Electronic Supplementary Information

for

A dual model logic gate for mercury and iodide ions sensing based on metal-organic framework MIL-101

Jing Mei Fang,[a] Peng Fei Gao,[b] Xiao Li Hu,[a] Yuan Fang Li*[a]

[a]*Key Laboratory of Luminescent and Real-Time Analytical Chemistry (Southwest University), Ministry of Education, College of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, PR China; E-mail: liyf@swu.edu.cn, Fax: (+86) 23 68367257; Tel: (+86) 23 68254659.*

[b]*College of Pharmaceutical Sciences, Southwest University, Chongqing, 400715, PR China.*

Principle of MIL-101 amplifying FA Strategy

It is well-known that the anisotropy value, *r*, is very sensitive to the rotational motion changes of the fluorescent molecule-linked object. It can be described by the Perrin equation:[1]

$$r = \frac{r_0}{1 + (\tau/\theta)} \qquad (1)$$

$$\theta = \eta V / RT \qquad (2)$$

So

$$\frac{1}{r} = \frac{1}{r_0} + \frac{\tau RT}{r_0 \eta V} \qquad (3)$$

where *r* is the observed anisotropy, r_0 is the fundamental anisotropy in the absence of rotational diffusion, θ is the rotational correlation time for the diffusion process, τ is excited state lifetime, *R* is the gas constant, *T* is the temperature in Kelvin, η is the viscosity of the solution and *V* is the effective volume of the rotating unit. The anisotropy of a fluorophore is proportional to its rotational relaxation time, which in turn depends on its molecular volume (molecular mass). Therefore, a small molecule in solution rotates fast and has small FA while larger molecules will have larger anisotropy due to their hindered motion.

1. Materials and apparatus

The probe DNA sequences used in this work were synthesized and purified by Sangon Biotech Co.Ltd (Shanghai, China), all ssDNAs were used without further purification. The sequence of the probe DNA 1 (P1) was 5′-TTC TTTCAT TTC TTT CTT CG-3′, the probe DNA 2 (P2) was 5′-CG TTG TTT GTT ATG TTT GTT-3′, and P1 was 13-base mismatch to P2. SG (10000×) was purchased from invitrogen inc, which was diluted to 1.25× with water to make a stock solution. According to the research of Liu et. al in 2008,[2] the concentration of 125× SG is 0.245 mM. $Cr(NO_3)_3 \cdot 9H_2O$ (99%), hydrofluoric acid (HF) (48%) and terephthalic acid (H_2BDC) (99%) were purchased from Aladdin

chemistry Co.Ltd. (Shanghai, China). The systhesis of MIL-101 is consistent with our former report, and its structure has been confirmed by means of XRD and SEM.[3] The surface area of MIL-101 is 5900 m^3/g, and pore aperture diameteris 12–16˚A.[4] In order to diffuse MIL-101 better, it was obtained by vacuum freeze-drying method.

Fluorescence spectra and fluorescence anisotropic were measured by an F-2500 fluorescence spectrophotometer (Hitachi, Tokyo, Japan). A QL-901 vortex mixer (Haimen, China) was employed to blend the solution in 1.5-mL tubes. A pH 510 precision pH meter (California, USA) was employed to measure pH values. A constant-temperature water-base boiler (Jiangsu, China) was employed to control the hybridization temperature to keep the temperature 40°C. A Milli-Q filtration syetem (Millipore, USA) was employed to prepare water (18.2 MΩ).

2. Detection of Hg^{2+}

The probe DNA P (20 nM P1 and 20 nM P2) were hybridized with different concentrations Hg^{2+} in 10 mM Tris-HCl (pH 7.6) buffer solution which containing 20 mM NaCl at 40°C for 10 min. Further, 50 μL of SG (2.45 μM) was added and incubated at room temperature for 2 min. At last a certain volume of MIL-101 (0.3 $mg \cdot mL^{-1}$) was added and the final mixture was diluted to 500 μL with doubly distilled water. After the mixture was incubated at room temperature for further 20 min, it was then transferred for fluorescence spectra and fluorescence anisotropic measurement by an F-2500 fluorescence spectrophotometer with an excitation wavelength at 490 nm, and the emission wavelength was recorded at 529 nm.

