Supplementary Materials

A luminescent sensor based on Zn(II) coordination polymer behave selective and sensitive detection for NACs and Fe$^{3+}$ ions

Xiao Zhang*, Xinrui Zhuang, Nanxi Zhang, Chunyu Ge, Xuan Luo, Jinxue Li, Jie Wu*, Qingfeng Yang, Rui Liu

Caption of Figures

Fig. S1 A view of the asymmetric unit and some symmetry-related atoms in 1.

Fig. S2 Disordered TBA$^{2-}$ anions in 1. (a) component 1, (b) component 2, (c) both components.

Fig. S3 Powder XRD of simulated from the single-crystal data of 1 (black) and synthesized compound 1 (red).

Fig. S4 Thermogravimetric analyses curve of 1, the weight loss of 77.6 % is close to the calculated value (78.3 %).

Fig. S5 Powder XRD of ZnO from the combustion residue and reference card of ZnO.

Fig. S6 The IR spectra of H$_2$TBA ligand and 1.

Fig. S7 Solid - state emission spectra of compound 1 and free H$_2$TBA and 4,4-bipy ligand when excited at 285 nm, 276 nm, 362 nm, respectively.

Fig. S8 Emission spectra of 1 dispersed in different solvents when excited at 290 nm.

Fig. S9 Power XRD patterns of 1 immersed in different solvents at room temperature.

Fig. S10 (a) The luminescence intensity of 1 upon incremental addition of PA solution (5 mM) in water. (b) Stern-Volmer plot for the luminescence intensity of 1 upon the addition of PA solution (5 mM) in water.

Fig. S11 The luminescence intensity of 1 upon incremental addition of NACs solution (5 mM) in water (a: NB, b: 4-Np, c: 2,4-DNT, d: m-NT, e: m-DNB, f: p-NT, g: o-NT).

Fig. S12 The fitting curve of the luminescence intensity of 1 at different PA concentration.

Fig. S13 HOMO and LUMO of ligand and NACs

Fig. S14. Spectral overlap between absorbance spectra of NACs and emission spectra of 1.

Fig. S15 The fitting curve of the luminescence intensity of 1 at different Fe$^{3+}$ concentration

Fig. S16 Powder XRD patterns of simulated from the single-crystal data of 1 and synthesized compound and Fe$^{3+}$-1.

Fig. S17 IR spectra of compound 1 and 1/Fe$^{3+}$. 
Fig. S18 The XPS of Fe$^{3+}$-1 shows the typical peak of Fe$^{3+}$ at 710 Ev.

Fig. S19 Spectral overlap between absorbance spectra of metal icons and emission spectra of 1.

Caption of Tables

Table S1 Selected bond lengths (Å) and angles (°) for 1.

Table S2 Summary of quenching constants (K$^{SV}$) for 1 sensing of NACs at room temperature.

Table S3 HOMO and LUMO energies for calculated NACs and ligand at B3LYP/6-31G* level of theory.

Fig. S1 A view of the asymmetric unit and some symmetry-related atoms in 1. (Symmetry codes: (i) x, -y, z, 2-z; (ii) x, 1+y, z; (iii) -1+x, y, z; (iv) -x, y).

Fig. S2 Disordered TBA$^{2-}$ anions in 1. (a) component 1, (b) component 2, (c) both components.
**Fig. S3** Powder XRD of simulated from the single-crystal data of 1 (black) and synthesized compound 1 (red).

**Fig. S4** Thermogravimetric analyses curve of 1, the weight loss of 77.6 % is close to the calculated value (78.3 %).
**Fig. S5** Powder XRD of ZnO from the combustion residue and reference card of ZnO.

**Fig. S6** The IR spectra of H₂TBA ligand and 1.
Fig. S7 Solid-state emission spectra of compound 1, free H$_2$TBA and 4,4'-bipy ligand when excited at 285 nm, 276 nm, 362 nm, respectively.

![Emission spectra graph]

Fig. S8 Emission spectra of 1 dispersed in different solvents when excited at 290 nm.

![Emission spectra graph]

Fig. S9 Power XRD patterns of 1 immersed in different solvents at room temperature.
**Fig. S10** (a) The luminescence intensity of 1 upon incremental addition of PA solution (5 mM) in water. (b) Stern-Volmer plot for the luminescence intensity of 1 upon the addition of PA solution (5 mM) in water.
Fig. S11 The luminescence intensity of 1 upon incremental addition of NACs solution (5 mM) in water (a: NB, b: 4-Np, c: 2,4-DNT, d: m-NT, e: m-DNB, f: p-NT, g: o-NT)

\[ R^2 = 0.98 \]
\[ \text{Slope} = -4.34 \times 10^6 \text{ M}^{-1} \]

Fig. S12 The fitting curve of the luminescence intensity of 1 at different PA concentration.
Fig. S13 HOMO and LUMO of ligand and NACs.

Fig. S14 Spectral overlap between normalized absorbance spectra of NACs and emission spectra of 1.
R² = 0.9901
Slope = -1.76 × 10⁶ M⁻¹

Linear Equation: Y = -1763.85X + 790.53

R = 0.9901
Slope = 1.76 × 10⁶ M⁻¹
δ = 4.21 (N = 10)

Limit detection = 3δ/Slope = 7.18 × 10⁻⁶ M

**Fig. S15** The fitting curve of the luminescence intensity of 1 at different Fe³⁺ concentration.

**Fig. S16** Powder XRD patterns of simulated from the single-crystal data of 1 and synthesized compound and Fe³⁺-1.
**Fig. S17** IR spectra of compound 1 and 1/Fe$^{3+}$.

**Fig. S18** The XPS of Fe$^{3+}$-1 shows the typical peak of Fe$^{3+}$ at 710 Ev.
Fig. S19 Spectral overlap between absorbance spectra of metal icons and emission spectra of 1.

Table S1 Selected bond lengths (Å) and angles (°) for 1.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Zn1-O1</th>
<th>Zn1-N5</th>
<th>O1-Zn1-N4²</th>
<th>O1¹-Zn1-N5</th>
<th>N1-Zn1-O1</th>
<th>N1-Zn1-N1¹</th>
<th>N1¹-Zn1-N3</th>
<th>N1¹-Zn1-N4²</th>
<th>O3¹-Zn1-O1¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.202(6)</td>
<td>2.522(10)</td>
<td>86.2(2)</td>
<td>29.31(18)</td>
<td>153.6(3)</td>
<td>110.9(4)</td>
<td>91.6(2)</td>
<td>89.56(19)</td>
<td>153.6(3)</td>
</tr>
</tbody>
</table>

Symmetry codes ¹+X,−Y,±Z; ²−1+X,±Y,±Z; ³−X,±Y,2−Z; ⁴+X,1−Y,±Z; ⁵1+X,±Y,±Z; ⁶−X,1−Y,2−Z

Table S2 Summary of quenching constants (K_{SV}) for 1 sensing of NACs at room temperature.

<table>
<thead>
<tr>
<th>Nitro explosives</th>
<th>K_{SV} (M⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA</td>
<td>4.83×10⁴</td>
</tr>
<tr>
<td>NB</td>
<td>4.94×10³</td>
</tr>
<tr>
<td>m-DNB</td>
<td>5.5×10³</td>
</tr>
<tr>
<td>o-NT</td>
<td>7.68×10³</td>
</tr>
<tr>
<td>m-NT</td>
<td>5.00×10³</td>
</tr>
<tr>
<td>p-NT</td>
<td>1.61×10⁴</td>
</tr>
<tr>
<td>2,4-DNT</td>
<td>1.49×10⁴</td>
</tr>
<tr>
<td>4-Np</td>
<td>1.62×10⁴</td>
</tr>
</tbody>
</table>
Table S3 HOMO and LUMO energies for calculated NACs, H₂TBA and 4,4'-bpy at B3LYP/6-31G* level of theory.

<table>
<thead>
<tr>
<th>Analytes</th>
<th>HOMO (ev)</th>
<th>LUMO (ev)</th>
<th>Bond gap</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA</td>
<td>-8.595166</td>
<td>-4.320934</td>
<td>4.27432</td>
</tr>
<tr>
<td>2,4-DNT</td>
<td>-8.41361</td>
<td>-3.409107</td>
<td>5.004502</td>
</tr>
<tr>
<td>p-NT</td>
<td>-7.655022</td>
<td>-2.79225</td>
<td>4.862798</td>
</tr>
<tr>
<td>NB</td>
<td>-7.887787</td>
<td>-2.912631</td>
<td>4.975156</td>
</tr>
<tr>
<td>m-DNB</td>
<td>-8.730522</td>
<td>-3.596104</td>
<td>5.134419</td>
</tr>
<tr>
<td>o-NT</td>
<td>-7.554773</td>
<td>-2.746777</td>
<td>4.807996</td>
</tr>
<tr>
<td>m-NT</td>
<td>-7.55031</td>
<td>-2.838932</td>
<td>4.711378</td>
</tr>
<tr>
<td>4-Np</td>
<td>-7.290064</td>
<td>-2.73967</td>
<td>4.550394</td>
</tr>
<tr>
<td>4,4'-bpy</td>
<td>-7.402589</td>
<td>-2.01690</td>
<td>5.273164</td>
</tr>
<tr>
<td>H₂TBA</td>
<td>-2.7089546</td>
<td>-0.7577181</td>
<td>1.9512364</td>
</tr>
</tbody>
</table>