Supporting Information

A Novel Highly Luminescent LnMOF Film: the Convenient Sensor for Hg$^{2+}$ Detecting

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S1. Deposition of 1 coating on ITO

$\text{Na}_2\text{bqdc}$ (0.023 g, 0.06 mmol) was dispersed in 6 mL DMF, 3 drops of 0.5 M HCl was added, resulting in a clear solution. To the solution EuCl$_3$·6H$_2$O (0.015 g, 0.04 mmol) in 6 mL DMF, the Na$_2$bqdc solution was added. After that, an ITO slide was placed vertically into the solution. The solution and the ITO slide were sealed in a 50 mL Teflon-lined stainless-steel autoclave and heated at 80 °C for 3 days. After cooling, a white coating of 1 grown on the ITO. The resulting film was rinsed with DMF and then immersed in a mixed solvent of 1 : 1 (v : v) DMF : H$_2$O before use.

S2. Experimental details for measurement of luminescence of 1 in the presence of various metal ions:

Preparation of 1-ion emulsions and measurement of their luminescence at room temperature: (i) The powder of 1 (0.2 mg) was introduced into 1.5 mL DMF; (ii) the resultant emulsion was treated by ultrasonic for 30 min to make the particles of 1 dispersing in DMF finely; (iii) 1.5 mL DMF containing $\text{M(NO}_3\text{)}_x$ (M = Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, Hg$^{2+}$) at $1 \times 10^{-3}$ M were added to the emulsion of 1 under continuous stirring; (iv) the mixtures were stirred for 3 days and then the emission spectra were measured.

Preparation of 1-ion films and measurement of their luminescence at room temperature: (i) A film of 1 was fixed in a cuvette vertically; (ii) 3 mL mixed solution of 1 : 1 (V : V) DMF : H$_2$O containing $\text{M(NO}_3\text{)}_x$ (M = Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, Hg$^{2+}$) at $1 \times 10^{-3}$ M was added to the cuvette; (iii) the emission of the 1-ion film was measured at once; (iv) the film was kept in the solution for 3 days and then the luminescence was measured again.
Measurement of time-dependent emission intensity of the 1 film immersed in Hg$^{2+}$ solution at room temperature: (i) A DMF-H$_2$O solution (3mL) containing Hg$^{2+}$ at different concentrations (0, 1×10$^{-5}$, 1×10$^{-4}$ and 1×10$^{-3}$ M, respectively) was added to a cuvette where a 1 film was fixed vertically, as mentioned above; (ii) the emission of 1 in film form was measured instantly; (iii) the emission was measured at different time points until its intensity reached to a stable state.

Measurement of time-dependent emission intensity of the 1 film immersed in Hg$^{2+}$ solution at 333 K: (i) A DMF-H$_2$O solution containing Hg$^{2+}$ at different concentrations (0, 1×10$^{-5}$, 1×10$^{-4}$ and 1×10$^{-3}$ M, respectively) was added to a screw-topped cuvette where a 1 film was fixed vertically, as mentioned above; (ii) the emission of 1 in film form was measured instantly at room temperature (298 K); (iii) the cuvette was sealed with a screw cap and placed in a water bath with temperature at 333 K for 1 h; (iv) the cuvette was taken out and then put in a mixture of ice and water to cool down quickly; (v) when temperature of the cell returned to 298 K, the luminescence was measured a second time; (vi) the cuvette was put back in the water bath for another 1 h; (vii) the operation of steps (iv) to (vi) were repeated (The emission of 1 in film form was measured every one hour in the first 4 h of the exposure to Hg$^{2+}$ and then the emission was measured every four hours after that time) until a constant value of luminescence intensity was reached.

S3. Measurement of number of binding sites within framework of 1 film:

A slice of 1 film was immersed in 5 mL DMF and then 5 drops of HCl (0.5 M) was added. Complex 1 solved completely and then absorption spectrum of the resulting solution was measured. The value of absorbance at 340 nm (the maximum of the absorption band) was compared with a standard curve derived from data of absorbance of H$_2$bdqc in DMF at 340 nm at a series of concentration. The quantity of bdqc in 1 film was calculated from the standard curve. The number of binding sites was calculated from the quantity of bdqc for each bdqc molecule contains two binding sites.

