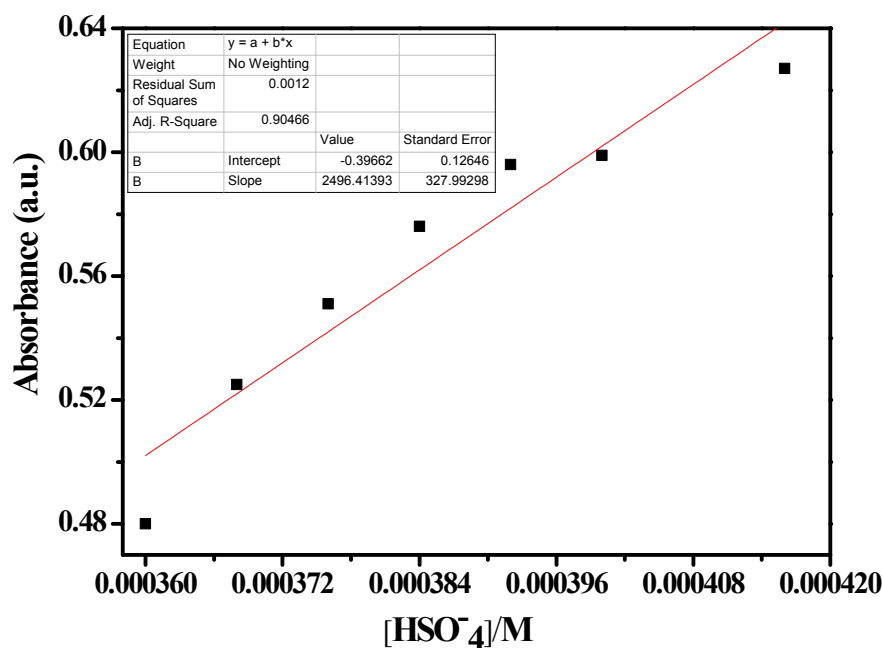


Figure S10 Plot of the absorbance at 410 nm for a mixture of the sensor **T** + CN⁻ and HSO₄⁻ in DMSO/H₂O (7: 3, v/v) solution in the range 0.00036 to 0.00042 M.

The result of the analysis as follows:

Linear Equation: $Y = 2496.413 \times X - 0.397$ $R^2 = 0.904$

$S = 2.496 \times 10^9$

$$\delta = \sqrt{\frac{\sum (A_0 - \bar{A}_0)^2}{N - 1}} = 6.372 \quad (N=20) \quad K = 3$$

