A highly luminescent terbium-organic framework for reversible detection of mercury ions in aqueous solution

Hong-Ming Wang$^{a,b}$ Yang-Yi Yang,*$^{a}$ Cheng-Hui Zeng,$^{a}$ Tian-Shu Chu,$^{a}$ Yi-Min Zhu$^{a}$ and Seik Weng Ng$^{c}$

$^{a}$MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, KLGHEI of Environment and Energy Chemistry, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou, 510275, P. R. China. E-mail: cesyyv@mail.sysu.edu.cn

$^{b}$Department of Chemistry, Guangdong University of Education, Guangzhou, P. R. China.

$^{c}$Department of Chemistry, University of Malaya, Kuala Lumpur, Malaysia and Department of Chemistry, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia
Luminescent Sensing Measurements

A well-ground powder of $[\text{TbL}_{1.5}(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (2 mg) was immersed in an aqueous solution (4 mL) containing different nitrate salts of metal cations and the mixture was well stirred for one hour at room temperature. The steady state luminescent emission of each sample was measured after two days of aging and stirred vigorously before testing.

Table S1 Crystal data and structure refinement parameters for complex 1

<table>
<thead>
<tr>
<th>Complex</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
<td>$\text{C}<em>{19.50}\text{H}</em>{16.50}\text{N}<em>{1.50}\text{O}</em>{9}\text{Tb}$</td>
</tr>
<tr>
<td><strong>Formula weight</strong></td>
<td>574.76</td>
</tr>
<tr>
<td><strong>Crystal system</strong></td>
<td>Triclinic</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>$P\bar{1}$</td>
</tr>
<tr>
<td><strong>$a$ / Å</strong></td>
<td>9.9199(4)</td>
</tr>
<tr>
<td><strong>$b$ / Å</strong></td>
<td>10.4905(4)</td>
</tr>
<tr>
<td><strong>$c$ / Å</strong></td>
<td>13.4316(8)</td>
</tr>
<tr>
<td><strong>$\alpha$ (°)</strong></td>
<td>105.687(4)</td>
</tr>
<tr>
<td><strong>$\beta$ (°)</strong></td>
<td>101.880(5)</td>
</tr>
<tr>
<td><strong>$\gamma$ (°)</strong></td>
<td>94.436(3)</td>
</tr>
<tr>
<td><strong>$V$/Å$^3$</strong></td>
<td>1303.68(11)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>2</td>
</tr>
<tr>
<td><strong>Calculated density / mg·m$^{-3}$</strong></td>
<td>1.464</td>
</tr>
<tr>
<td><strong>Absorption coefficient/ mm$^{-1}$</strong></td>
<td>2.755</td>
</tr>
<tr>
<td><strong>Crystal size / mm</strong></td>
<td>0.35 x 0.15 x 0.05</td>
</tr>
<tr>
<td><strong>Reflections collected / unique</strong></td>
<td>14207 / 9460</td>
</tr>
<tr>
<td><strong>GOF</strong></td>
<td>1.065</td>
</tr>
<tr>
<td>$R_1$ a/ $wR_2$ b/[ $I &gt; 2\sigma(I)$]</td>
<td>0.0521/0.1490</td>
</tr>
<tr>
<td>$R_1$, $wR_2$ (all data)</td>
<td>0.0738/0.1734</td>
</tr>
</tbody>
</table>

\[ aR_1 = \Sigma||F_o|| - |F_c||/|F_o|, \]
\[ bR_2 = [\Sigma w (F_o - F_c)^2]/ \Sigma w(F_o)^2]^{1/2}. \]
Table S2 Selected bond lengths (Å) and angles (°) for 1