S4. Additional figures

Fig. S1 Packing diagram of 1 viewed along the c axis showing channels. H atoms as well as lattice H$_2$O and DMF molecules are omitted for clarity. Color scheme: Eu atoms, pink; C atoms, grey; O atoms, red; N atoms, blue.
**Fig. S2** Emission spectra of 1 emulsion after introducing various metal ions at 1×10⁻³ M at 298 K (excited at 368 nm). The data were normalized to the intensity of the blank sample.

**Fig. S3** Emission spectra of H₂bqdc and its complexes with Cd²⁺, Zn²⁺ and Hg²⁺ in DMF at concentration of 0.005 M (excited at 388 nm).
Fig. S4  Powder XRD patterns of as-synthesized Eu(OH)₃ coating and reference XRD pattern of Eu(OH)₃ (PDF: 17-0781). * indicates ITO reflection.

Fig. S5  PXRD patterns: a) calculated from single crystal data I; b) I film after being immersed in water solutions at pH = 3 for 24 h; c) I film after being immersed in water solutions at pH = 9 for 24 h.

Fig. S6  Photographs of Gd-bqdc thin film (a), Tb-bqdc thin film (b), Eu-terephthalate thin film (c).
Fig. S7 Ratio of intensity of the $^{5}D_{0} \rightarrow ^{7}F_{2}$ transition (at 621 nm) of the 1 film immersed in solutions containing various metal ions at $1 \times 10^{-3}$ M for 3 days at 298 K ($I$) to that of the film just immersed in the solution containing the same metal ion ($I_0$) (excited at 373 nm).

Fig. S8 Photographs of 1 thin film. The film illuminated by lab UV lamp: a) before and b) after immersion in Hg$^{2+}$ at $1 \times 10^{-3}$ M.
Fig. S9  Emission spectra of 1 film after being immersed in Hg$^{2+}$ at concentration of 0~1x10$^{-5}$ M at 298 K (excited at 373 nm).

S5. Additional Table

Table S1  The selected bond lengths and angles of 1.

| Bond Length/Angles | Eu(1)-O(1W) | Eu(1)-O(1#1) | Eu(1)-O(1) | Eu(1)-O(3) | Eu(1)-O(5) | O(1W)-Eu(1)-O(2)#1 | O(1W)-Eu(1)-O(1) | O(2)#1-Eu(1)-O(1) | O(1W)-Eu(1)-O(3) | O(2)#1-Eu(1)-O(3) | O(1W)-Eu(1)-O(5) | O(2)#1-Eu(1)-O(5) | O(1W)-Eu(1)-O(7) | O(2)#1-Eu(1)-O(7) | O(1W)-Eu(1)-O(8) | O(2)#1-Eu(1)-O(8) | O(1W)-Eu(1)-O(3) | O(2)#1-Eu(1)-O(3) |
|--------------------|-------------|-------------|-------------|-------------|-------------|-------------------|-------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
|                    | 2.335(17)   | 2.373(4)    | 2.375(4)    | 2.377(4)    | 2.454(4)    | 79.4(4)           | 138.9(4)          | 133.16(15)       | 147.8(4)         | 73.38(15)        | 73.23(15)        | 105.0(6)          | 126.06(15)       | 77.20(14)        | 78.56(14)        | 68.4(4)          | 146.7(2)         |
|                    |             |             |             |             |             | O(2)#1-Eu(1)-O(6) | O(1)-Eu(1)-O(6)   | O(3)-Eu(1)-O(6)  | O(5)-Eu(1)-O(6)  | O(7)-Eu(1)-O(6)  | O(8)-Eu(1)-O(6)  | O(5)-Eu(1)-O(4)#1 | O(2)#1-Eu(1)-O(4)#1 | O(1)-Eu(1)-O(4)#1 | O(3)-Eu(1)-O(4)#1 | O(5)-Eu(1)-O(4)#1 | O(2)#1-Eu(1)-O(4)#1 | O(1)-Eu(1)-O(4)#1 |
|                    |             |             |             |             |             | 2.458(5)         | 2.489(17)         | 81.71(15)        | 52.51(14)        | 101.13(19)       | 75.7(4)          | 76.2(5)           | 90.08(17)         | 79.25(16)        | 75.9(4)          | 143.74(16)       | 74.70(17)        | 75.8(4)          |
|                    |             |             |             |             |             |                  |                   |                  |                  |                  |                  |                   |                   |                  |                  |                  |                  |                  |
|                    |             |             |             |             |             |                  |                   |                  |                  |                  |                  |                   |                   |                  |                  |                  |                  |                  |
|                    |             |             |             |             |             |                  |                   |                  |                  |                  |                  |                   |                   |                  |                  |                  |                  |                  |
|                    |             |             |             |             |             |                  |                   |                  |                  |                  |                  |                   |                   |                  |                  |                  |                  |                  |
S6. Modeling of the diffusion kinetics and calculation of the diffusion coefficient and activation energy of Hg\(^{2+}\) from solution to the \(1\) film