The anisotropy, *r*, of the test solution was calculated by

$$r = \frac{I_{VV} - G \times I_{VH}}{I_{VV} + 2G \times I_{VH}} \qquad (4)$$

and

$$G = \frac{I_{HV}}{I_{HH}} \qquad (5)$$

where *I* represents the intensity of the fluorescence signal and the subscripts define the orientation H for horizontal and V for vertical of the excitation and emission polarizers, respectively. *G* is the grating factor of the fluorescence spectrophotometer, which is used to correct for the wavelength response to polarization of the emission optics and detectors.[5]

3. Detection of I^-

The probe DNA P (20 nM P1 and 20 nM P2) were hybridized with a certain amount of Hg^{2+} in 10 mM Tris-HCl (pH 7.6) buffer solution which containing 20 mM NaCl at 40°C for 10 min. Then different concentrations of I^- were added to the reaction solution and incubated at room temperature for 5 min. Further, 50 μL of SG (2.45 μM) was added and incubated at room temperature for 2 min. At last a certain volume of MIL-101 (0.3 $mg \cdot mL^{-1}$) was added and the final mixture was diluted to 500 μL with doubly distilled water. After the mixture was incubated at room temperature for further 20 min, it was then transferred for fluorescence spectra and fluorescence anisotropic measurement by an F-2500 fluorescence spectrophotometer with an excitation wavelength at 490 nm, and the emission wavelength was recorded at 529 nm.

4. Optimization of the logic gate conditions

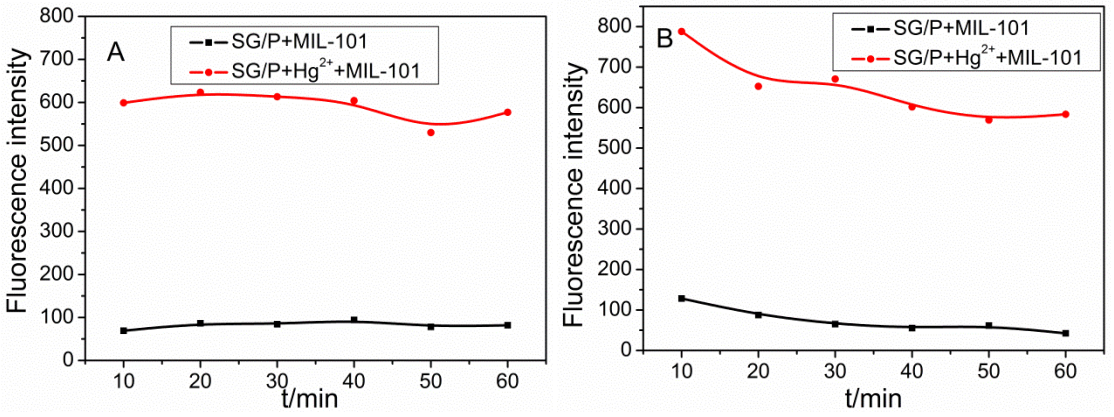

Fig. S1 (A) The hybridization time of formation the duplex T-Hg^{2+}-T structure. (B) The reaction time between MIL-101 and SG/P complex or SG/P/Hg^{2+}. Concentrations: P1, 20 nM; P2, 20 nM; Hg^{2+}, 300 nM; SG, 0.245 μM; MIL-101, 36 $\mu g \cdot mL^{-1}$; Tris-HCl buffer, pH 7.6.

For better quantification of the Hg^{2+} and I^{-}, several sensing conditions are investigated and optimized in the proposed strategy. Firstly, the formation of T-Hg^{2+}-T between P and Hg^{2+} were completely in 10 min at 40°C (Fig. S1A). Then the fluorescence intensity of the SG/P complex and SG/P/Hg^{2+} were gradually stabilized within 20 min after the adding of MIL-101 (Fig. S1B), so 20 min was chosen as the reaction time.

Because of the electrostatic interaction between the MIL-101 and probe DNA, there is a great impact on the acidity of the system. To investigate the effect of pH, 10 mM Tris-HCl buffer solution was used. Experiments show that the F/F_0 is improving with increasing the pH value and reaching a maximum when the pH is 7.6 (Fig. S2).

