Supporting information

Fabrication and application of ratiometric and colorimetric fluorescent probe for Hg$^{2+}$ based on dual-emissive metal-organic framework hybrids with carbon dots and Eu$^{3+}$

Xiao-Yu Xu and Bing Yan*

Shanghai Key Lab of Chemical Assessment and Sustainability, Department of Chemistry, Tongji University, Siping Road 1239, Shanghai 200092, China.

*E-mail: byan@tongji.edu.cn.
**Fig. S1** A synthetic route using citric acid and ethylenediamine to from carbogenic CDs in aqueous solution.

**Fig. S2** FTIR spectra of (a) CDs and (b) MOF-253, CDs@MOF-253 and Eu³⁺/ CDs@MOF-253. In the FTIR analysis of CDs, broad absorption bands at 3000-3500 cm⁻¹ are assigned to ν(O-H) and ν(N-H). The hydrophilicity and stability of CDs in aqueous system can be improved by this functional groups. The following were observed simultaneously: ν(C=O) at 1126 cm⁻¹, δ(N-H) at 1570 cm⁻¹, and the ν(C=N) at 1635 cm⁻¹.⁵¹
Fig. S3 N\textsubscript{2} adsorption and desorption isotherms of MOF-253, CDs@MOF-253 (the CDs content is 100 mg for (1) and 200 mg for (2)) and Eu\textsuperscript{3+}/CDs@MOF-253. The BET surface areas of MOF-253, CDs@MOF-253 (1), CDs@MOF-253 (2) and Eu\textsuperscript{3+}/CDs@MOF-253 were calculated to be 723, 386, 215 and 207 m\textsuperscript{2}/g. And the N\textsubscript{2} sorption isotherms and BET surface area are considerably different from the previous work.\textsuperscript{32} We speculate the following points which are different from others could be responsible for this: 1) Sodium acetate has been added for size adjustment in our work; 2) Our reaction vessel (15 mL) is a bit smaller than the reported one; 3) The much higher dried temperature under dynamic vacuum on a Schlenk line cannot be achieved in our work.

Fig. S4 EDS pattern and SEM mapping of as-prepared Eu\textsuperscript{3+}/CDs@MOF-253 samples.
**Fig. S5** (a) Room temperature excitation (blue line) and emission spectra (red line) of CDs aqueous solution; (b) the corresponding photographs of CDs solution (top) and dried CDs (bottom) under day light and UV light irradiation at 365 nm.

**Fig. S6** Room temperature excitation (black line) and emission spectra (red line) of MOF-253 in aqueous environment. The inset is its corresponding CIE chromaticity diagram.
Fig. S7 Stability of PL intensity of Eu³⁺/CDs@MOF-253 (a) after immersing in different pH aqueous solutions for 1 h and (b) after treated in aqueous solution for 9 days; (c) PXRD patterns of Eu³⁺/CDs@MOF-253 after exposure to different pH and different storage time in H₂O.

Fig. S8 PL response of Eu³⁺/CDs@MOF-253 at I_{Eu}/I_{CD} with immersion time in the aqueous solution of Hg²⁺ (100 μM), λ_ex = 360 nm.
**Fig. S9** UV-vis absorption spectra of fine suspensions of powdered CDs, MOF-253, Eu$^{3+}$/CDs@MOF-253 and Hg$^{2+}$ treated Eu$^{3+}$/CDs@MOF-253 in aqueous solution.

**Fig. S10** PL emission spectra of Eu$^{3+}$/CDs@MOF-253 in the presence of different concentration (0-200 μM) of Hg$^{2+}$ in aqueous solution, $\lambda_{ex}$ = 360 nm.
**Fig. S11** Selectivity of the Eu$^{3+}$/CDs@MOF-253 (3 mg) based sensor for Hg$^{2+}$ over other metal ions (100 μM) in aqueous solution.

**Fig. S12** PL emission spectra of Eu$^{3+}$/CDs@MOF-253 in aqueous solution (black line) and in supernatant fluid of Hg$^{2+}$ removal (red line), $\lambda_{ex} = 360$ nm.
Table S1  Hg\textsuperscript{2+} removal ability by Eu\textsuperscript{3+}/Cd\textsubscript{S}@MOF-253 in its aqueous solution.

<table>
<thead>
<tr>
<th>C\textsubscript{Hg2+} (μM)</th>
<th>M\textsubscript{Eu/CdS@MOFs} (mg)\textsuperscript{a}</th>
<th>I\textsubscript{Eu}/I\textsubscript{CD}</th>
<th>C\textsubscript{Hg2+} (μM)</th>
<th>M\textsubscript{Eu/CdS@MOFs} (mg)\textsuperscript{a}</th>
<th>I\textsubscript{Eu}/I\textsubscript{CD}</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.3±4.0%</td>
<td>1.48</td>
<td>30</td>
<td>2.0±9.5%</td>
<td>1.43</td>
</tr>
<tr>
<td>10</td>
<td>0.6±8.2%</td>
<td>1.45</td>
<td>50</td>
<td>3.5±13.4%</td>
<td>1.44</td>
</tr>
<tr>
<td>20</td>
<td>1.0±11.2%</td>
<td>1.52</td>
<td>60</td>
<td>4.0±17.3%</td>
<td>1.41</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The result was expressed as mean of five measurements ± standard deviation (SD).

References
