

Supporting Information

A Novel Highly Luminescent LnMOF Film: the Convenient Sensor for Hg²⁺ Detecting

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S1. Deposition of **1** coating on ITO

Na₂bqdc (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 EuCl₃·6H₂O (0.015 g, 0.04 mmol) in 6 mL DMF, the Na₂bqdc 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 : H₂O before use.

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

Preparation of I-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 M(NO₃)_x (M = Na⁺, K⁺, Mg²⁺, Ca²⁺, Zn²⁺, Cd²⁺, Hg²⁺) at 1×10⁻³ 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 I-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 : H₂O containing M(NO₃)_x (M = Na⁺, K⁺, Mg²⁺, Ca²⁺, Zn²⁺, Cd²⁺, Hg²⁺) at 1×10⁻³ 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 Hg²⁺ solution at room temperature: (i) A DMF-H₂O solution (3mL) containing Hg²⁺ 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 Hg²⁺ solution at 333 K: (i) A DMF-H₂O solution containing Hg²⁺ 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 Hg²⁺ 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 H₂bqdc in DMF at 340 nm at a series of concentration. The quantity of bqdc in **1** film was calculated from the standard curve. The number of binding sites was calculated from the quantity of bqdc for each bqdc molecule contains two binding sites.

S4. Additional figures

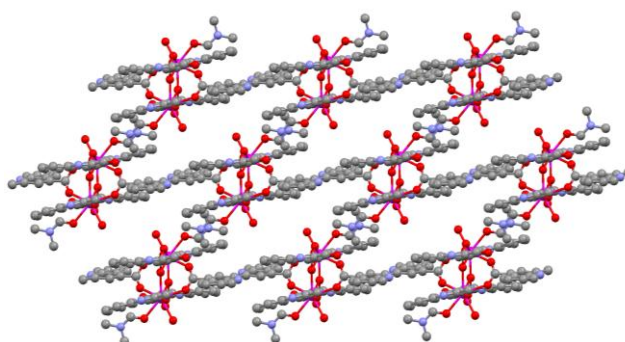


Fig. S1 Packing diagram of **1** viewed along the *c* axis showing channels. H atoms as well as lattice H₂O and DMF molecules are omitted for clarity. Color scheme: Eu atoms, pink; C atoms, grey; O atoms, red; N atoms, blue.

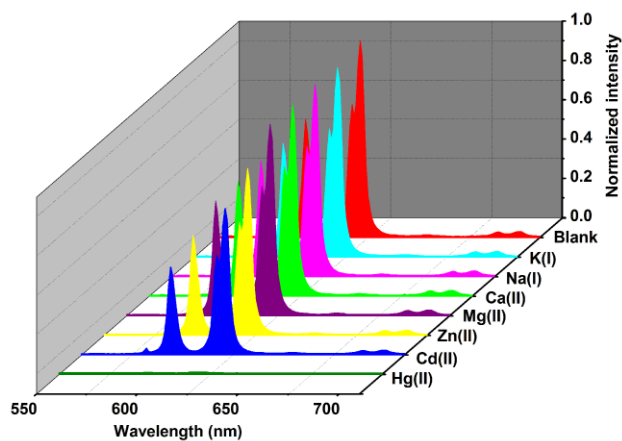


Fig. S2 Emission spectra of **1** emulsion after introducing various metal ions at 1×10^{-3} M at 298 K (excited at 368 nm). The data were normalized to the intensity of the blank sample.

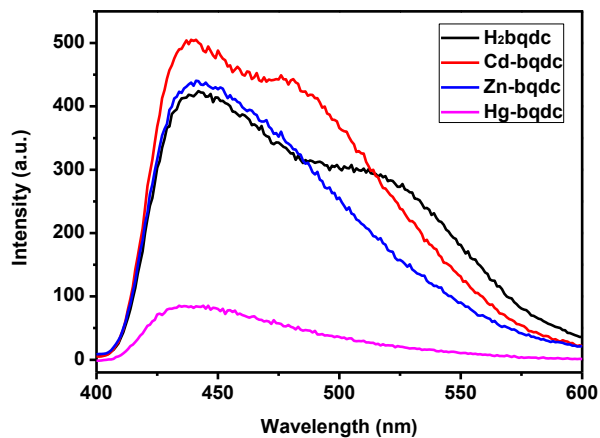


Fig. S3 Emission spectra of H₂bqdc and its complexes with Cd²⁺, Zn²⁺ and Hg²⁺ in DMF at concentration of 0.005 M (excited at 388 nm).