$LOD = K \times \delta / S = 7.65 \times 10^{-9} \text{ M}$

12. Determination of fluorescence detection limit of HSO_4^-

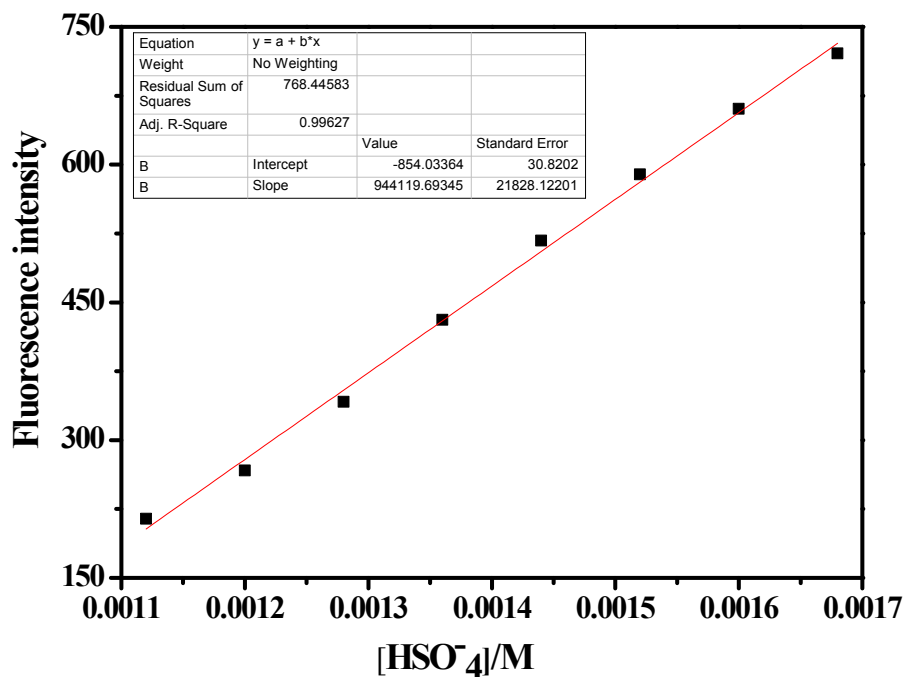


Figure S11 Plot of the intensity at 550 nm for a mixture of the sensor $\text{T} + \text{CN}^-$ and HSO_4^- in the DMSO/ H_2O (7: 3, v/v) solution in the range 0.0011 to 0.0017 M ($\lambda_{\text{ex}} = 430\text{nm}$).

The result of the analysis as follows:

$$\text{Linear Equation: } Y = 944119.693 \times X - 854.336 \quad R^2 = 0.996$$

$$S = 9.44 \times 10^{11}$$

$$\delta = \sqrt{\frac{\sum (F_0 - \bar{F}_0)^2}{N - 1}} = 46.1548 \quad (N=20) \quad K = 3$$

$$\text{LOD} = K \times \delta / S = 1.46 \times 10^{-10} \text{ M}$$

13. Time-dependent fluorescence change of T with CN⁻ and T + CN⁻ with HSO₄⁻

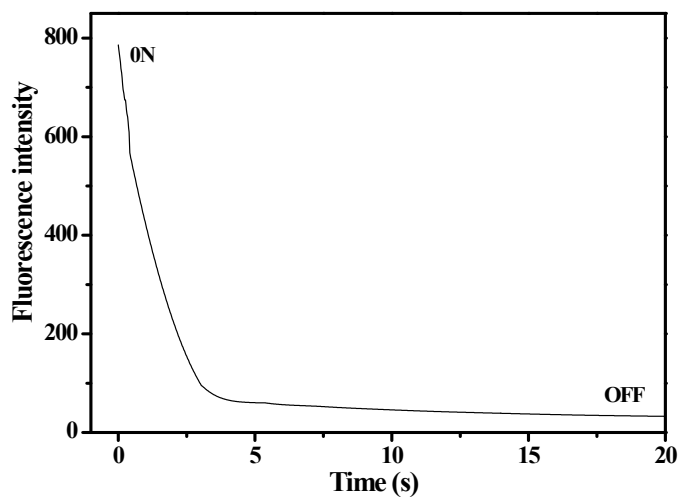


Figure S12 Fluorescence intensity at 550 nm for T (2.0×10^{-4} M) in DMSO/H₂O (7: 3, v/v) solution addition of CN⁻ (50 equiv.), after a period of time.

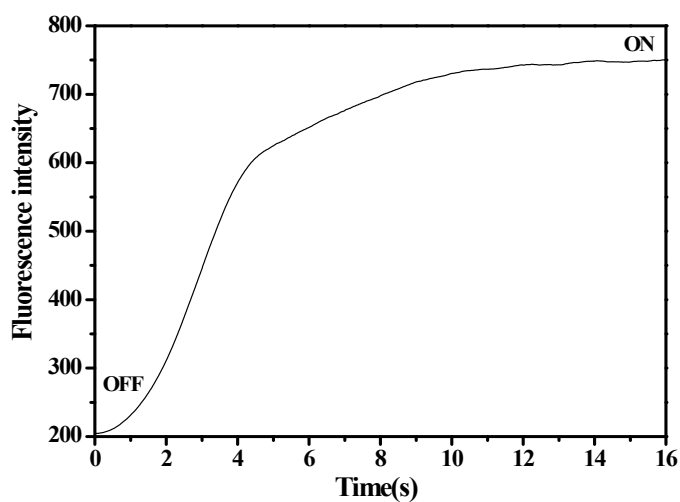


Figure S13 Fluorescence intensity at 550 nm for T + CN⁻ in DMSO/H₂O (7: 3, v/v) solution addition of HSO₄⁻ (50 equiv.), after a period of time.