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th>Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb(1)-O(2)#1</td>
<td>2.300(5)</td>
</tr>
<tr>
<td>Tb(1)-O(3)#2</td>
<td>2.309(5)</td>
</tr>
<tr>
<td>Tb(1)-O(1)</td>
<td>2.328(4)</td>
</tr>
<tr>
<td>Tb(1)-O(4)#3</td>
<td>2.333(4)</td>
</tr>
<tr>
<td>Tb(1)-O(2W)</td>
<td>2.435(5)</td>
</tr>
<tr>
<td>Tb(1)-O(1W)</td>
<td>2.436(5)</td>
</tr>
<tr>
<td>O(2)#1-Tb(1)-O(3)#2</td>
<td>146.90(18)</td>
</tr>
<tr>
<td>O(2)#1-Tb(1)-O(1)</td>
<td>100.87(17)</td>
</tr>
<tr>
<td>O(3)#2-Tb(1)-O(1)</td>
<td>86.91(17)</td>
</tr>
<tr>
<td>O(2)#1-Tb(1)-O(4)#3</td>
<td>85.09(19)</td>
</tr>
<tr>
<td>O(3)#2-Tb(1)-O(4)#3</td>
<td>102.07(18)</td>
</tr>
<tr>
<td>O(1)-Tb(1)-O(2W)</td>
<td>142.07(19)</td>
</tr>
<tr>
<td>O(3)#2-Tb(1)-O(2W)</td>
<td>70.47(18)</td>
</tr>
<tr>
<td>O(1)-Tb(1)-O(2W)</td>
<td>82.86(17)</td>
</tr>
<tr>
<td>O(4)#3-Tb(1)-O(2W)</td>
<td>77.22(18)</td>
</tr>
<tr>
<td>O(2)#1-Tb(1)-O(2W)</td>
<td>142.07(19)</td>
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<tr>
<td>O(4)#3-Tb(1)-O(2W)</td>
<td>77.22(18)</td>
</tr>
<tr>
<td>O(2)#1-Tb(1)-O(1W)</td>
<td>71.58(18)</td>
</tr>
<tr>
<td>O(3)#2-Tb(1)-O(1W)</td>
<td>141.00(18)</td>
</tr>
<tr>
<td>O(1)-Tb(1)-O(1W)</td>
<td>75.28(18)</td>
</tr>
<tr>
<td>O(4)#3-Tb(1)-O(1W)</td>
<td>82.62(18)</td>
</tr>
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<td>O(4)#3-Tb(1)-O(1W)</td>
<td>82.62(18)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Symmetry codes for 1: #1 -x+1,-y+1,-z+1; #2 -x+1,-y+2,-z+1; #3 x+1,y-1,z; #4 x-1,y+1,z; #5 x+2,-y+1,-z+2.

![Fig. S1. FT-IR spectra.](Image)
Fig. S2 The distorted square antiprism coordination polyhedron of the Tb$^{3+}$ in 1.

Fig. S3 Coordination modes of ligand in 1.
Fig. S4 Space-filled model of 1 showing the 1D channels viewed along the $a$-axis; the guest water are omitted for clarity.

Fig. S5 The (4, 4)-connected topological network. Hydrogen atoms and lattice solvent molecules have been omitted for clarity.
**Fig. S6** TGA curves of 1 in nitrogen (black) and air (red) atmosphere.

**Fig. S7** The π-π stacking of adjacent aromatic rings
**Fig. S8** Emission spectra of 1 in different metal ionic aqueous solutions at various concentrations (excited at 314 nm).

**Fig. S9** Luminescence decay profiles of 1 (black) and Hg$^{2+}$-incorporated 1 (red).
**Fig. S10** The emission intensities of 1 at 545 nm in different $10^{-3}$ mol L$^{-1}$ metal ions (red) or mixture of $10^{-3}$ mol L$^{-1}$ metal ions and $10^{-4}$ mol L$^{-1}$ Hg$^{2+}$ ions (blue) aqueous solutions (excited at 314 nm).

**Table S3** Quenching effect coefficients (Ksv) of different metal ions on the luminescence intensity of 1.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Ba$^{2+}$</th>
<th>Mg$^{2+}$</th>
<th>Ca$^{2+}$</th>
<th>Co$^{2+}$</th>
<th>Cd$^{2+}$</th>
<th>Ni$^{2+}$</th>
<th>Zn$^{2+}$</th>
<th>Pb$^{2+}$</th>
<th>Cu$^{2+}$</th>
<th>Hg$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ksv [M$^{-1}$]</td>
<td>61</td>
<td>62</td>
<td>69</td>
<td>116</td>
<td>118</td>
<td>135</td>
<td>211</td>
<td>525</td>
<td>880</td>
<td>7465</td>
</tr>
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</table>