Electronic Supplementary Information

A simple chemiluminesce aptasensor for detection of α-fetoprotein based on

iron-based metal organic frameworks

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1.Experimental Section

1.1. Reagents and Solutions.

FeCl$_3$·6H$_2$O was obtained from fengchuan Chemical Co., Ltd. (Tianjin,China).

Trimesic acid (H$_3$BTC) and terephthalate (H$_2$BDC) were purchased from Shanghai

Macklin Biochemical Co., Ltd. (Shanghai, China). Luminol was ordered from West

Asia Chemical Industry Co., Ltd. (Shandong, China). N, N-dimethylformamide (DMF)

was obtained from Damao Chemical Reagent Factory (Tianjin, China). α-fetoprotein

(AFP), Bovine serum albumin (BSA), adrenaline and Glucose (Glc) were purchased

from Solebo Biological Technology Co. Ltd. (Beijing, China). Sodium hydroxide,

sodium chloride, ethanol, hydrogen peroxide and all other chemicals unless specified

were analytical reagent grade and used without further purification. AFP aptamer

(AFP-Apt): 5'-ATCAGGTGCAGTTCTCGACTCGGTCTTGATGTGGG-3' was purchased from Sangon Biotech Company (Shanghai, China). Regarding the preparation of the aptamer solution, the AFP aptamer was slowly heated to 90 °C for 10 minutes before use of the aptamer, and then cooled to room temperature to unwind the single-stranded oligonucleotide. Redistilled water was used throughout the work. Phosphate buffer (PBS, pH = 7.4, 0.01 moL/L) solution was used as working buffer solution.

1.2. Equipment.

Regulus 8100 scanning electron microscope was utilized to characterize the morphology of Fe-MOFs. The determination of zeta potential was carried out by using a Malvern Zetasizer 2000. All functional groups or chemical bonds contained in the material were identified by VERTEX70 Fourier infrared spectrometer. The specific surface area of Fe-MOFs was measured by a fully automatic surface area and pore size analyzer. All electrochemical measurements were performed on a CHI 760D electrochemical workstation. UV-vis absorption spectra was obtained from a Lambda 35 UV-vis spectrometer. Fluorescence experiments were carried out on a Shimadzu RF-5301 Fluorescence. The results of the wavelength measurement of the chemiluminescence system were obtained by adding a filter to a fluorescent device.

1.3. Preparation of Fe-MOFs.

MIL-53 (Fe): 1.00 mM of $FeCl_3 \cdot 6H_2O$ and 1.00 mM of H_2BDC were added to 6 mL of DMF and stirred at room temperature. Then the reaction mixture was transferred to a reactor with teflon liner and reacted for 3 h at 150 °C. After cooling to

room temperature, the mixture was centrifuged and washed with DMF, ethanol and water, respectively. Finally, the brown powder was obtained by vacuum drying at 60 °C [1].

MIL-88B (Fe): 1.00 mM $FeCl_3 \cdot 6H_2O$ and 0.43 mM H_2BDC were transfered to the mixture of 5 mL DMF and 0.4 mL 2 M NaOH solution. The reaction mixture were stirred at room temperature to a reactor with teflon liner and reacted for 12 h at 100 °C. After cooling to room temperature, the mixture was centrifuged and washed with DMF, ethanol and water, respectively. Finally, the brown powder was obtained by vacuum drying at 60 °C [2].

MIL-100 (Fe): 1.00 mM $FeCl_3 \cdot 6H_2O$, 0.52 mM H_3BTC, and 6 mL of ultrapure water were stirred at room temperature, then the reaction mixture was transferred to a reaction kettle and reacted for 72 h at 130 °C. After that, the product was purified by 70 mL ultrapure water and 70 mL absolute ethanol for 12 h at 70 °C, Finally, the mixture was centrifuged and the brown powder was obtained by vacuum drying at 60 °C [3, 4].
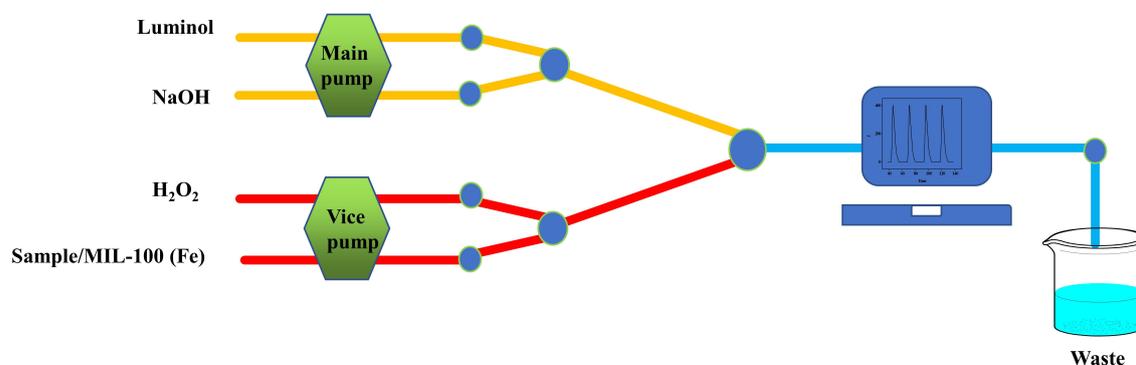
1.4. AFP detection process

Fig. S1. The schematic of MPI-F flow injection chemiluminescence analyzer.
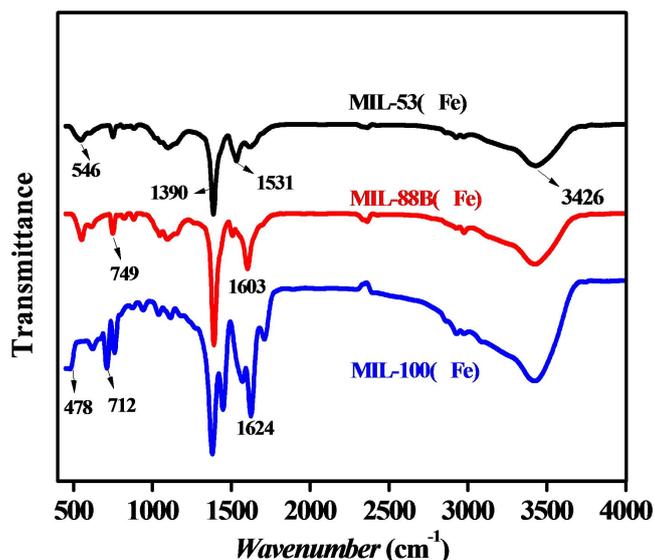
1.5. FTIR of Fe-MOFs

Fig. S2. FTIR spectra of Fe-MOFs.

Fig. S2 showed the FTIR of Fe-MOFs in the wavenumber range of 500cm^{-1} - 4000 cm^{-1}. In the spectrum of Fe-MOFs, a broad and strong absorption peak appears at 3426 cm^{-1}, which belongs to the stretching vibration peak of O-H. The strong peaks at 1531 cm^{-1} and 1390 cm^{-1} in MIL-53 (Fe) curve are attributed to the asymmetric and symmetric vibrations of carboxyl groups, respectively. The strong peaks at the 1603 cm^{-1} and 1390 cm^{-1} in MIL-88B (Fe) curve are correspond to the asymmetric and symmetric vibrations of carboxyl groups. Furthermore, in the spectrum of MIL-53 (Fe) and MIL-88B (Fe), the absorption peaks at 749 cm^{-1} and 546 cm^{-1} belong to the stretching vibration peak of C-H on benzene ring and Fe-O, respectively. The characteristic peaks at 1624 cm^{-1}, 1390 cm^{-1}, 712 cm^{-1} and 478 cm^{-1} in the spectra of MIL-100 (Fe) are ascribed to asymmetric vibrations of -O-C-O-, the symmetric vibrations of -O-C-O-, the stretching vibration of C-H and the stretching vibration of Fe-O, respectively.
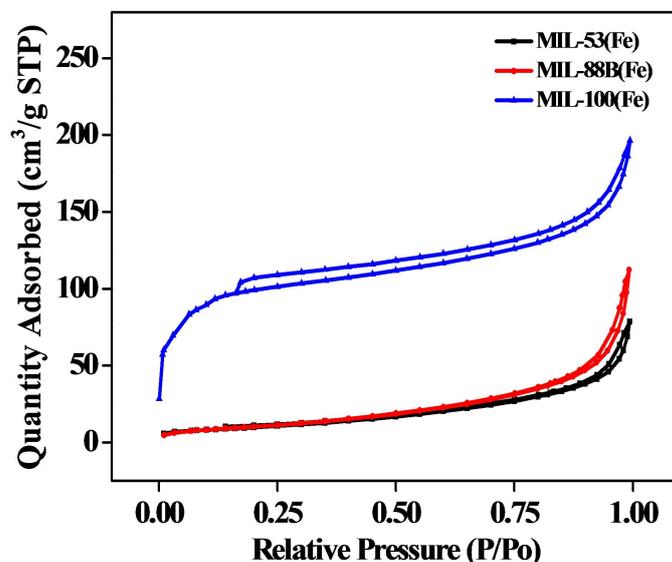
1.6. BET of Fe-MOFs

Fig. S3. BET of Fe-MOFs.

The specific surface area of Fe-MOFs were as follows: MIL-100 (Fe) (316.95 m^2/g) > MIL-88B (Fe) (39.86 m^2/g) > MIL-53 (Fe) (36.44 m^2/g). The corresponding average pore size showed a different order: MIL-88B (Fe) (13.01 nm) > MIL-53 (Fe) (10.64 nm) > MIL-100 (Fe) (9.12 nm).

1.7. The immobilization capacity calculation formula

$$Q_e=(c_0-c_e)V/m$$

Where Q_e (mol/mg) was the mass of AFP-apt adsorbed per unit mass of dry MIL-100 (Fe), c_0 (mol/L) and c_e (mol/L) were the concentration of AFP-apt in the initial and final solution, respectively, V (L) was the volume of the adsorption mixture, and m (mg) was the mass of the MIL-100 (Fe).

Table S1

Determination of AFP in real samples.

Samples	Added (10^{-8} g/L)	Found[a] (10^{-8} g/L)	Recovery (%)	RSD[b] (n = 3, %)
1	Not	Not	-	-
2	10.00	10.15	101.5	2.2
3	25.00	24.45	97.8	1.5
4	5.00	4.98	99.6	1.8
5	50.00	51.10	102.2	2.3
6	100.00	103.7	103.7	3.0

[a] Mean values of three determinations.
[b] Standard deviation.

Reference

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