Biphenyl Containing Amido Schiff base Derivative as a Turn-on Fluorescent Chemosensor for Al\(^{3+}\) and Zn\(^{2+}\) ions

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1. General

1.1. Materials

All reagents and spectroscopic grade solvents were used as received from commercial sources without further purification. All cations in the form of perchlorate / nitrate salts were purchased from Sigma-Aldrich Chemical Company. Solvents used for spectroscopic studies were of spectroscopic grade. Aqueous medium experiments have been done in deionized water.

1.2. Methods

Hitachi UV–vis (Model U-3501) spectrophotometer and Perkin Elmer LS-55 spectrofluorometer, were used to record the absorption spectra and emission spectra respectively. IR spectra (KBr pellet, 4000–400 cm⁻¹) were recorded on a Parkin Elmer model 883 infrared spectrophotometer. Shimadzu LCMS-2020 was used for recording mass spectrum.¹H NMR and ¹³C NMR spectra were recorded on a Bruker, Avance 500 spectrometer, where chemical shifts (δ in ppm) were determined with respect to tetramethylsilane (TMS) as internal standards.
2. Benesi-Hildebrand Plot:

Figure S1. B–H plot for UV-vis titration of 1 with Al$^{3+}$
Figure S2. B–H plot for UV-vis titration of 1 with Zn$^{2+}$.
3. UV-vis titration:

**Figure S3.** UV-vis titration of 1 ($1 \times 10^{-5}$ M) in DMF- H$_2$O solvent (v/v, 7:3) upon addition of (0-3 equivalents) of Zn$^{2+}$ ion (inset: absorbance at 386 nm as a function of the equivalence of Zn$^{2+}$ ion).
Figure S4. Job's plot for determining the stoichiometry of sensor 1 and Al$^{3+}$ in the complex.
Figure S5. Job's plot for determining the stoichiometry of molecule 1 and Zn$^{2+}$ in the complex.
5. Fluorescence spectra

Figure S6. Changes in fluorescence spectra of sensor 1 ($1 \times 10^{-6}$ M) in the DMF-H$_2$O solution (v/v, 7:3) induced by Zn$^{2+}$ ion.
6. Detection limit:

![Graph showing emission intensity vs. [Al^{3+}] \text{µM}}]

**Figure S7.** Detection limit of molecule 1 to Al^{3+} based on 3σ/slope

\[ Y = 631.90X - 435.35266 \]

\[ R^2 = 0.9942 \]

\[ \text{LOD} = 3\sigma / K \]

\[ = 0.042 \text{µM} \]
Figure S8. Detection limit of molecule 1 to Zn$^{2+}$ based on 3σ/slope.
7. $^1$H NMR titration spectra:

**Figure S9.** Partial $^1$H NMR titration spectra of sensor 1 in $d_6$-DMSO upon addition of different amount of Zn$^{2+}$ ion
8. Mass spectra:

Figure S10. Mass spectrum of 1-Al$^{3+}$ complex.

Figure S11. Mass spectrum of 1-Zn$^{2+}$ complex.
9. Probable structure:

\[
\begin{align*}
&\text{Figure S12. Probable structure of } 1- \text{ Al}^{3+} \text{ complex}
\end{align*}
\]
Figure S13. Probable structure of 1- Zn$^{2+}$ complex
10. Effect of pH

Figure S14. Change in fluorescence intensity sensor 1 (1×10^{-6} M) (●), its Al^{3+} (●) and Zn^{2+} (●) complexes in different pH values.
11. Competition experiment:

Figure S15 Competition experiments of 1, a plot of fluorescence intensity at 458 nm of 1 with addition of 3.0 equiv. of Al\(^{3+}\), and then 10.0 equiv. of various metal ions, (\(\lambda_{ex}: 350\) nm).
Figure S16. Competition experiments of 1, a plot of fluorescence intensity at 478 nm of 1 with addition of 3.0 equiv. of Zn$^{2+}$, and then 10.0 equiv. of various metal ions, ($\lambda_{ex}$: 350 nm).
12. UV-Vis spectra with EDTA:

Figure S17. UV-Vis titration of 1- Zn$^{2+}$ complex with EDTA in DMF- H$_2$O solvent (v/v, 7:3).
Figure S18. UV-Vis titration of Al$^{3+}$-1 complex with EDTA in DMF- H$_2$O solvent (v/v, 7:3).
13. Emission spectra with EDTA:

**Figure S19.** Fluorescence titration of $1$-$\text{Zn}^{2+}$ complex in DMF-$\text{H}_2\text{O}$ solvent (v/v, 7:3) upon addition of (0-5 equivalents) of EDTA.
Figure S20. Fluorescence intensity change of 1 and 1-Zn$^{2+}$ complex upon addition of Zn$^{2+}$ and EDTA sequentially in DMF-H$_2$O solvent (v/v, 7:3)
**Figure S21.** Fluorescence titration of 1-Al$^{3+}$ complex in DMF- H$_2$O solvent (v/v, 7:3) upon addition of (0-5 equivalents) of EDTA.
### 14. Comparative table:

**Table S1**: Comparative table of past reported probes on the basis of their medium, binding constant, limit of detection and application.

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Analyte</th>
<th>Medium</th>
<th>Method</th>
<th>Binding Constant(Kₘ)</th>
<th>Detection limit (M)</th>
<th>Applications</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Al³⁺, Cu²⁺</td>
<td>EtOH/Water</td>
<td>Fluorometric Colorimetric</td>
<td>Al³⁺: 2.83 x 10¹⁰ Cu²⁺: 5.69 x 10⁹</td>
<td>Al³⁺: 9.10 x 10⁻⁸ Cu²⁺: 3.54 x 10⁻⁷</td>
<td>Logic gate, Live cell imaging and paper strips</td>
<td>1</td>
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<tr>
<td>2</td>
<td>Al³⁺, F⁻</td>
<td>DMSO/ H₂O</td>
<td>Fluorometric</td>
<td>Al³⁺: 8.50 x 10⁵</td>
<td>Al³⁺: 1.05 x 10⁻⁸</td>
<td>Logic gate, Live cell imaging</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>Al³⁺ H₂PO₄⁻</td>
<td>CH₃OH</td>
<td>Fluorometric</td>
<td>Al³⁺: 3.6 x 10⁴</td>
<td>Al³⁺: 8.30 x 10⁻⁷ H₂PO₄⁻: 1.7 x 10⁻⁶</td>
<td>Paper strips</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>Al³⁺ Zn²⁺</td>
<td>CH₃OH/HEPES Buffer</td>
<td>Fluorometric</td>
<td>Al³⁺: 1.3 x 10⁶ Zn²⁺: 7.9 x 10⁴</td>
<td>Al³⁺: 8.30 x 10⁻⁸ Zn²⁺: 1.24 x 10⁻⁷</td>
<td>Logic gate Live cell imaging</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>Al³⁺</td>
<td>CH₃OH / H₂O</td>
<td>Fluorometric</td>
<td>Al³⁺: 5.42 x 10⁵</td>
<td>Al³⁺: 3.55 x 10⁻⁷</td>
<td>Paper strips</td>
<td>5</td>
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<tr>
<td>6</td>
<td>Al³⁺ Cr³⁺</td>
<td>CH₃CN</td>
<td>Fluorometric</td>
<td>Al³⁺: 5.44 x 10⁴</td>
<td>Al³⁺: 3.1 x 10⁻⁷ Cr³⁺: 2.5 x 10⁻⁷</td>
<td>-</td>
<td>6</td>
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<tr>
<td>7</td>
<td>Al³⁺</td>
<td>DMSO/ H₂O</td>
<td>Fluorometric</td>
<td>Al³⁺: 4.09 x 10⁴</td>
<td>Al³⁺: 1.20 x 10⁻⁷</td>
<td>Live cell imaging</td>
<td>7</td>
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<tr>
<td>8</td>
<td>Al³⁺</td>
<td>DMSO/ H₂O</td>
<td>Fluorometric</td>
<td>Al³⁺: 1.90 x 10⁻⁶</td>
<td>-</td>
<td>-</td>
<td>8</td>
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<tr>
<td>9</td>
<td>Al³⁺</td>
<td>CH₃OH / H₂O</td>
<td>Fluorometric</td>
<td>2.85 x 10⁸ Al³⁺: 1.1 x 10⁻⁷</td>
<td>-</td>
<td>-</td>
<td>9</td>
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<tr>
<td>10</td>
<td>Al³⁺ Zn²⁺ Cd²⁺</td>
<td>CH₃OH/ HEPES Buffer</td>
<td>Fluorometric</td>
<td>Al³⁺: 1.5 x 10⁶ M⁻¹ Zn²⁺: 5 x 10⁵ Cd²⁺: 3.5 x 10⁵</td>
<td>Al³⁺: 5.7 x 10⁻⁹ Zn²⁺: 1.09 x 10⁻⁶ Cd²⁺: 1.64 x 10⁻⁶</td>
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<tr>
