Electronic Supplementary Information (ESI)

for

The tongs role of L-histidine: a strategy of grasping Tb$^{3+}$ by ZIF-8 to design sensors for monitoring anthrax biomarker on-the-spot

Lan Guo, Maosheng Liang, Xiuli Wang, Rongmei Kong, Guang Chen, Lian Xia$^*$, Fengli Qu$^*$

Key Laboratory of Life-Organic Analysis of Shandong Province, Qufu Normal University, Qufu 273165, China

*E-mail: fengliquhn@hotmail.com (F.L. Qu)

*E-mail: xialian01@163.com (L. Xia)

Table of Contents

1. Experimental Section

2. Supporting Figures and Tables

Fig. S1 TGA curve of the synthesized His@ZIF-8 (A) and His@ZIF-8/Tb$^{3+}$ (B).

Fig. S2 FT-IR spectra of ZIF-8, His@ZIF-8 and His@ZIF-8/Tb$^{3+}$.

Fig. S3 Zeta potential of His@ZIF-8, His@ZIF-8/Tb$^{3+}$ and His@ZIF-8/Tb$^{3+}$ upon adding DPA.

Fig. S4 SEM images of His@ZIF-8 (A) and His@ZIF-8/Tb$^{3+}$ (B).

Fig. S5 The EDX of His@ZIF-8 (A) and His@ZIF-8/Tb$^{3+}$ (B).

Fig. S6 (A) Effects of pH values on fluorescence intensity of His@ZIF-8/Tb$^{3+}$ with DPA (red line) and without DPA (black line). (B) Effects of reaction time on fluorescence intensity of His@ZIF-
8/Tb$^{3+}$ with DPA.

**Fig. S7** (A) The fluorescence emission spectra of ZIF-8/Tb$^{3+}$ and ZIF-8/Tb$^{3+}$ with DPA. (B) The fluorescence emission spectra of His@ZIF-8/Tb$^{3+}$ and His@ZIF-8/Tb$^{3+}$ with DPA. (C) The comparison of fluorescence response ability of ZIF-8/Tb$^{3+}$ and His@ZIF-8/Tb$^{3+}$, respectively.

**Fig. S8** SEM images of His@ZIF-8/Tb$^{3+}$ before (A) and after (B) reacting with DPA. (C) XRD patterns of His@ZIF-8/Tb$^{3+}$ before and after reacting with DPA.

**Table S1** The comparison of different fluorescent probe for DPA detection.

**Table S2** Analytical results of real samples.

3. **Supporting References**
1. Experimental Section

Preparation of ZIF-8 nanocrystals. ZIF-8 nanocrystals were synthesized according to reporting literature. Briefly, a solution of Zn(NO$_3$)$_2$·6H$_2$O (1.173 g) in 80 mL methanol was added into a solution of 2-methylimidazole (2.595 g) in 80 mL methanol under stirring with a magnetic bar. After keeping at room temperature for 1 h, ZIF-8 was formed, and then separated by centrifugation at 7000 rpm for 5 min and washed with methanol three times. The collected white powder was dried in the oven at 60 °C overnight.

Preparation of ZIF-8/Tb$^{3+}$. The synthesis of ZIF-8/Tb$^{3+}$ was performed by dispersing 30.0 mg His@ZIF-8 to 60.0 mL Tb(NO$_3$)$_3$ ethanol solution (10 mmol L$^{-1}$). Then the above solution was stirred for 2 h at room temperature. The product was collected by centrifugation at 7000 rpm for 5 min and repeatedly washed with ethanol for 3 times. The collected white powder was dried in the oven at 60 °C overnight.
2. Supporting Figures and Tables

**Fig. S1** TGA curve of the synthesized His@ZIF-8 (A) and His@ZIF-8/Tb$^{3+}$ (B).

**Fig. S2** FT-IR spectra of ZIF-8, His@ZIF-8 and His@ZIF-8/Tb$^{3+}$.
**Fig. S3** Zeta potential of His@ZIF-8, His@ZIF-8/Tb$^{3+}$ and His@ZIF-8/Tb$^{3+}$ upon adding 1 μmol L$^{-1}$ DPA.

