A dual-channel chemosensor could successively detect CN⁻ and HSO₄⁻ in aqueous solution and act as a keypad lock

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CONTENTS

1. General Methods .....................................................................................................................3
2. Synthesis of T ..........................................................................................................................5
3. Determination of association constant .....................................................................................6
4. UV-vis and fluorescence responses of T, T + CN⁻ and T + CN⁻ with HSO₄⁻ ....................7
5. UV-vis and fluorescence responses of T, T + CN⁻ and T + CN⁻ with HSO₄⁻, HCl, HNO₃, H₂PO₄, and HClO₄ ......................................................................................................................8
6. ¹H-NMR titration of compound T ..........................................................................................9
7. UV-vis spectroscopy and fluorescence spectroscopy of T, T + CN⁻ and T + OH⁻ ..........10
8. The proposed mechanism of T for CN⁻ and T + CN⁻ for HSO₄⁻ ........................................11
9. Determination of UV-vis detection limit of CN⁻ ..................................................................12
10. Determination of fluorescence detection limit of CN⁻ ......................................................13
11. Determination of UV-vis detection limit of HSO₄⁻ ............................................................14
12. Determination of fluorescence detection limit of HSO₄⁻ ....................................................15
13. Time-dependent fluorescence change of T with CN⁻ and T + CN⁻ with HSO₄⁻ ............16
14. Truth table and logic gate ..................................................................................................17
15. Fluorescence naked eye detection ......................................................................................18
16. ¹H NMR spectra of compound T .......................................................................................19
17. ¹³C NMR spectra of compound T .....................................................................................20
18. ESI-MS spectrum of T ........................................................................................................21
19. ESI-MS spectrum of T + CN⁻+HSO₄⁻ ..............................................................................22
20. Reference .............................................................................................................................23
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\(_2\)PO\(_4^-\), 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. \(^1\)H 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 \(\times\) 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\(_2\)PO\(_4^-\), HSO\(_4^-\) and ClO\(_4^-\)) and sodium salt of anions (CN\(^-\) and SCN\(^-\)). All the UV-vis experiments were carried out in DMSO/H\(_2\)O (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 \(\times\) 10\(^{-5}\) M) in all experiments.

1.4. General procedure for Fluorescence spectra experiments

The solution of sensor \(T\) (2.0 \(\times\) 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\(_2\)PO\(_4^-\), HSO\(_4^-\) and ClO\(_4^-\)) and sodium salt of anions (CN\(^-\) and SCN\(^-\)). All the fluorescence spectra experiments were carried out in DMSO/H\(_2\)O (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 DMSO-\textit{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

\[
\begin{align*}
\text{NH}_2 & \quad \begin{array}{c} \text{HCl FeCl}_3 \\ \text{RT} \end{array} \\
\text{NH}_2 & \quad \begin{array}{c} \text{CHO} \\ \text{DMF, AcO, 85°C} \end{array} \\
\text{NH}_2 & \quad \begin{array}{c} \text{HO} \\ \text{RT} \end{array}
\end{align*}
\]

Scheme S1 Structure and synthesis of the sensor T

Synthesis of 2, 3-diamino-phenazinewas synthesized according to the reported procedure \(^1\)-\(^2\).

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-H\(_2\)O to get brown powdery product T. The other compound T was prepared by similar procedures.

T: yield: 75%; m.p. > 300 C; \(^1\)H NMR (DMSO-d\(_6\), 400 MHz) \(\delta\) 13.45 (1H, NH), \(\delta\) 12.95 (1H, OH), \(\delta\) 8.43-8.24 (2H, ArH) 7.91-7.89 (2H, ArH) 7.56-7.53 (1H, ArH) 7.17-7.11 (2H, ArH). \(^1\)C NMR (DMSO-d\(_6\), 150 MHz) \(\delta\) 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 C\(_{19}\)H\(_{12}\)N\(_4\)O 313.2; Found 313.3; Anal. Calcd. For C\(_{19}\)H\(_{12}\)N\(_4\)O: 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.

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

\[K = 1.24 \times 10^{10} \text{M}^{-2}\]

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

\[
\log \frac{I - I_{\text{min}}}{I_{\text{max}} - I} = \log K + 2 \log [\text{HSO}_4^-]
\]

\[K = 1.70 \times 10^4 \text{M}^{-2}\]

I is the observed the fluorescence intensity of T-CN\(^-\) at the fixed concentrations of HSO\(_4^-\). \(I_{\text{max}}\) and \(I_{\text{min}}\) are the corresponding maximum and minimum, respectively.
4. UV-vis and fluorescence responses of T, T + CN\(^{-}\) and T + CN\(^{-}\) with HSO\(_4\)\(^{-}\)

**Figure S1** UV-vis absorbance spectra of T (2.0 × 10\(^{-4}\) M) in the presence of CN\(^{-}\) (50 equiv.) and HSO\(_4\)\(^{-}\) (50 equiv.) in DMSO/H\(_2\)O (7: 3, v/v) solution. Inset: photograph from left to right shows the color changes of only T, T + CN\(^{-}\) and T + CN\(^{-}\) plus HSO\(_4\)\(^{-}\) in DMSO/H\(_2\)O (7: 3, v/v) solution

**Figure S2** Fluorescence emission (\(\lambda_{ex}= 430\) nm) spectra of T (2.0 × 10\(^{-4}\) M) in the presence of CN\(^{-}\) (50 equiv.) and HSO\(_4\)\(^{-}\) (50 equiv.) in DMSO/H\(_2\)O (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 HSO\(_4\)\(^{-}\) in DMSO/H\(_2\)O (7: 3, v/v) solution under irradiation at 365 nm.
5. UV-vis and fluorescence responses of $T$, $T + CN^-$ and $T + CN^-$ with $\text{HSO}_4^-$, $\text{HCl}$, $\text{HNO}_3$, $\text{H}_2\text{PO}_4$, and $\text{HClO}_4$

![UV-vis absorbance spectra](image1)

**Figure S3** UV-vis absorbance spectra of $T$ ($2.0 \times 10^{-4}$ M), $T + CN^-$, $T + CN^-$ with $\text{HSO}_4^-$, $\text{HCl}$, $\text{HNO}_3$, $\text{H}_2\text{PO}_4$, and $\text{HClO}_4$ (50 equiv.) in DMSO/H$_2$O (7: 3, v/v) solution.

![Fluorescence emission spectra](image2)

**Figure S4** Fluorescence emission ($\lambda_{ex} = 430$ nm) spectra of $T$ ($2.0 \times 10^{-4}$ M), $T + CN^-$, $T + CN^-$ with $\text{HSO}_4^-$, $\text{HCl}$, $\text{HNO}_3$, $\text{H}_2\text{PO}_4$, and $\text{HClO}_4$ (50 equiv.) in DMSO/H$_2$O (7: 3, v/v) solution.
6. $^1$H-NMR titration of compound T

Figure S5 $^1$H NMR spectra (600 MHz, DMSO-d6) of free T and in the presence of CN$^-$ and HSO$_4^-$, respectively.
7. UV-vis spectroscopy and fluorescence spectroscopy of $T$, $T + \text{CN}^-$ and $T + \text{OH}^-$

![UV-vis absorbance spectra](image)

**Figure S6** UV-vis absorbance spectra of $T$ ($2.0 \times 10^{-4}$ M), $T$ ($2.0 \times 10^{-4}$ M) in the presence of $\text{CN}^-$ (50 equiv.) and $T$ ($2.0 \times 10^{-4}$ M) in the presence of $\text{OH}^-$ (50 equiv.) in DMSO/\(H_2O\) (7: 3, v/v) solution.

![Fluorescence emission spectra](image)

**Figure S7** Fluorescence emission ($\lambda_{ex} = 430$ nm) spectra of $T$ ($2.0 \times 10^{-4}$ M), $T$ ($2.0 \times 10^{-4}$ M) in the presence of $\text{CN}^-$ (50 equiv.) and $T$ ($2.0 \times 10^{-4}$ M) in the presence of $\text{OH}^-$ (50 equiv.) in DMSO/\(H_2O\) (7: 3, v/v) solution.
8. The proposed mechanism of T for CN⁻ and T + CN⁻ for HSO₄⁻.

Scheme S2 The proposed mechanism of T for CN⁻ and T + CN⁻ for HSO₄⁻.
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/H$_2$O (7: 3, v/v) solution in the range 0 to 18.8 μM.

The result of the analysis as follows:

Linear Equation: $Y = -0.012 \times X +0.774$ \hspace{1cm} $R^2 = 0.962$

$S = 1.2 \times 10^3$

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

$\text{LOD} = K \times \delta / S = 2.55 \times 10^{-7}$ 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/H_2O (7: 3, v/v) solution in the range 0.00 to 7.23μM (λ_ex =430nm).

The result of the analysis as follows:

Linear Equation: Y = -52.35× X +836.33   \hspace{1cm} R^2 = 0.982

S = 5.23× 10^7

\[ \delta = \sqrt{\frac{\sum (F_0 - \bar{F}_0)^2}{N - 1}} = 1.5534 \] \hspace{1cm} (N=20) \hspace{1cm} K = 3

LOD = K × \delta / S = 8.90 × 10^{-8} 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: \( Y = 2496.413 \times X - 0.397 \) \( \quad R^2 = 0.904 \)

\[ S = 2.496 \times 10^9 \]

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

\[ \text{LOD} = K \times \delta / S = 7.65 \times 10^{-9} \text{ M} \]
12. Determination of fluorescence detection limit of HSO$_4^-$

Figure S11 Plot of the intensity at 550 nm for a mixture of the sensor T + CN$^-$ and HSO$_4^-$ in the DMSO/H$_2$O (7: 3, v/v) solution in the range 0.0011 to 0.0017 M ($\lambda_{ex}$ =430nm).

The result of the analysis as follows:

Linear Equation: $Y = 944119.693 \times X -854.336$ \hspace{1cm} $R^2 = 0.996$

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

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

$LOD = K \times \delta / S = 1.46 \times 10^{-10}$ M
13. Time-dependent fluorescence change of T with CN\(^-\) and T + CN\(^-\) with 
\(\text{HSO}_4\)^- 

**Figure S12** Fluorescence intensity at 550 nm for T (2.0 \(\times 10^{-4}\) M) in DMSO/H\(_2\)O (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/H\(_2\)O (7: 3, v/v) solution addition of HSO\(_4\)^- (50 equiv.), after a period of time.
14. Truth table and logic gate

Table (1)

The truth table of this logic gate

<table>
<thead>
<tr>
<th>Input</th>
<th>CN-</th>
<th>HSO₄⁻</th>
<th>Output</th>
<th>Fluorescence single</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
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<td>0</td>
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<td>0</td>
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<tr>
<td>0</td>
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<td>1</td>
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<td>1</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

**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/H$_2$O (7: 3, v/v) solution under irradiation at 365 nm.

**Figure S17** Fluorescent changes of T + CN$^-$ upon the addition of HSO$_4^-$ at the indicated concentrations in DMSO/H$_2$O (7: 3, v/v) solution under irradiation at 365 nm.
16. $^1$H NMR spectra of compound T

Figure S18 $^1$H NMR spectra of compound T
17. $^{13}$C NMR spectra of compound T

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