<td>11</td>
<td>Al³⁺ Cu²⁺</td>
<td>CH₃CN</td>
<td>Fluorometric Colorimetric</td>
<td>Al³⁺: 1.80 x 10⁴ Cu²⁺: 2.02 x 10⁴</td>
<td>Al³⁺: 1.48 x 10⁻⁶ Cu²⁺: 2.05 x 10⁻⁶</td>
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<td>11</td>
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<tr>
<td>12</td>
<td>Al³⁺</td>
<td>DMF/ H₂O</td>
<td>Fluorometric</td>
<td>Al³⁺: 2.75 x 10³</td>
<td>Al³⁺: 4.9 x 10⁻⁷</td>
<td>Paper strips</td>
<td>12</td>
</tr>
<tr>
<td>13</td>
<td>Al³⁺</td>
<td>CH₃OH</td>
<td>Fluorometric</td>
<td>Al³⁺: 1.6 x 10⁴</td>
<td>Al³⁺: 2.7 x 10⁻⁷</td>
<td>Paper strips</td>
<td>13</td>
</tr>
<tr>
<td>14</td>
<td>Al³⁺</td>
<td>DMSO</td>
<td>Fluorometric</td>
<td>Al³⁺: 1.4 x 10⁴</td>
<td>Al³⁺: 2.0 x 10⁻⁷</td>
<td>Paper strips</td>
<td>14</td>
</tr>
<tr>
<td>15</td>
<td>Al³⁺ Zn²⁺</td>
<td>CH₃OH / H₂O Buffer</td>
<td>Fluorometric</td>
<td>Al³⁺: 1.94 x 10⁴ Zn²⁺: 1.19 x 10⁵</td>
<td>Al³⁺: 1.45 x 10⁻⁷ Zn²⁺: 1.29 x 10⁻⁸</td>
<td>-</td>
<td>15</td>
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<tr>
<td>16</td>
<td>Al³⁺ Zn²⁺</td>
<td>Tris-HCl buffer EtOH / H₂O</td>
<td>Fluorometric</td>
<td>Al³⁺: 3.5 x 10⁹ M⁻² Zn²⁺: 4.27 x 10⁴ M⁻¹</td>
<td>Al³⁺: 1.27 x 10⁻⁷ M Zn²⁺: 5.5 x 10⁻⁸ M</td>
<td>Recovery in real samples</td>
<td>16</td>
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<tr>
<td>17</td>
<td>Al³⁺ Zn²⁺</td>
<td>DMF/ H₂O</td>
<td>Fluorometric</td>
<td>Al³⁺: 2.43 x 10⁸ M⁻² Zn²⁺: 2.59 x 10⁷ M⁻²</td>
<td>Al³⁺: 4.2 x 10⁻⁸ M Zn²⁺: 3.4 x 10⁻⁸ M</td>
<td>Paper strips Logic gate This work</td>
<td></td>
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</tbody>
</table>
15. Application study table:

Table S2: Determination of Al\(^{3+}\) recovery sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al(^{3+}) added (µmol L(^{-1}))</th>
<th>Al(^{3+}) found (µmol L(^{-1}))</th>
<th>Recovery (%)</th>
<th>R.S.D (n=3)(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap water</td>
<td>0.00</td>
<td>0.00</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td>10.00</td>
<td>9.60</td>
<td>96.0</td>
<td>1.52</td>
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<tr>
<td>Drinking water</td>
<td>0.00</td>
<td>0.00</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td>10.00</td>
<td>9.80</td>
<td>98.0</td>
<td>0.73</td>
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</tbody>
</table>

Table S3: Determination of Zn\(^{2+}\) recovery sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zn(^{2+}) added (µ mol L(^{-1}))</th>
<th>Zn(^{2+}) found (µ mol L(^{-1}))</th>
<th>Recovery (%)</th>
<th>R.S.D (n=3)(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap water</td>
<td>0.00</td>
<td>0.00</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td>10.00</td>
<td>9.33</td>
<td>93.3</td>
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<tr>
<td>Drinking water</td>
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<td></td>
<td>10.00</td>
<td>9.50</td>
<td>95.0</td>
<td>1.78</td>
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</table>
16. References:


