Supplementary Information

A robust and efficient aqueous electrochemiluminescence emitter constructed by sulfonate porphyrin-based metal-organic framework and its application in ascorbic acid detection

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Experimental section

1. Reagents and materials

Briefly, 1,3,5-benzenetricarboxylic acid (BTC), zinc nitrate ($Zn(NO_3)_2$), methanol (CH_3OH), potassium persulfate ($K_2S_2O_8$), *N*,*N*-dimethylformamide (DMF), potassium chloride (KCl), ascorbic acid (AA), dopamine (DA), uric acid (UA), glucose (Glu), ammonium ferrous sulfate ($(NH_4)_2Fe(SO_4)_2$), resorcinol (R-80) and hydroquinone (HQ) were acquired from Shanghai Aladdin Chemical Reagent Company (Shanghai, China). Zn(II)meso-tetra (4-sulfonatophenyl) porphine (ZnTSPP) was received from J&K Scientific Ltd (Shanghai, China). The ECL measurements were conducted in the 0.1 M phosphate buffer solution (PBS, pH 7.4) as supporting electrolyte, which was obtained by mixing the freshly-prepared 0.1 M K_2HPO_4 and 0.1 M KH_2PO_4 solutions together with the specific proportion in the presence of 0.25 M KCl. Human serum samples were obtained from Jinhua City Central Hospital and stored at -20 °C. The N_2-saturated electrolyte was gained by bubbling with high-purity N_2 into the solution for 20 min and preserving the N_2 atmosphere during the test. The ultrapure water used in all the experiments was prepared on the Millipore water purification system (≥18 MΩ, Milli-Q, Millipore).

2. Characterization

The morphology and structure of the as-synthetized product were characterized by transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) on a JEM-2100 HR transmission electron microscope (Japan Electronics Co. Ltd, Japan)

operating at an acceleration voltage of 200 kV. The X-ray photoelectron spectroscopy (XPS) measurements were performed at a K-Alpha XPS spectrometer (Thermo Fisher Scientific, America, SCIENTIFIC ESCALAB 250) with the excitation source of Al Kα X-ray radiation (1486.6 eV). The ultraviolet-visible (UV-vis) absorption spectra were acquired by the thermo Nicolet evolution 500 UV-vis spectrometers (Beijing Puxi general instrument Co. Ltd. China) with the wavelength window of 200-800 nm. The fluorescence (FL) spectra were recorded on a FLS980 spectrofluorometer (Edinburgh Instruments Co., Ltd., Britain).

All the cyclic voltammetry (CV) measurements were conducted with the CHI 660D electrochemical workstation (Shanghai Chenhua Instruments Inc. China). The ECL experiments were performed on an MPI-E multifunctional electrochemical and chemiluminescent analytical system (Xi'an Remax Analytical Instrument Co. Ltd. China), coupled with the emission wavelength region from 280 to 850 nm under the photomultiplier tube biased at -1000 V for signal collection.

All the ECL and electrochemical measurements were performed with a conventional three-electrode system, a bare glassy carbon electrode (GCE, 5 mm in diameter, Shanghai Xianren Technology Co. Ltd. China) behaved as the working electrode, Ag/AgCl electrode (filling liquid: saturated KCl) and a Pt wire acted as the reference electrode and counter electrode, respectively.

For all of the electrochemical measurements, all the potentials were quoted against the Ag/AgCl electrode, and the scan rate was 100 mV s^{-1} if not specifically mentioned otherwise.

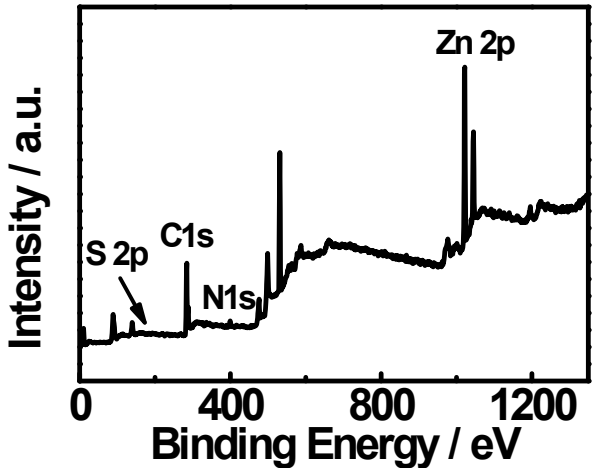

Fig. S1. The survey XPS spectrum of (Zn)porphMOF.

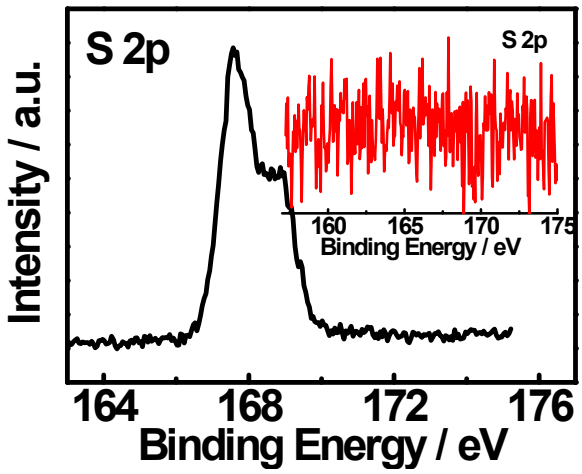

Fig. S2. The high-resolution S 2p XPS spectrum of Zn-TSPP. Inset is the respective spectrum of (Zn)porphMOF.

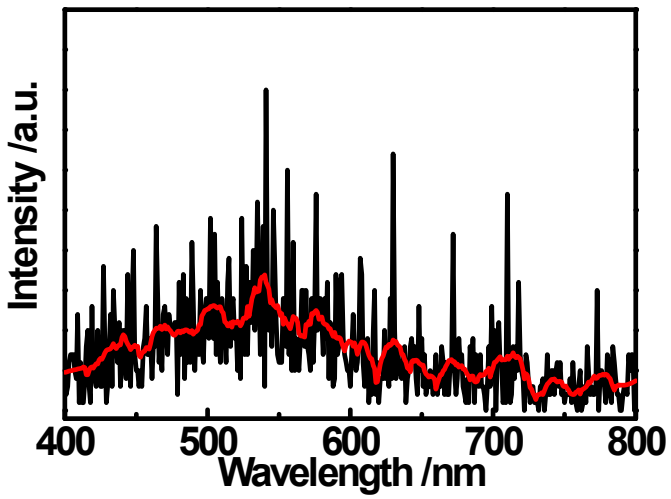

Fig. S3. The ECL responses of (Zn)porphMOF in the PBS containing 20 mM $K_2S_2O_8$ at the potential of -2.0 V.

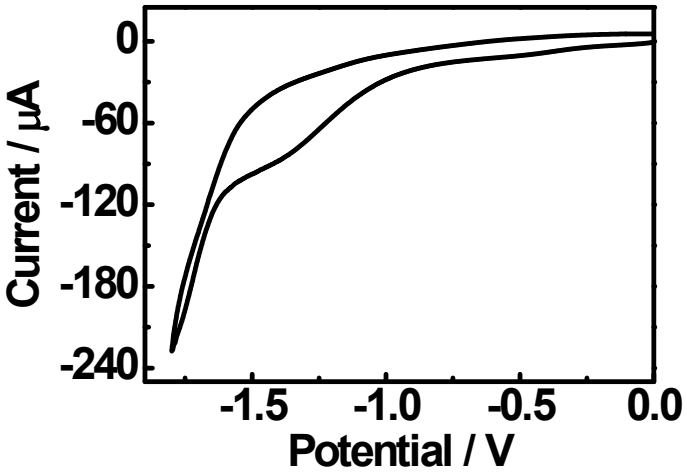

Fig. S4. The CV curve of (Zn)porphMOF in the air-saturated electrolyte.

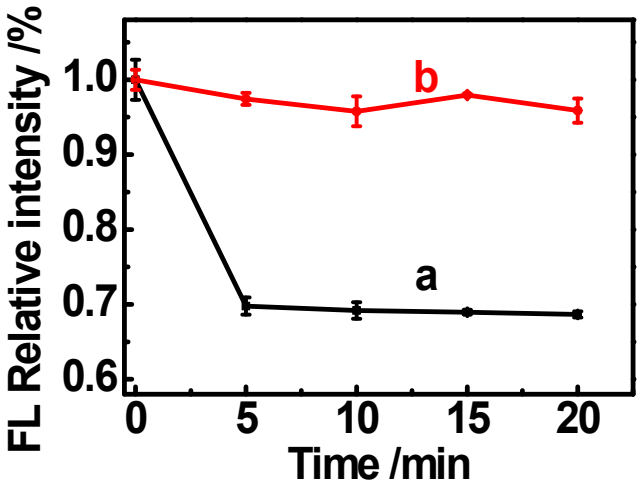

Fig. S5. The plots of the FL relative intensity *vs*. detection time of the Zn-TSPP (curve a) and (Zn)porphMOF (curve b).

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

Methods	**Linear ranges/**μM	**Detection limits/**μM	**References**
Fluorescent	1.5-10	0.2	1
Amperometry	568-5680	568	2
[a]DPV	100-1000	49.8	3
Colorimetry	5-30	3.6	4
ECL	3.77-26.4	0.29	This work

Note: [a]DPV stands for differential pulse voltammetry;

Table S2. The detection results of AA in the diluted serum samples (n = 4)

Samples	C_{Added} (μM)	C_{Found} (μM)	Recovery (%)	RSD (%)
1	1	0.966	96.6	2.6
2	1.5	1.46	97.3	4.9
3	1.8	1.76	97.8	3.9
4	2	2.05	102.5	2.9

References

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