14. Truth table and logic gate

Table (1)

The truth table of this logic gate

Input		Output
CN ⁻	HSO ₄ ⁻	Fluorescence single
0	0	1
1	0	0
0	1	1
1	1	1

Figure S14 IMP truth table. Output is represented by the fluorescence intensity at 550 nm.

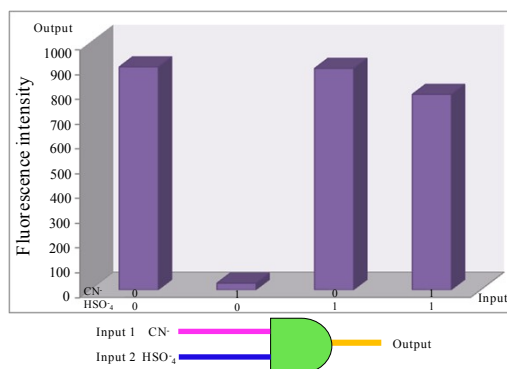


Figure S15 The fluorescence response in the presence of different inputs and the symbol of **T** logic gate.

15. Fluorescence naked eye detection

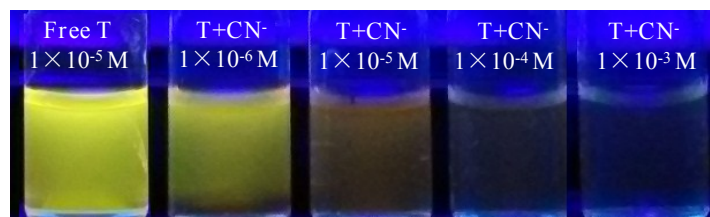


Figure S16 Fluorescent changes of **T** upon the addition of **CN⁻** at the indicated concentrations in DMSO/H₂O (7: 3, v/v) solution under irradiation at 365 nm.

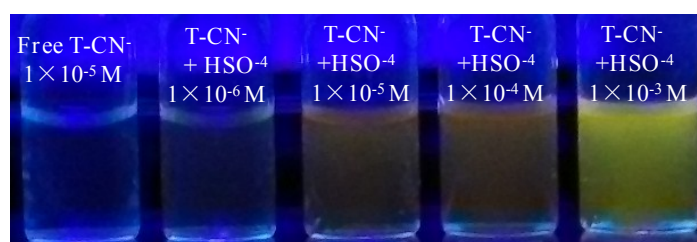


Figure S17 Fluorescent changes of **T + CN⁻** upon the addition of **HSO₄⁻** at the indicated concentrations in DMSO/H₂O (7: 3, v/v) solution under irradiation at 365 nm.

16. ^1H NMR spectra of compound T

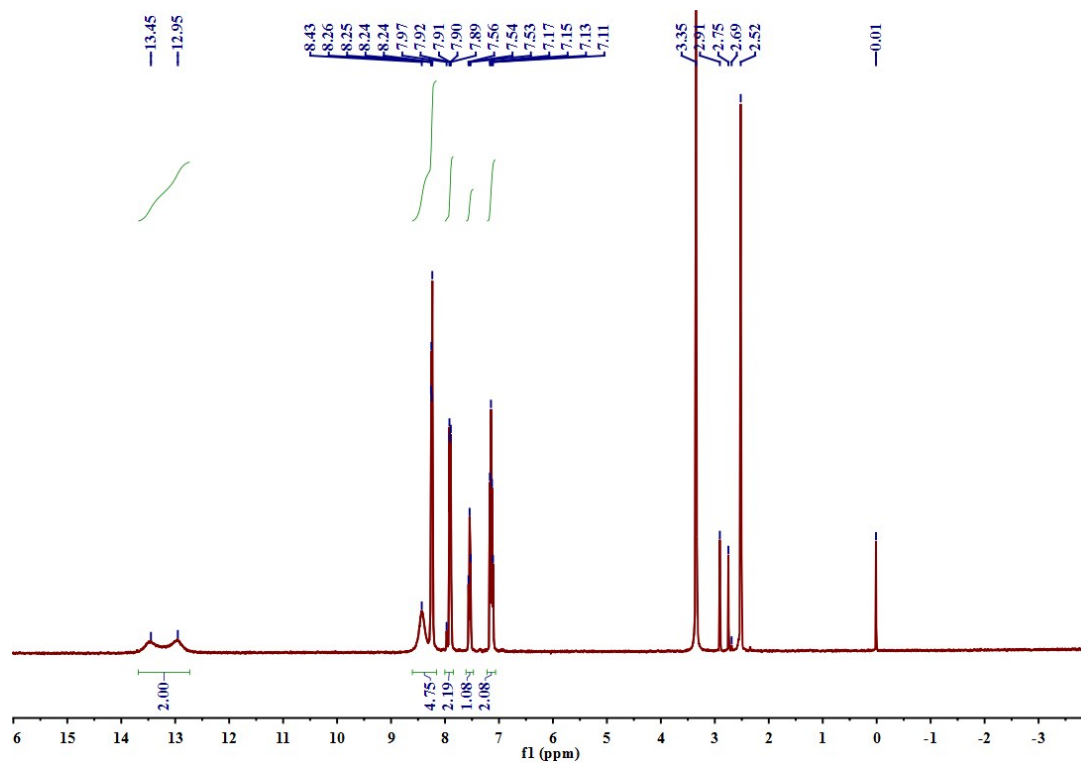


Figure S18 ^1H NMR spectra of compound T

17. ^{13}C NMR spectra of compound T