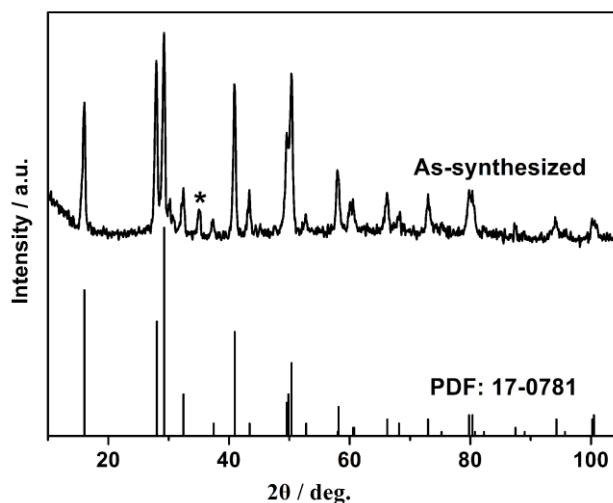


Fig. S4 Powder XRD patterns of as-synthesized $\text{Eu}(\text{OH})_3$ coating and reference XRD pattern of $\text{Eu}(\text{OH})_3$ (PDF: 17-0781). * indicates ITO reflection.

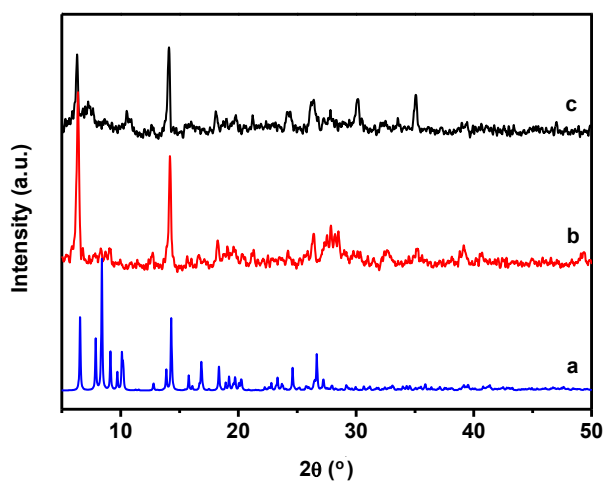


Fig. S5 PXRD patterns: a) calculated from single crystal data **1**; b) **1** film after being immersed in water solutions at pH = 3 for 24 h; c) **1** film after being immersed in water solutions at pH = 9 for 24 h.

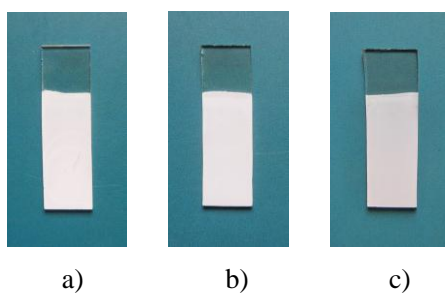


Fig. S6 Photographs of Gd-bqdc thin film (a), Tb-bqdc thin film (b), Eu-terephthalate thin film (c).

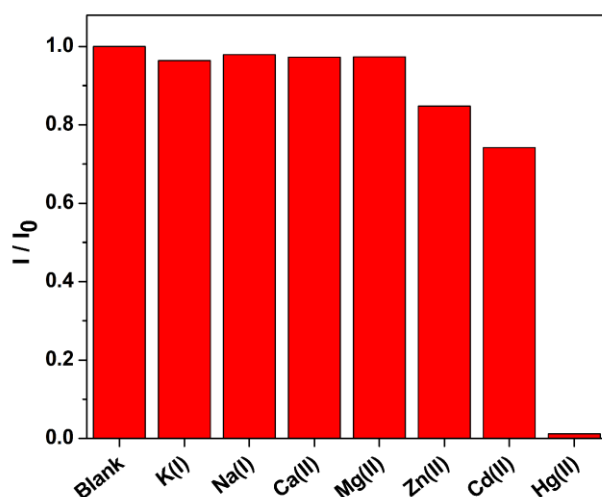


Fig. S7 Ratio of intensity of the ${}^5D_0 \rightarrow {}^7F_2$ transition (at 621 nm) of the **1** film immersed in solutions containing various metal ions at 1×10^{-3} M for 3 days at 298 K (I) to that of the film just immersed in the solution containing the same metal ion (I_0) (excited at 373 nm).

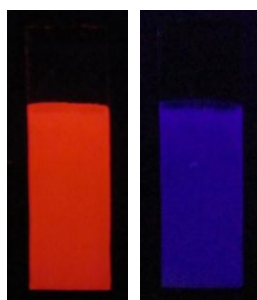


Fig. S8 Photographs of **1** thin film. The film illuminated by lab UV lamp: a) before and b) after immersion in Hg^{2+} at 1×10^{-3} M.