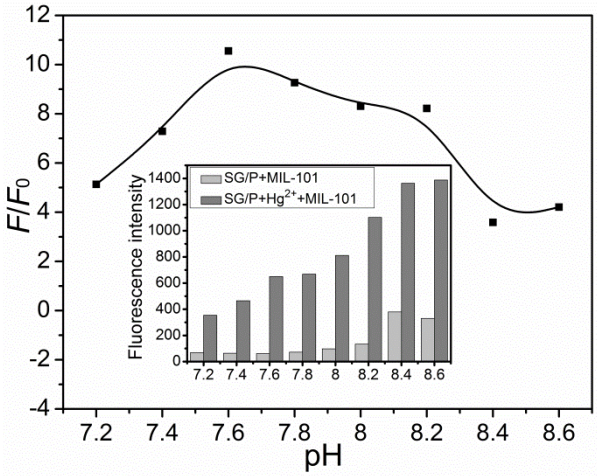

Fig. S2 The signal-to-background ratio (F/F_0) at different pH values of Tris-HCl buffer. Inset: Fluorescence intensity of SG at different pH values of Tris-HCl buffer. Key: light gray columns, without Hg^{2+}; dark gray columns, 300 nM Hg^{2+}. Concentrations: P1, 20 nM; P2, 20 nM; SG, 0.245 μM; MIL-101, 36 $\mu g \cdot mL^{-1}$.

The effects of the dosage of MIL-101 are shown in Fig. S3. For the fluorescence method, in the absence of MIL-101, due to the high background fluorescence of SG/P complex, the F/F_0 is relatively low. When MIL-101 is introduced, the background fluorescence is gradually decreased, and the F/F_0 increases with the addition of MIL-101. The results show that the F/F_0 can reach ~ 12 when 36 $\mu g \cdot mL^{-1}$ of MIL-101 is employed (Fig. S3A). While further increasing the amount of MIL-101, as the more dsDNAs are absorbed by MIL-101, the fluorescence intensity of SG/P/T/MIL-101 is much lower (Fig.

S3A, the inset), then resulting in the decrease of F/F_0. So 36 μg·mL^{-1} of MIL-101 is chosen as the best dosage for the following experiments. For the FA method, in the absence of MIL-101, the value change of FA ($|\Delta r_1|$) is almost undetectable. With increasing amount of MIL-101, both the FA values of SG/P and SG/P/Hg^{2+} are increased and their difference also enlarged (Fig. S3B). In this situation, 33 μg·mL^{-1} of MIL-101 was employed since reached maximum while all of the FA values were less than 0.4.

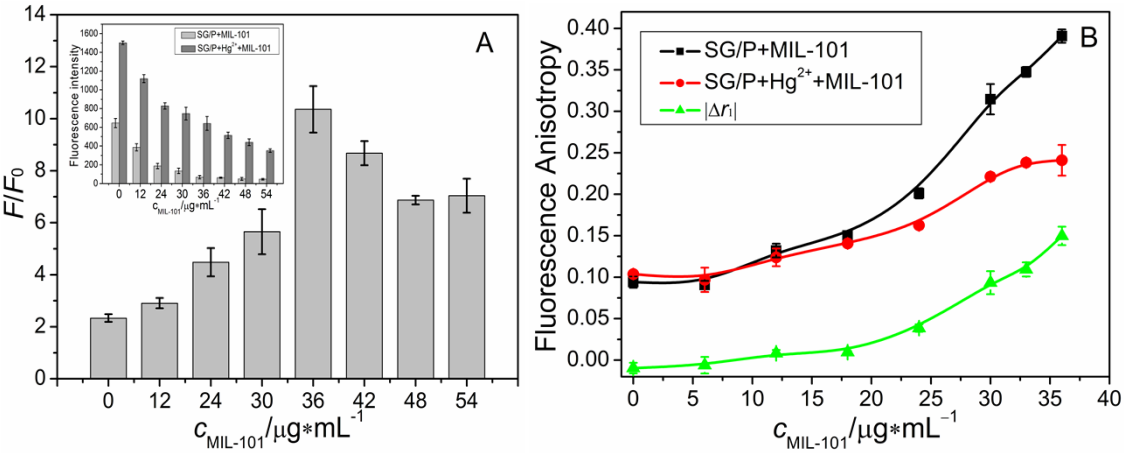

Fig. S3 (A) The signal-to-background ratio (F/F_0) at different concentrations of MIL-101. Inset: Fluorescence intensities of SG in the presence of different concentrations of MIL-101, key: light gray columns, without Hg^{2+}; dark gray columns, 300 nM Hg^{2+}. (B) The value change of FA at different concentrations of MIL-101, 100 nM Hg^{2+}. Concentrations: P1, 20 nM; P2, 20 nM; SG, 0.245 μM. Tris-HCl buffer, pH 7.6.