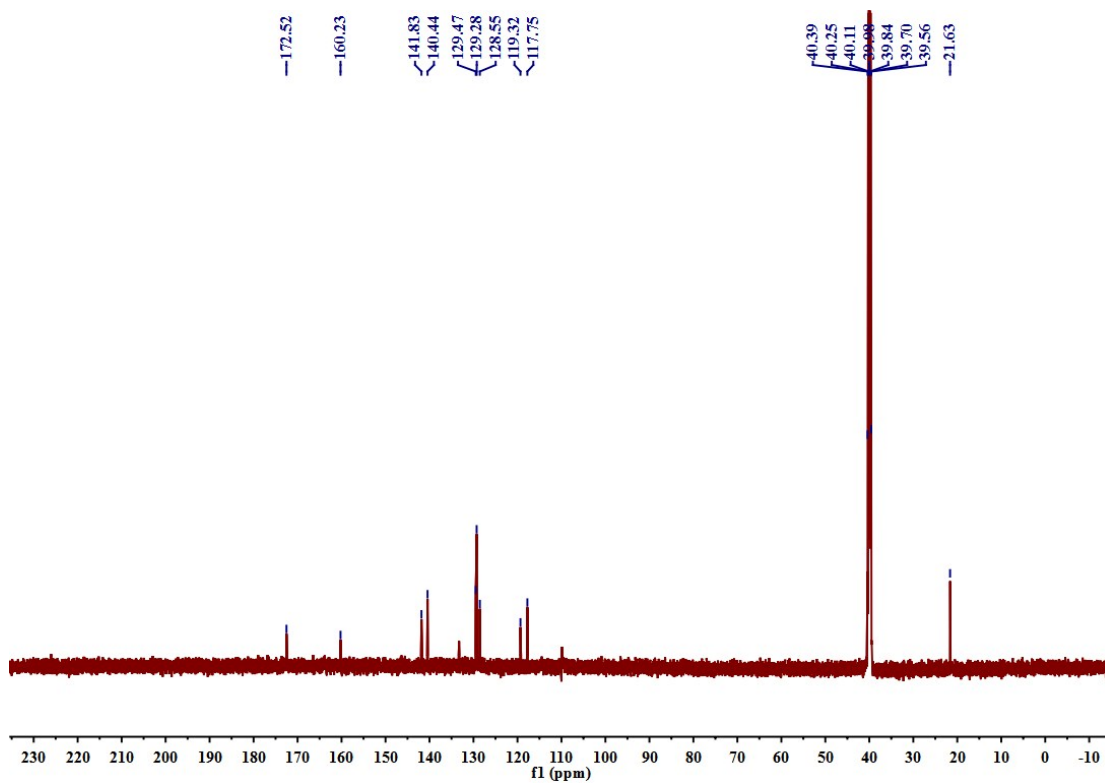


Figure S19 ^{13}C NMR spectra of compound T

18. ESI-MS spectrum of T

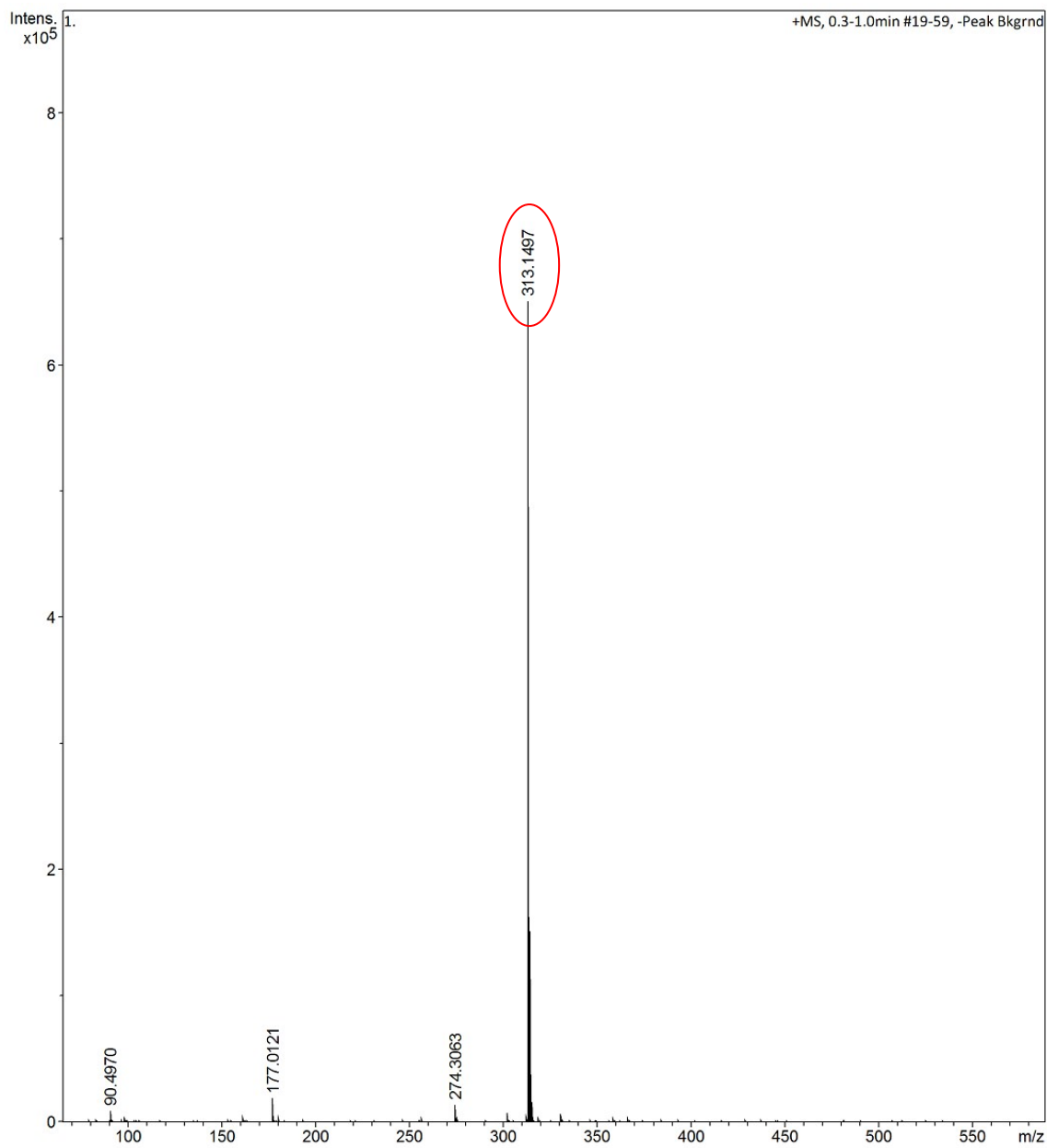
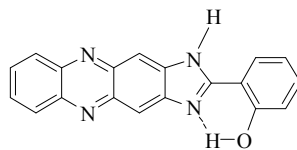