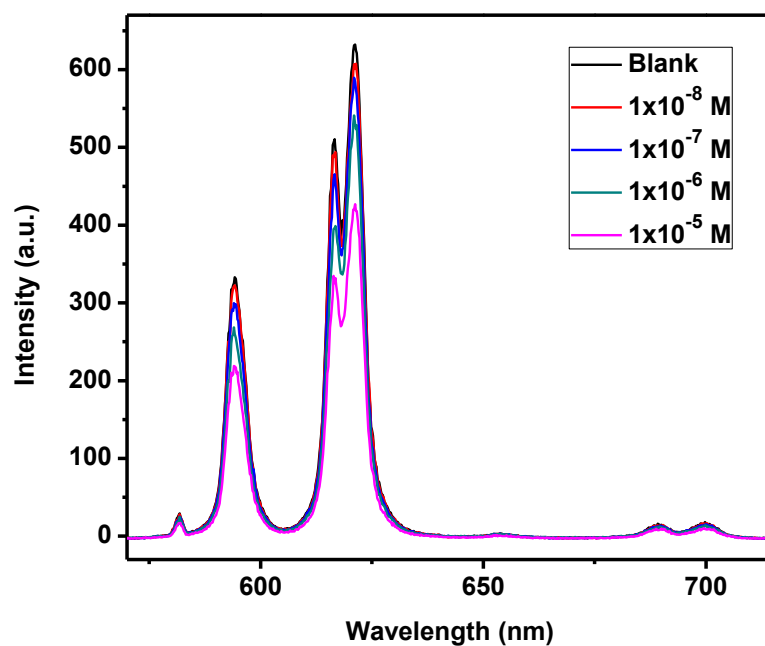


Fig. S9 Emission spectra of **1** film after being immersed in Hg^{2+} at concentration of $0 \sim 1 \times 10^{-5}$ M at 298 K (excited at 373 nm).

S5. Additional Table

Table S1 The selected bond lengths and angles of **1**.

Eu(1)-O(1W)	2.335(17)	Eu(1)-O(7)	2.458(5)
Eu(1)-O(2)#1	2.373(4)	Eu(1)-O(8)	2.489(17)
Eu(1)-O(1)	2.375(4)	Eu(1)-O(6)	2.494(4)
Eu(1)-O(3)	2.377(4)	Eu(1)-O(4)#1	2.516(4)
Eu(1)-O(5)	2.454(4)	Eu(1)-O(3)#1	2.666(4)
O(1W)-Eu(1)-O(2)#1	79.4(4)	O(2)#1-Eu(1)-O(6)	78.24(15)
O(1W)-Eu(1)-O(1)	138.9(4)	O(1)-Eu(1)-O(6)	127.37(15)
O(2)#1-Eu(1)-O(1)	133.16(15)	O(3)-Eu(1)-O(6)	81.71(15)
O(1W)-Eu(1)-O(3)	147.8(4)	O(5)-Eu(1)-O(6)	52.51(14)
O(2)#1-Eu(1)-O(3)	73.38(15)	O(7)-Eu(1)-O(6)	101.13(19)
O(1)-Eu(1)-O(3)	73.23(15)	O(8)-Eu(1)-O(6)	75.7(4)
O(1W)-Eu(1)-O(5)	105.0(6)	O(1W)-Eu(1)-O(4)#1	76.2(5)
O(2)#1-Eu(1)-O(5)	126.06(15)	O(2)#1-Eu(1)-O(4)#1	90.08(17)
O(1)-Eu(1)-O(5)	77.20(14)	O(1)-Eu(1)-O(4)#1	79.25(16)
O(3)-Eu(1)-O(5)	78.56(14)	O(3)-Eu(1)-O(4)#1	119.99(14)
O(1W)-Eu(1)-O(7)	68.4(4)	O(5)-Eu(1)-O(4)#1	143.74(16)
O(2)#1-Eu(1)-O(7)	146.7(2)	O(7)-Eu(1)-O(4)#1	74.70(17)
O(1)-Eu(1)-O(7)	73.7(2)	O(8)-Eu(1)-O(4)#1	75.8(4)
O(3)-Eu(1)-O(7)	139.86(18)	O(6)-Eu(1)-O(4)#1	151.52(17)
O(5)-Eu(1)-O(7)	72.46(17)	O(1W)-Eu(1)-O(3)#1	114.8(6)
O(1W)-Eu(1)-O(8)	14.4(5)	O(2)#1-Eu(1)-O(3)#1	69.35(14)
O(2)#1-Eu(1)-O(8)	65.1(3)	O(1)-Eu(1)-O(3)#1	69.30(13)
O(1)-Eu(1)-O(8)	149.2(4)	O(3)-Eu(1)-O(3)#1	71.04(14)
O(3)-Eu(1)-O(8)	135.7(3)	O(5)-Eu(1)-O(3)#1	139.76(14)