The diffusion of Hg\(^{2+}\) from solution toward the thin film of \(1\) is a case of diffusion in a plane sheet, for the thickness of the film is very thin (10 \(\mu\)m) so that the amount diffusing through the edges is negligible. If \(M_t\) is the amount of Hg\(^{2+}\) diffused into the film at time \(t\) and \(M_\infty\) is the corresponding amount after infinite time, \(l\) is the thickness of the film, and diffusion coefficient \(D\) is constant, then the Fick’s equation of diffusion is:

\[
\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp \left( -\frac{D \pi^2 (2n+1)^2}{4l^2} t \right)
\]

Eq. (1) can be written as follow for short times: \(^{[1]}\)

\[
\frac{M_t}{M_\infty} = 2 \left( \frac{Dt}{l^2} \right)^{1/2}
\]

(2)

We hypothesize the amount of Hg\(^{2+}\) diffusing into the film is proportional to the decrease in luminescence intensity of \(1\) in film form, then

\[
\frac{I_0 - I_t}{I_0 - I_\infty} = \frac{M_t}{M_\infty}
\]

(3)

where \(I_0\), \(I_t\), and \(I_\infty\) are respectively the luminescence intensities of \(1\) in film form at time 0 (namely at the time when the film was just immersed in the solution containing Hg\(^{2+}\)), at time \(t\), and at the end of diffusion process. The diffusion coefficient can be calculated from the following equation:

\[
\frac{I_0 - I_t}{I_0 - I_\infty} = 2 \left( \frac{Dt}{l^2} \right)^{1/2} = \frac{2D^{1/2}}{\pi^{1/2} l} l^{1/2}
\]

(4)

Figure S10 shows the dependence of the ratio \(\frac{I_0 - I_t}{I_0 - I_\infty}\) versus square root of time (\(t^{1/2}\)) at the beginning of the diffusion of Hg\(^{2+}\) at 1\(\times\)10\(^{-4}\) M from the solution into the \(1\) film at 298 and 333 K, respectively. The experimental data of the two diffusion processes were fitted linearly and the diffusion coefficient can be calculated from the slopes, which are equal to the values of the term \(\frac{2D^{1/2}}{\pi^{1/2} l}\) in Eq. (4). The values of diffusion coefficient for Hg\(^{2+}\) at 298 and 333 K are 1.70\(\times\)10\(^{-15}\) and 4.01\(\times\)10\(^{-15}\) m\(^2\) s\(^{-1}\), respectively.
Fig. S10  Plot of $\frac{I_0 - I_t}{I_0 - I_\infty}$ versus $t^{1/2}$ at the beginning of the diffusion processes of Hg$^{2+}$ at $1\times10^{-4}$ M leaving the solution coming into the I film at 298 and 333 K, respectively.

Besides the method above, a simplification of Eq. (1) in combination with a fit of all the experimental data of the diffusion processes can deduce the diffusion coefficient. The approach is presented in detail as follows.

Eq. (1) can be written as:

$$\frac{M_t}{M_\infty} = 1 - \left( \frac{8}{\pi^2} \exp\left( \frac{-D\pi^2 t}{4l^2} \right) + \frac{8}{9\pi^2} \exp\left( \frac{-9D\pi^2 t}{4l^2} \right) + \frac{8}{25\pi^2} \exp\left( \frac{-25D\pi^2 t}{4l^2} \right) + \cdots \right)$$  \hspace{1cm} (5)

In Eq. (5), the value of the term $\exp\left( \frac{-D\pi^2 t}{4l^2} \right)$ is higher than that of the term $\exp\left( \frac{-9D\pi^2 t}{4l^2} \right)$.