Figure S20 ESI/MS of compound T

19. ESI-MS spectrum of T+CN⁻+HSO₄⁻

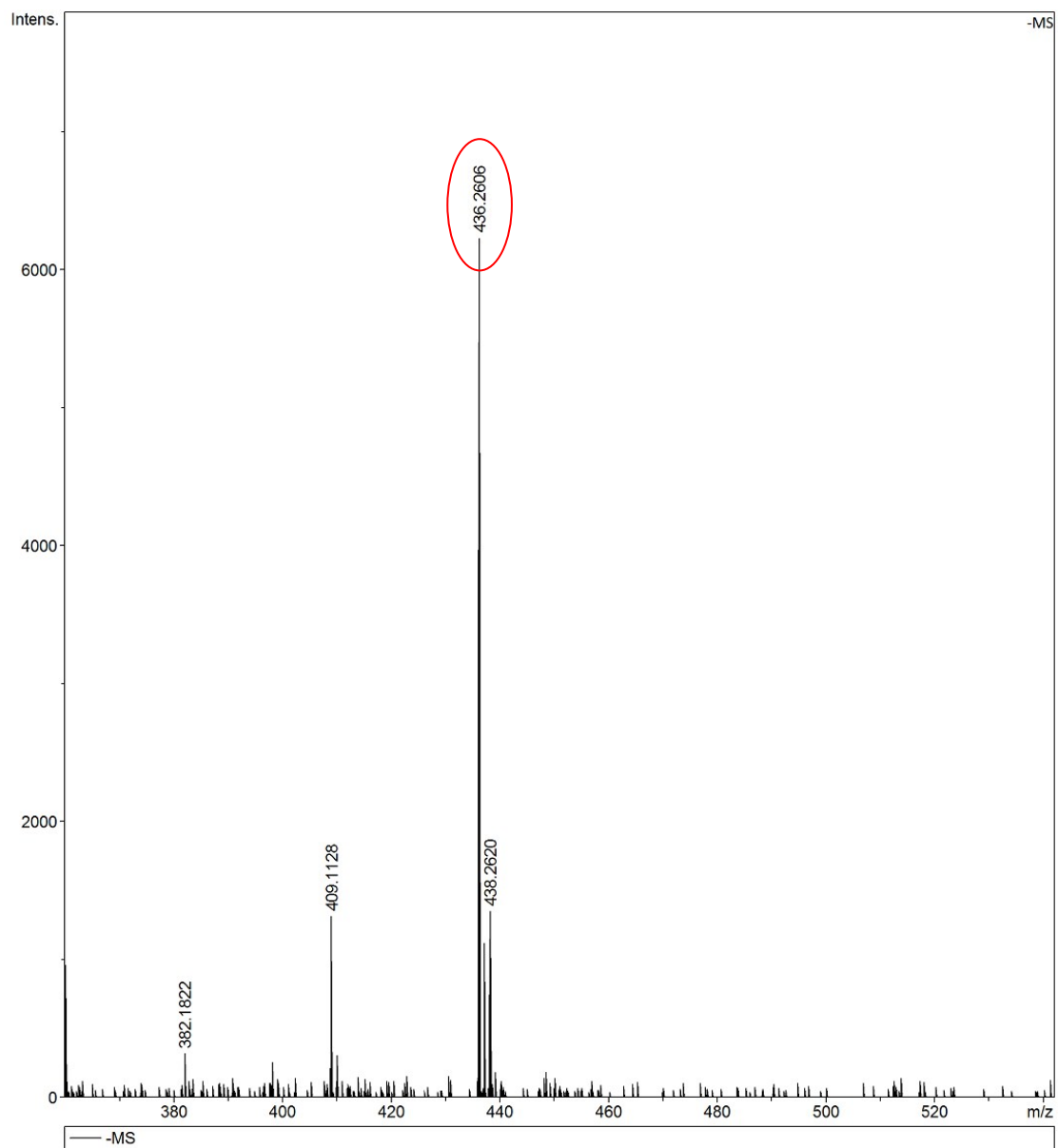
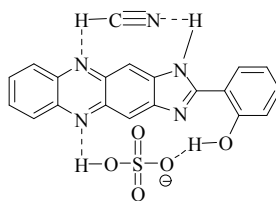


Figure S21 ESI/MS of T+CN⁻+HSO₄⁻

20. Reference

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- (2) A. M. Amer, A. A. Bahnasawi, M. R. Mahran, M. Lapib *onatshefte für Chemie.*, 1999, **130**, 1217-1225.