O(5)-Eu(1)-O(8)	114.0(4)	O(7)-Eu(1)-O(3)#1	116.58(16)
O(7)-Eu(1)-O(8)	82.4(3)	O(8)-Eu(1)-O(3)#1	106.1(4)
O(1W)-Eu(1)-O(6)	76.2(5)	O(6)-Eu(1)-O(3)#1	142.23(14)

Symmetry transformations used to generate equivalent atoms: #1: -x,-y,-z-2

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 μm) 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_∞ 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:

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

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

$$\frac{M_t}{M_\infty} = \frac{2}{\pi^{1/2}} \left(\frac{Dt}{l^2}\right)^{1/2} \quad (2)$$

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

$$\frac{I_0 - I_t}{I_0 - I_\infty} = \frac{M_t}{M_\infty} \quad (3)$$

where I_0 , I_t and I_∞ 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:

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

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 1×10^{-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 1.70×10^{-15} and $4.01 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$, respectively.

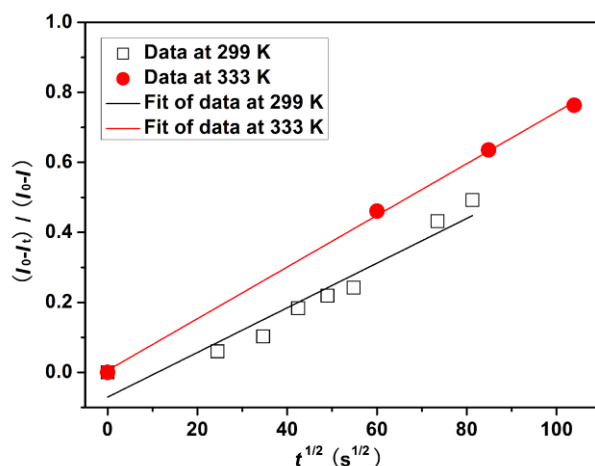


Fig. S10 Plot of $\frac{I_0 - I_t}{I_0 - I_\infty}$ versus $t^{1/2}$ at the beginning of the diffusion processes of Hg^{2+} at 1×10^{-4} M leaving the solution coming into the **1** film at 298 and 333 K, respectively.

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:

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

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:

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

If the ratio M_t/M_∞ was displaced by evolution of luminescence intensity, then

$$\frac{I_0 - I_t}{I_0 - I_\infty} = 1 - \frac{8}{\pi^2} \exp\left(\frac{-D\pi^2 t}{4l^2}\right) \quad (7)$$

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:

$$\frac{I_0 - I_t}{I_0 - I_\infty} = 1 - \exp\left(\frac{-D\pi^2 t}{4l^2}\right) \quad (8)$$

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.

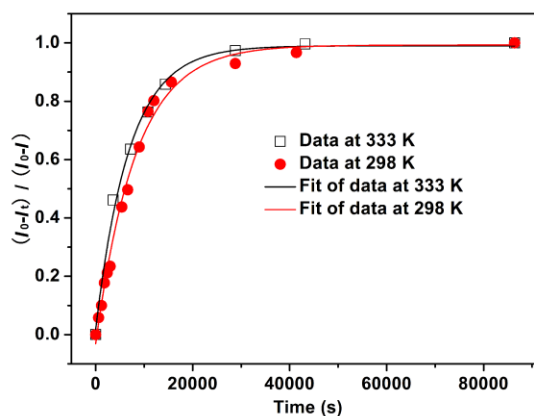


Fig. S11 Diffusion kinetics of Hg^{2+} at 1×10^{-4} M from the solution penetrating into the **1** film at 298 and 333 K, respectively.

Table S2 Results of the fit and values of the diffusion coefficient of Hg²⁺ leaving the solution entering the 1 film

	Fitted parameters			R ²	D [m ² s ⁻¹]
	y ₀	A	B		
298 K	0.99269	-1.02431	8235.08578	0.992	4.93×10 ⁻¹⁵
333 K	0.99013	-0.97209	6905.42067	0.994	5.88×10 ⁻¹⁵

The diffusion activation energy of Hg²⁺ in the **1** film was calculated from the Arrhenius approach:

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

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

1. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution*, University of Göttingen, Göttingen, Germany, 1997.
2. R.-Q. Zou, R.-Q. Zhong, M. Du, T. Kiyobayashi and Q. Xu, *Chem. Commun.*, 2007, 2467.