Electronic Supplementary Material (ESI) for Analyst.

The electrochemiluminescence coreactant accelerator of metal organic frameworks grafted with N-(aminobutyl)-N-(ethylisoluminol) for ultrasensitive detection of chloramphenicol

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Reagents and materials

Zinc nitrate hydrate, melamine, thiophenedicarboxylic acid (TPDA), mercaptopropanoic acid (MPA), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC), *N*-hydroxysuccinimide (NHS) and mercaptoethanol (MCH) were obtained from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Bovine serum albumin (BSA) and tripropylamine (TPA) were purchased from Sigma-Aldrich (Shanghai, China). *N*-(4-Aminobutyl)-*N*-ethylisoluminol (ABEI) and *N*,*N*-dimethylformamide (DMF) were acquired from J & K Chemical Technology (Beijing, China). Tripropylamine (TPA), methanol and sodium hydroxide (NaOH) were purchased from Sigma-Aldrich (Shanghai, China). Human serum albumin (HSA) was received from Jinhua City Central Hospital. Chloramphenicol (CAP) was received from Macklin biochemical Co., Ltd. (Shanghai, China). The CAP concentration was adjusted with standard CAP sample from National Institute for food, where the drug control and purity ratio is 1.17±0.14 by UV-vis spectroscopy. The materials used to compare CAP, such as Kanamycin (Kana), thiamphenicol (TAP), amoxicillin (AMC) and tobramycin (TOB) were obtained from Macklin Biochemical Co., Ltd. (Shanghai, China). The CAP eye drops was purchased from Handan KANGYE Pharmaceutical Co., Ltd (labeled amount of 8 mL:20 mg, Handan, China) and diluted to 0.01 mM as medical sample with phosphate buffer solution (PBS, pH 7.4, 10 mM) for the recovery experiments.

All oligonucleotides were purchased from Sangon Biotech Co., Ltd. (Shanghai, China), which include capture DNA (cDNA), aptamer DNA (aptDNA) and link DNA (L-DNA). These primers were distilled with sterilization PBS (pH 7.4, 10 mM) from

Sangon Biotechnology (Shanghai, China) too. The sequences were described as following:

Capture DNA (cDNA): 5'-SH-

AACTTCAGTGAGTTGTCCCACGGTCGGCGAGTCGGTGGTAGCACTAAGT-

Fc-'3

Aptamer DNA (aptDNA):

5'-ACTTCAGTAGTTGTCCCACGGTCGGCGAGTCGGTGGTAG-'3

Link DNA (L-DNA)

5'- CTACCACCGACTCGCCGACCGTGGGACAACTCACTGAAGT-3'

Human serum samples were gained from Jinhua City Central Hospital and stored at -20 °C. The PBS (pH 8.0, 0.1 M NaH_2PO_4/Na_2HPO_4) performed as the detection buffer. All of the analyses were carried out with high-purity water acquired from Millipore water purification system (≥18MΩ, Milli-Q, Millipore) in this system.

Apparatus

Transmission electron microscopy (TEM) images were obtained with the JEM-2100 HR transmission electron microscope (Japan Electronics Co., Ltd, Japan). Scanning electron microscopy (SEM) images were obtained by using JSM-6360LV SEM (Japan Electronics Co., Ltd, Japan). X-ray photoelectron spectroscopy (XPS) images were obtained on a K-Alpha XPS spectrometer excited with AlKα X-ray radiation ($h\nu$ = 1486.6 eV, Thermo Fisher Scientific, America). UV-visible (UV-vis) spectra were acquired at the Thermo nicolet evolution 500 UV-vis spectrophotometer

(Beijing Puxi general instrument Co., Ltd., China) in the wavelength range of 200-800 nm. Fluorescence (FL) measurements were conducted at an RF-6000 spectrometer (Thermo Fisher Scientific, America). After full dispersion of the sample into KBr particles, Fourier transform infrared spectroscopy (FT-IR) measurement was performed at a Nicolet 670 spectrometer only in the mid-infrared range of 400-4000 cm^{-1} (Shimadzu Co., Japan).

Electrochemistry and electrochemiluminescence (ECL) experiments were performed at CHI 660D electrochemical workstation and MPI-E multi-function ECL analyzer (Xi'an Remax Analytical Instrument Co., Ltd., China), respectively. The ECL spectroscopy experiments were carried out by galvanizing ABEI-Zn-MOF-1 in the above buffer under the hydrodynamic electrolysis conditions with an applied potential of 0.9 V. Electrochemical impedance spectra (EIS) were recorded in 0.1 M KCl containing 5 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ with an amplitude of 10 mV in the frequency range from 0.1 to 100,000 Hz. Photoelectrochemical measurements were performed on the electrochemical workstation ZAHNER Zennium IM6 by using a white LED as the light source. Herein, the classic three-electrode system was used: A glassy carbon electrode (GCE, Φ = 5 mm) behaved as the working electrode, an Ag/AgCl electrode (saturated KCl) as the reference electrode, and a platinum wire as the counter electrode (ZAHNER, Germany).

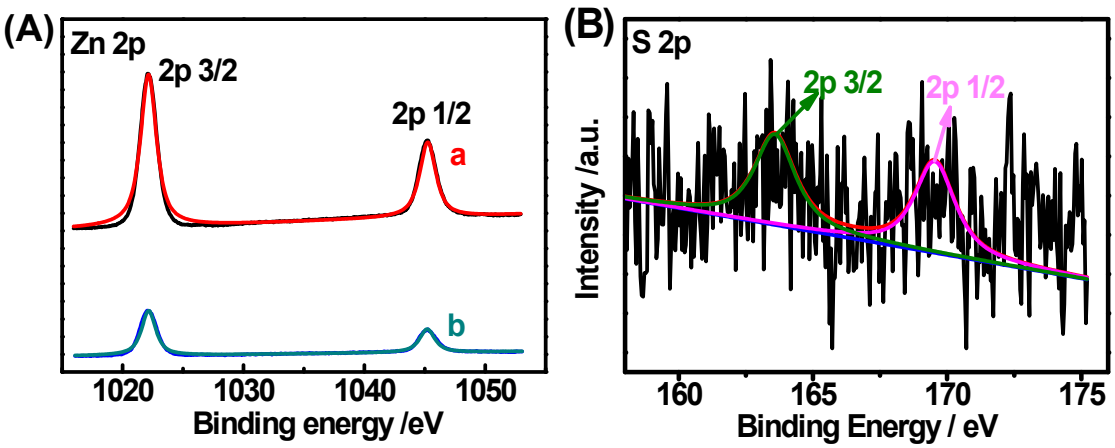

Figure S1. (A) High-resolution Zn 2P XPS spectra of MPA/MOF-Zn-1 (curve a) and MOF-Zn-1 (curve b); (B) The S 2P XPS spectra of cDNA/ABEI-MOF-Zn-1.

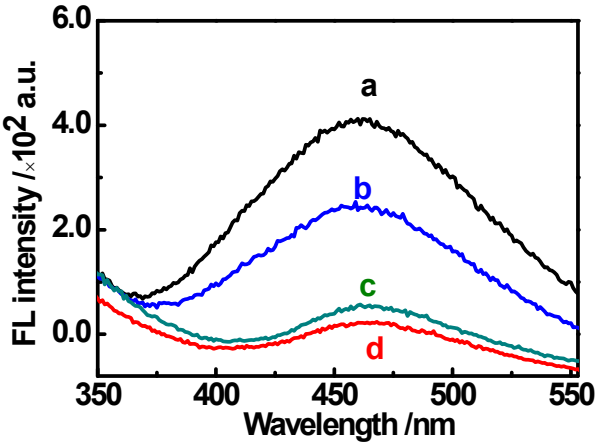

Figure S2. FL spectra of ABEI-MOF-Zn-1 (curve a), ABEI (curve b), TPA (curve c), and MOF-Zn-1 (curve d).

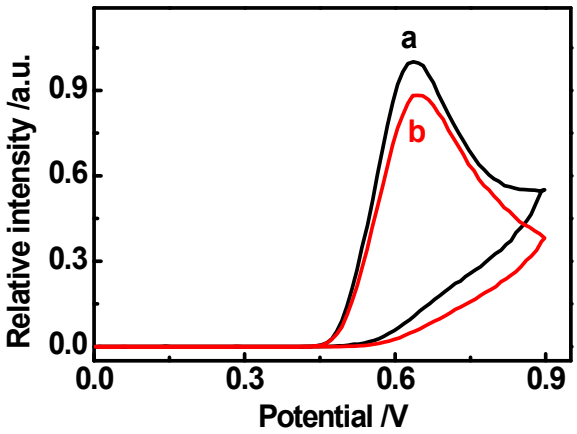

Figure S3. The ECL plots of ABEI-MOF-Zn-1 in the air- (curve a) and N_2-saturated (curve b) TPA system.

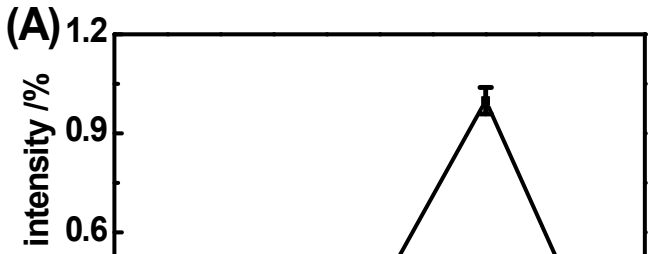

Figure S4. Influences of the ABEI-MOF-Zn-1 (A) and TPA (B) concentrations, and the incubation time at 37°C (C) on the ECL responses.

Table S1. Comparison of the analytical data of the as-fabricated biosensor for the determination of CAP with those reported previously.

Methods	Linear ranges	Detection limits	References
ELISA	0.03 nM-0.31 μM	0.93 nM	[1]
Microtiter	3.09-6.19 μM	324.95 nM	[2]
CV	0.010-0.10 μM	5200 nM	[3]
Fluorescent	0.005-0.2 μM	1.20 nM	[4]
ECL	**1.00 nM-100 μM**	**0.11 nM**	**This work**

Table S2. Detection results of CAP in the serum samples and eye drops (n = 3).

Samples	Added (mM)	Found (mM)	Recovery (%)	RSD (%)
1	0.1	0.102	101.67	7.5
2	0.01	0.01	100.67	8.3
3	0.001	0.00095	95.00	4.8
eye drops	0.01	0.0103	103.0	1.5

References

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