5. The confirm of the low background signal platform

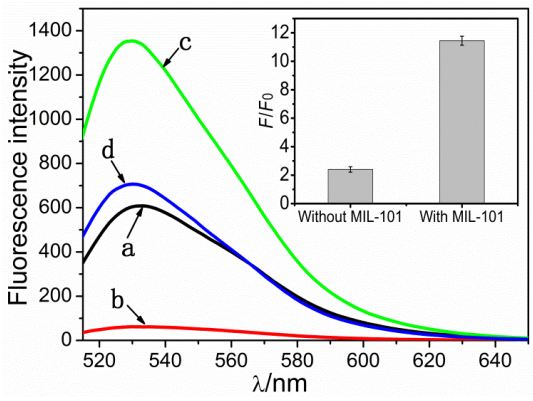

Fig. S4 Fluorescence emission spectra of SG in the presence of P, Hg^{2+} and MIL-101, respectively. (a) SG/P; (b) SG/P+MIL-101; (c) SG/P+Hg^{2+}; (d) SG/P+Hg^{2+}+MIL-101. Inset: the signal-to-background ratio (F/F_0) histogram in the absence and presence of MIL-101. Concentrations: SG, 0.245 μM; P1, 20 nM; P2, 20 nM; Hg^{2+} 300 nM; MIL-101, 36 μg·mL^{-1}. Tris-HCl buffer, pH 7.6.

6. The comparison of value change of FA

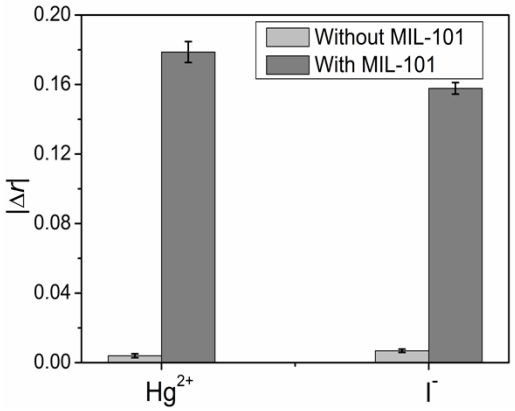

Fig. S5 The value change of FA in the absence or presence of MIL-101. Concentrations: SG, 0.245 μM; P1, 20 nM; P2, 20 nM; Hg^{2+}, 200 nM; I^-, 3.0 μM; MIL-101, 33 μg·mL^{-1}. Tris-HCl buffer, pH 7.6.

7. Selectivity of mercury

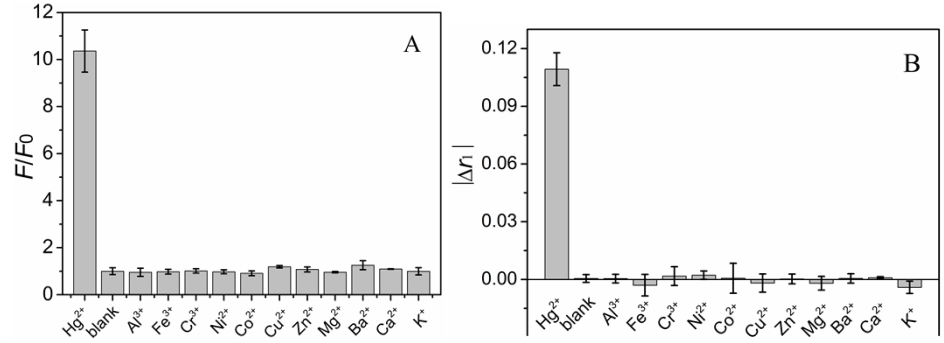

Fig. S6 The interference test of different metal ions for the detection of Hg^{2+}. (A) Fluorescence method, 300 nM Hg^{2+}; other metal ions, 1.5 μM; MIL-101, 36 μg·mL^{-1}. (B) FA method, 100 nM Hg^{2+}; other metal ions, 500 nM; MIL-101, 33 μg·mL^{-1}. Concentrations: P1, 20 nM; P2, 20 nM; SG, 0.245 μM. Tris-HCl buffer, pH 7.6.