Accordingly, the value of the term $\frac{8}{9\pi^2} \exp\left( \frac{-9D\pi^2 t}{4l^2} \right)$ is more than eight times lower than that of the term $\frac{8}{\pi^2} \exp\left( \frac{-D\pi^2 t}{4l^2} \right)$, and the values of other terms in the polynomial expression are even lower. The contribution mainly comes from the term $\frac{8}{\pi^2} \exp\left( \frac{-D\pi^2 t}{4l^2} \right)$ while the others are negligible. Therefore, Eq. (5) can be simplified as follow:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \exp\left( \frac{-D\pi^2 t}{4l^2} \right)$$  \hspace{1cm} (6)

If the ratio $M_t/M_\infty$ was displaced by evolution of luminescence intensity, then

$$\frac{I_0 - I_t}{I_0 - I_\infty} = 1 - \frac{8}{\pi^2} \exp\left( \frac{-D\pi^2 t}{4l^2} \right)$$  \hspace{1cm} (7)
An exponential fit of all the experimental data of the diffusion kinetics of Hg$^{2+}$ at 1×10$^{-4}$ M from the solution penetrating inside the 1 film at 298 and 333 K respectively give a model representing the evolution of emission intensity $\frac{I_0 - I_t}{I_0 - I_\infty}$ as a function of time. The diffusion coefficient can be calculated from values of the fitted model parameter. The fit was performed in Origin program with a formula $y = y_0 + A \cdot \exp(-x/B)$ (Figure S11). The results show that the model fits the experimental data well and the values of the parameters $y_0$ and $A$ are almost equivalent to those of the corresponding coefficients in Eq. (7), namely 1 and $8/\pi^2$, respectively (Table S2). This demonstrates that the technique described here is feasible. The diffusion kinetics of Hg$^{2+}$ can be expressed by a simple model:

$$\frac{I_0 - I_t}{I_0 - I_\infty} = 1 - \exp\left(\frac{-D\pi^2 t}{4l^2}\right)$$

(8)

1 was assigned as the value of the coefficient in front of the term $\exp\left(\frac{-D\pi^2 t}{4l^2}\right)$ in Eq. (8) instead of $8/\pi^2$, which allows for the contribution of other terms in the polynomial expression in Eq. (5). The diffusion coefficient can be calculated from the values of the parameter B which represent the term $\frac{4l^2}{D\pi^2}$ (Table S2). The values of $D$ calculated from this approach are similar to those from the known one.

![Graph of diffusion kinetics](image)

**Fig. S11** Diffusion kinetics of Hg$^{2+}$ at 1×10$^{-4}$ M from the solution penetrating into the 1 film at 298 and 333 K, respectively.
Table S2  Results of the fit and values of the diffusion coefficient of Hg$^{2+}$ leaving the solution entering the 1 film

<table>
<thead>
<tr>
<th></th>
<th>Fitted parameters</th>
<th></th>
<th></th>
<th>R²</th>
<th>D $[m^2 s^{-1}]$</th>
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<tbody>
<tr>
<td>298 K</td>
<td>y₀ = 0.99269 A = -1.02431 B = 8235.08578</td>
<td>0.992</td>
<td>4.93×10⁻¹⁵</td>
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</tr>
<tr>
<td>333 K</td>
<td>y₀ = 0.99013 A = -0.97209 B = 6905.42067</td>
<td>0.994</td>
<td>5.88×10⁻¹⁵</td>
<td></td>
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</tr>
</tbody>
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The diffusion activation energy of Hg$^{2+}$ in the 1 film was calculated from the Arrhenius approach:

$$E_a = R \ln \left( \frac{D_2}{D_1} \right) \left( \frac{T_1 T_2}{T_2 - T_1} \right)$$  \hspace{1cm} (9)

where $E_a$ is diffusion activation energy; $R$ is the gas constant (8.314 J mol⁻¹ K⁻¹); $D_1$ and $D_2$ are the values of diffusion coefficient at 298 and 333 K, respectively; $T_1 = 298$ K and $T_2 = 333$ K.

References