Supporting Information

Cobalt metal-mixed organic complex-based hybrid micromaterials: ratiometric detection of cyanide

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Table S1 Comparison of a few recent examples for CN− sensors based on organic-metal complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Mechanism</th>
<th>Specificity</th>
<th>Detection mode</th>
<th>Detection limit</th>
<th>pH</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Complex 1" /></td>
<td>Strategy (iii)</td>
<td>CN−</td>
<td>$A_{456nm}/A_{537nm}$</td>
<td>1.8 μM</td>
<td>2.5–9.5</td>
<td>This work</td>
</tr>
<tr>
<td><img src="image2.png" alt="Complex 2" /></td>
<td>Strategy (iii)</td>
<td>CN−</td>
<td>$A_{450nm}/A_{517nm}$</td>
<td>10 μM</td>
<td>–</td>
<td>¹</td>
</tr>
<tr>
<td><img src="image3.png" alt="Complex 3" /></td>
<td>Strategy (iii)</td>
<td>HCO$_3^-$</td>
<td>$F_{610nm}$</td>
<td>–</td>
<td>7.5</td>
<td>²</td>
</tr>
<tr>
<td>Strategy</td>
<td>Ligand</td>
<td>F&lt;sub&gt;λ&lt;/sub&gt;</td>
<td>Concentration</td>
<td>λ&lt;sub&gt;exc&lt;/sub&gt;</td>
<td>λ&lt;sub&gt;em&lt;/sub&gt;</td>
<td>Ratio</td>
</tr>
<tr>
<td>----------</td>
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</tr>
<tr>
<td>(iii)</td>
<td>NO</td>
<td>F&lt;sub&gt;505nm&lt;/sub&gt;</td>
<td>50-100 µM</td>
<td>505nm</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>(ii)</td>
<td>CN&lt;sup&gt;-&lt;/sup&gt;</td>
<td>F&lt;sub&gt;460nm&lt;/sub&gt;</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>--</td>
</tr>
<tr>
<td>(ii)</td>
<td>CN&lt;sup&gt;-&lt;/sup&gt;</td>
<td>A&lt;sub&gt;562nm&lt;/sub&gt;/F&lt;sub&gt;580nm&lt;/sub&gt;</td>
<td>0.14 µM</td>
<td>7.0</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>(ii)</td>
<td>CN&lt;sup&gt;-&lt;/sup&gt;</td>
<td>F&lt;sub&gt;550nm&lt;/sub&gt;</td>
<td>30 nm</td>
<td>–</td>
<td>–</td>
<td>--</td>
</tr>
<tr>
<td>(ii)</td>
<td>CN&lt;sup&gt;-&lt;/sup&gt;</td>
<td>F&lt;sub&gt;600nm&lt;/sub&gt;, A&lt;sub&gt;495/A325&lt;/sub&gt;</td>
<td>–</td>
<td>5–11</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>(i)</td>
<td>CN&lt;sup&gt;-&lt;/sup&gt;</td>
<td>A&lt;sub&gt;400nm&lt;/sub&gt;</td>
<td>4.0 µM</td>
<td>–</td>
<td>–</td>
<td>--</td>
</tr>
<tr>
<td>(i)</td>
<td>CN&lt;sup&gt;-&lt;/sup&gt;</td>
<td>F&lt;sub&gt;748nm&lt;/sub&gt;</td>
<td>5 µM</td>
<td>2.7–10.4</td>
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</tr>
</tbody>
</table>
Strategy (i): CN\(^{-}\) (no study for S\(^{2-}\))

\(\text{A}_{500\text{nm}}, \text{F}_{525\text{nm}}\) 724 nm 5.5–11.5 8

Strategy (i): CN\(^{-}\) (no study for S\(^{2-}\))

\(\text{F}_{590\text{nm}}\) – 7.5 9

Abbreviations used: A–Absorbance; F–Fluorescence

Strategy (i): “displacement” approach;
Strategy (ii): “binding site–signaling subunit” protocol;
Strategy (iii): partial replacement of the bound ligand/antenna, accompanied by the formation of a new organic–metal–anion adduct;

References

Fig. S1 Examples in Table S1 based on strategy (iii).
Fig. S2 FTIR spectra of DHAB, TAC, CoSO\textsubscript{4}·7H\textsubscript{2}O and complex 1.

Fig. S3 QTOF–MS spectrum of 1 in acetonitrile.
Fig. S4 Powder X-ray diffraction patterns of 1.

Fig. S5 Absorption spectra of DHAB (2×10^{-5} M) and TAC (2×10^{-5} M) in the absence and presence of Co^{2+} (1.0×10^{-4} M), and absorption spectra of complex 1 (2×10^{-5} M) in DMF-HEPES buffer solutions (4/1, v/v, pH 7.0).
**Fig. S6** Absorption spectra of 1 (2×10^{-5} M) upon titrating S^{2−} (0–2.0×10^{-3} M) (a) and SO_{3}^{2−} (0–2.0×10^{-3} M) (b) in DMF-HEPES buffer solutions (4/1, v/v, pH 7.0).

**Fig. S7** Changes in the absorption spectra of 1 upon titrating CN^{−} (0–2.0×10^{-3} M) at 765 nm, 456 nm and 537 nm in DMF-HEPES buffer solutions (4/1, v/v, pH 7.0).
Fig. S8 (a) Absorption spectra and (b) visual colors of 1 (2×10⁻⁵ M) with 10 equivalents of CN⁻ and 20 fold concentrations of other anions with respect to CN⁻, in DMF-HEPES buffer solutions (4/1, v/v, pH 7.0). Blank: 1 in the presence of 10 equivalents of CN⁻.

Fig. S9 Absorption spectra of 1 (2×10⁻⁵ M) in the absence (a) and presence of 10 equivalents of CN⁻ (b), and (c) absorption spectra of DHAB-Co(II) (2×10⁻⁵ M/2×10⁻⁵ M) in presence of 10 equivalents of CN⁻, and (d) absorption spectra of TAC (2×10⁻⁵ M), in DMF-HEPES buffer solutions (4/1, v/v, pH 7.0).
Fig. S10 TLC experiments of 1 with CN\textsuperscript{−}. The TLC plate was developed by 4:1 petroleum ether/ethyl acetate. Results indicated that TAC was released from complex 1 upon adding CN\textsuperscript{−}, while the dissociation of DHAB from complex 1 was not observed.

Fig. S11 QTOF–MS spectra of 1 with CN\textsuperscript{−} in acetonitrile.
Fig. S12 QTOF–MS spectra of DHAB in the presence of Co$^{2+}$ and CN$^{-}$ in acetonitrile.

Fig. S13 Schematic illustration of CN$^{-}$ detection using complex 1.