Amide based dipodal Zn$^{2+}$ complex: a nano-molar detection of HSO$_4^-$ in semi-aqueous system

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Table S1. A comparison of literature reported sensors with present work

<table>
<thead>
<tr>
<th>Group</th>
<th>Technique</th>
<th>Solvent System</th>
<th>Detection Limit</th>
<th>Interference</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yang et al.</td>
<td>Fluorescence</td>
<td>MeOH</td>
<td>1.39×10$^{-6}$ M</td>
<td>NO</td>
<td>1</td>
</tr>
<tr>
<td>Li et al.</td>
<td>Fluorescence</td>
<td>CH$_3$CN</td>
<td>N.E.</td>
<td>N.E.</td>
<td>2</td>
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<tr>
<td>Xue et al.</td>
<td>Fluorescence</td>
<td>CH$_3$Cl/CH$_3$OH (9:1; v/v)</td>
<td>N.E.</td>
<td>N.E.</td>
<td>3</td>
</tr>
<tr>
<td>Zhou et al.</td>
<td>Fluorescence</td>
<td>CH$_3$CN</td>
<td>N.E.</td>
<td>H$_2$PO$_4^-$</td>
<td>4</td>
</tr>
<tr>
<td>Chawla et al.</td>
<td>NMR</td>
<td>CDCl$_3$</td>
<td>N.E.</td>
<td>N.E.</td>
<td>5</td>
</tr>
<tr>
<td>Nam et al.</td>
<td>NMR and Electrochemistry</td>
<td>CDCl$_3$</td>
<td>N.E.</td>
<td>N.E.</td>
<td>6</td>
</tr>
<tr>
<td>Tan et al.</td>
<td>Fluorescence</td>
<td>H$_2$O</td>
<td>5.0×10$^{-5}$ M</td>
<td>H$_2$PO$_4^-$</td>
<td>7</td>
</tr>
<tr>
<td>Present Work</td>
<td>Fluorescence</td>
<td>DMSO/H$_2$O (50:50, v/v)</td>
<td>50nM</td>
<td>No</td>
<td>-</td>
</tr>
</tbody>
</table>

N.E. represent not evaluated

1 Binding constant

1.1 The Benesi-Hildebrand Plot

Using the Benesi-Hildebrand Plot$^8$ (Eq.1) methodologies. We made the calculation of association constant K.

\[
\frac{1}{F-F_0} = \frac{1}{(F_\infty - F_0)K[G]} + \frac{1}{(F_\infty - F_0)}
\]  

(Eq.1)
Figure S1. Benesi-Hildebrand Plot (adjusted equation: 1/F-F₀ = -2E-11x+7E-07 1/[G], R=0.9918) and the K value for HSO₄⁻ at 3.5 x 10⁴ M⁻¹.

1.2 The Stern–Volmer quenching constant

The quenching can be mathematically expressed by the Stern–Volmer Eq. (2), which allows for calculating quenching constants.

\[
F₀/F = 1 + k_q \tau_0 [Q] = 1 + K_{sv}[Q] \tag{2}
\]

Where \(F_0\) and \(F\) are the fluorescence intensities in the absence and presence of the quencher, \(k_q\) is the bimolecular quenching constant, \(\tau_0\) is the lifetime of the fluorescence in the absence of the quencher \([Q]\) is the concentration of the quencher, and \(K_{sv}\) is the Stern–Volmer quenching constant. In the presence of a quencher \((Lns)\), the fluorescence intensity is reduced from \(F_0\) to \(F\). The ratio \((F_0/F)\) is directly proportional to the quencher concentration \([Q]\).

Evidently:

\[
K_{sv} = k_q \tau_0 \tag{3}
\]

\[
F_0/F = 1 + K_{sv}[Q] \tag{4}
\]

According to Eq, a plot of \(F_0/F\) versus \([Q]\) shows a linear graph with an intercept of \(4\) and a slope of \(K_{sv}\). A typical plot of \(F_0/F\) versus HSO₄⁻ concentration is shown in Fig S2.

Figure S2. The Stern–Volmer plot of the titrations of probe 4 with different concentrations of HSO₄⁻ anion salt.

2 Stoichiometry of complexations

To determine the binding stoichiometry between receptor 4 and HSO₄⁻ the continuous variation method was used. Fig. S3 shows the Job’s plot of the fluorescence intensity of free receptor 4 and the intensity of the system with the molar fraction of the host \([(H)/(H+G)]\) for a series of solutions, in which the total concentration of host and
guest was constant, with the molar fraction of host continuously varying. The results show that the formation of a 1:1 (Host: Guest) complex. Using the equation: \[ [G]_{\text{tot}} = a/2K(1-a)^2[H]_{\text{tot}} + a[H]_{\text{tot}}/2, \] where \([G]_{\text{tot}}\) is total concentration of guest, \([H]_{\text{tot}}\) is the total concentration of host, \(a = (I - I_0)/(I_i - I_0)\) with \(I\) being the fluorescent intensity at a particular guest ion concentration while \(I_0\) and \(I_i\) are the intensities at zero and infinite guest concentrations, respectively.

**Figure S3.** 1:1 Stoichiometry of the host guest relationship realised from the Job plot between receptor 4 and HSO₄⁻.

**Figure S4.** Absorbance spectrum of probe 4 (\(c = 10\mu M\)) upon the addition of HSO₄⁻ salt (\(c = 100\mu M\)) in DMSO/H₂O (50:50, v/v). The inset corresponding colorimetrically colour change in the DMSO/H₂O (50:50, v/v) solution of 4 induced by HSO₄⁻ (from left to right: 4 only and 4+ HSO₄⁻).

**Figure S5.** Titration of absorbance spectrum of probe 4 (\(c = 10\mu M\)) upon the gradually addition of increase amount of HSO₄⁻ salt (\(c = 100\mu M\)) in DMSO/H₂O (50:50, v/v).
Figure S6. Infra red spectra of receptor 3
Figure S7. ESI MASS of receptor 4
Figure S8. Infra red spectra of receptor 4

Reference


2. Q. Li, Y. G. Shao, Analyst, 2012, 137, 4497.