8. Selectivity of iodide

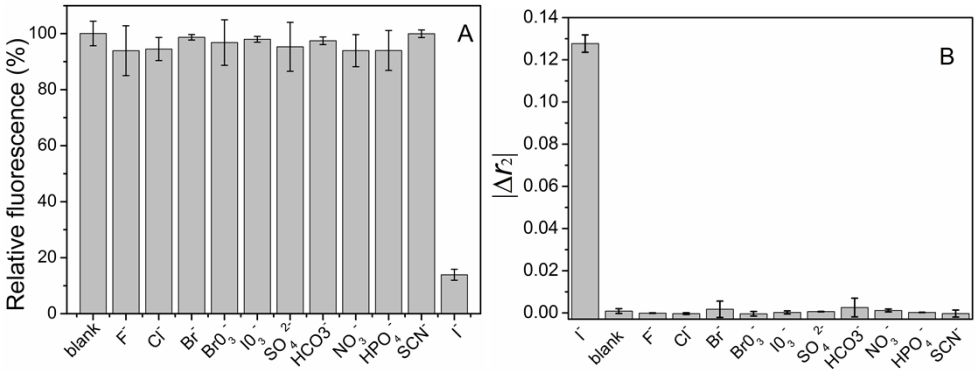

Fig. S7 The interference test of different anions for the detection of I^-. (A) Fluorescence method, 500 nM Hg^{2+}, 0.8 μM I^-; other anions, 4.0 μM; MIL-101, 36 μg·mL^{-1}. (B) FA method, 200 nM Hg^{2+}, 2

μM I^-; other anions, 10 μM; MIL-101, 33 μg·mL^{-1}. Concentrations: P1, 20 nM; P2, 20 nM; SG, 0.245 μM. Tris-HCl buffer, pH 7.6.

9. Determination of Hg^{2+} and I^- in tap water sample

To demonstrate the real application of the proposed methods, we detected Hg^{2+} and I^- in tap water using the logic gate of fluorescence intensity and anisotropy. Different amounts of Hg^{2+} and I^- were added into the tap water.

Table S1 Detection of Hg^{2+} and I^- in tap water samples using the proposed method (n=5)

Fluorescence method

Sample	Target	Background Content	Concentration		Recovery (%)	RSD (%)
			Added/nM	Found/nM		
Tap water 1		ND	100	101	101	3.27
Tap water 2	Hg^{2+}	ND	200	205	102.5	2.13
Tap water 3		ND	300	301	100	3.29
Tap water 1		ND	400	392	98	3.51
Tap water 2	I^-	ND	600	604	101	3.56
Tap water 3		ND	800	790	99	3.31

ND: not detected

Fluorescence anisotropy method

Sample	Target	Background Content/nM	Concentration		Recovery (%)	RSD(%)
			Added/nM	Found/nM		
Tap water 1		ND	100	98.2	98.21	3.56
Tap water 2	Hg^{2+}	ND	150	150	99.97	2.96
Tap water 3		ND	200	202	101.2	0.996
Tap water 1		ND	1000	998.8	99.88	2.76
Tap water 2	I^-	ND	2000	2029	101.4	2.54
Tap water 3		ND	3000	3003	100.1	2.53

ND: not detected

Refrences

1. D. M. Jameson and J. A. Ross, *Chem. Rev.*, 2010, **110**, 2685.
2. J. Wang and B. Liu, *Chem. Commun.*, 2008, 4759.
3. J. M. Fang, F. Leng, X. J. Zhao, X. L. Hu and Y. F. Li, *Analyst*, 2014, **139**, 801.
4. F. Leng, W. Wang, X. J. Zhao, X. L. Hu and Y. F. Li, *Colloid. Surface. , A*, 2014, **441**, 164.
5. D. Zhang, H. Shen, G. Li, B. Zhao, A. Yu, Q. Zhao and H. Wang, *Anal. Chem.*, 2012, **84**, 8088.