**Fig. S4** SEM images of His@ZIF-8 (A) and His@ZIF-8/Tb$^{3+}$ (B).
Fig. S5 The EDX of His@ZIF-8 (A) and His@ZIF-8/Tb^{3+} (B).
Fig. S6 (A) Effects of pH values on fluorescence intensity of His@ZIF-8/Tb³⁺ with DPA (red line) and without DPA (black line). (B) Effects of reaction time on fluorescence intensity of His@ZIF-8/Tb³⁺ with DPA (1 μmol L⁻¹); HEPES buffer: 20 mmol L⁻¹, pH 7.4.

Fig. S7 (A) The fluorescence emission spectra of ZIF-8/Tb³⁺ and ZIF-8/Tb³⁺ with 1 μmol L⁻¹ DPA. (B) The fluorescence emission spectra of His@ZIF-8/Tb³⁺ and His@ZIF-8/Tb³⁺ with 1 μmol L⁻¹ DPA. (C) The comparison of fluorescence response ability of ZIF-8/Tb³⁺ and His@ZIF-8/Tb³⁺, respectively. (F₀ is the fluorescence of ZIF-8/Tb³⁺ and His@ZIF-8/Tb³⁺; F is the fluorescence of ZIF-8/Tb³⁺ and His@ZIF-8/Tb³⁺ with 1 μmol L⁻¹ DPA.)
Fig. S8 SEM images of His@ZIF-8/Tb$^{3+}$ before (A) and after (B) reacting with DPA aqueous solution (1 mmol L$^{-1}$) for 3 min. (C) XRD patterns of His@ZIF-8/Tb$^{3+}$ before and after reacting with DPA aqueous solution (1 mmol L$^{-1}$) for 3 min.

Table S1 The comparison of different fluorescent probe for DPA detection.

<table>
<thead>
<tr>
<th>Probes</th>
<th>Linear range</th>
<th>Detection limit</th>
<th>Response time</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TbP-CPs</td>
<td>0-8 μM</td>
<td>0.005 μM</td>
<td>30 s</td>
<td>2S</td>
</tr>
<tr>
<td>RiP/Eu$^{3+}$ CPs</td>
<td>0-1 μM</td>
<td>0.0415 μM</td>
<td>/</td>
<td>3S</td>
</tr>
<tr>
<td>Tb/Eu@bio-MOF</td>
<td>0.05-1 μM</td>
<td>0.034 μM</td>
<td>20 s</td>
<td>4S</td>
</tr>
<tr>
<td>CDs-Cu$^{2+}$ systems</td>
<td>0.25-20 μM</td>
<td>0.079 μM</td>
<td>1 min</td>
<td>5S</td>
</tr>
<tr>
<td>EBT-Eu$^{3+}$</td>
<td>0-32 μM</td>
<td>2 μM</td>
<td>/</td>
<td>6S</td>
</tr>
<tr>
<td>Terbium functionalized micelle</td>
<td>0-7 μM</td>
<td>0.054 μM</td>
<td>/</td>
<td>7S</td>
</tr>
<tr>
<td>His@ZIF-8/Tb$^{3+}$</td>
<td>0-10 μM</td>
<td>0.02 μM</td>
<td>10 s</td>
<td>This work</td>
</tr>
</tbody>
</table>

/: Not mentioned.
Table S2 Analytical results of real samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Added (µM)</th>
<th>Found (µM)</th>
<th>Recovery (%)</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Human Urine</td>
<td>0</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>0.51</td>
<td>102.0</td>
<td>2.76</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>0.99</td>
<td>99.0</td>
<td>1.28</td>
</tr>
<tr>
<td></td>
<td>5.00</td>
<td>5.16</td>
<td>103.2</td>
<td>0.92</td>
</tr>
<tr>
<td>10% Bovine Serum</td>
<td>0</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>0.49</td>
<td>98.0</td>
<td>3.12</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>1.03</td>
<td>103.0</td>
<td>1.36</td>
</tr>
<tr>
<td></td>
<td>5.00</td>
<td>5.09</td>
<td>101.8</td>
<td>2.21</td>
</tr>
</tbody>
</table>

/: Not detected.
3. Supporting References


