

Ratiometric electrochemical detection of tryptophan based on ferrocene and carboxylated-pillar[6]arene hybrid metal-organic layers

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Supporting Information

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1. Materials and instruments

All solvents and chemical reagents were purchased from commercial reagents corporation and used without further purification. All aqueous solutions were prepared with ultrapure Milli-Q water ($\rho > 18.0 \text{ M}\Omega \text{ cm}^{-1}$).

The morphologies and compositions of the materials were characterized by transmission electron microscopy (TEM; FEI Tecnai G₂ F20, USA), atomic force microscopy (AFM; Bruker Dimension Icon, Germany). thermogravimetric analysis (TGA; NETZSCH STA 449F5, Germany), fourier transform infrared spectroscopy (FT-IR; Thermo Nicolet iS10, USA), 400M Hz nuclear magnetic resonance spectrometer (BUXI-I NMR; Zhongke Niujin, China) and ultraviolet-visible spectroscopy (UV-Vis; Agilent Technologies Cary 60 UV-Vis, USA). Zeta potential was passed through ZETASizer Nanolink SZ900 (Malvern, U.K.) for the measurement. Powder X-ray diffraction instrument (XRD; Bruker D8 ADVANCE, Germany) was used for obtaining the XRD patterns with Cu K α radiation.

The electrochemical measurements were performed on an electrochemical workstation (CHI 760E, Shanghai, China) with a standard three-electrode system, consisting of a glassy carbon electrode (GCE, 3 mm in diameter) as the working electrode, a platinum wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode.

2. Synthesis and characterization

Synthesis of WP6: the synthesis route has been reported by previous literatures.^{S1}
¹H NMR (400 MHz, CDCl₃) δ 6.78 (s, 10H), 3.77 (s, 10H), 3.66 (s, 30H).

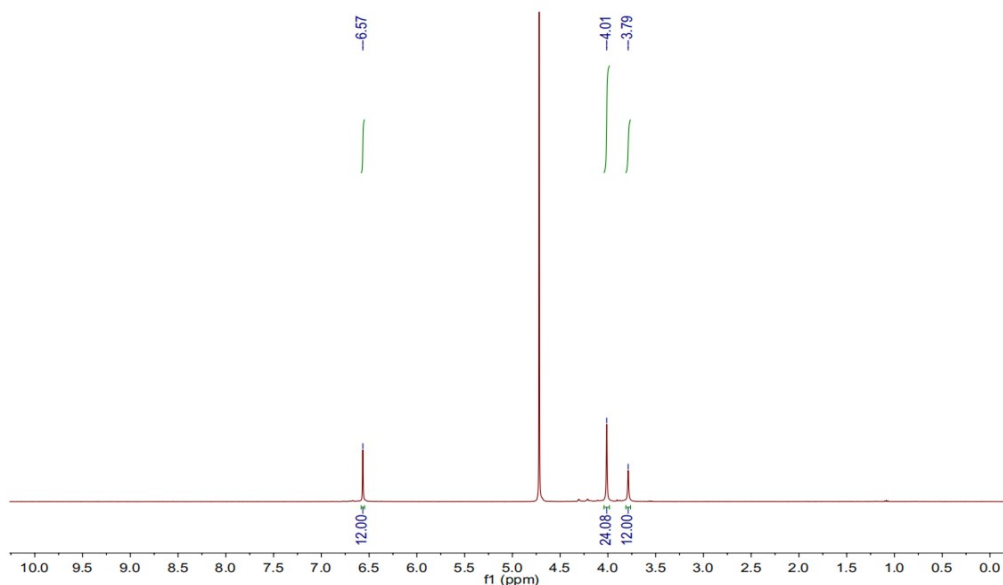


Figure S1. ¹H NMR spectrum (400 MHz, D₂O) of WP6.

Synthesis of Zr-MOL: the synthesis method has been reported by previous literatures.^{S2} ZrOCl₄·8H₂O (50 mg) and H₃BTB (62.5 mg) were added into a mixed solution containing DMF (7.5 mL), acetic acid (3.75 mL) and H₂O (0.75 mL) in a pressure tube. The mixture was kept at 120°C for 3 days. Then the mixture was centrifuged. The precipitate was washed with DMF and EtOH, and dried.

Preparation of Fc-MOL: 49.15 mg Zr-MOL was added into a ferrocenecarboxylic acid solution (2.4 mL, 0.1 M). The mixture was stirred at 60°C for 12 h. The mixture was centrifuged. The precipitate was washed with DMF and EtOH, and dried.

Preparation of WP6@Fc-MOL: 30 mg Fc-MOL and 30 mg WP6 was dispersed in water. And the mixture was sonicated and stirred at room temperature for 1 h. The mixture was centrifuged. The precipitate was washed with water and dried.

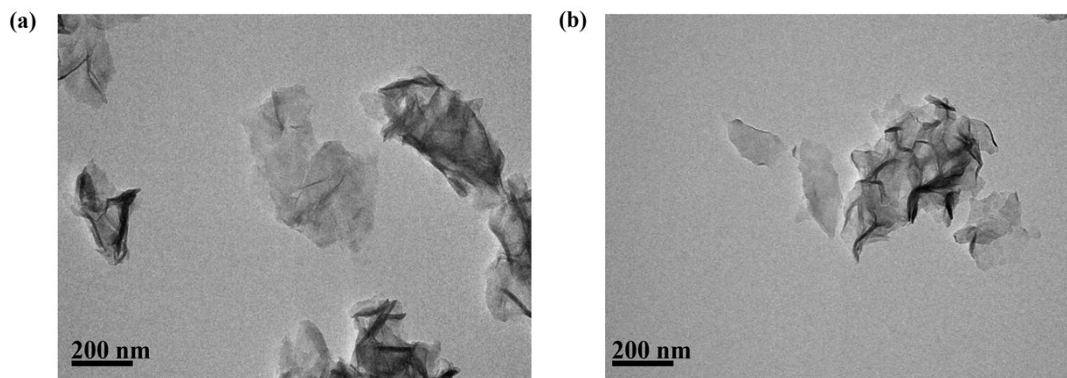


Figure S2. TEM images of Zr-MOL (a) and Fc-MOL (b).

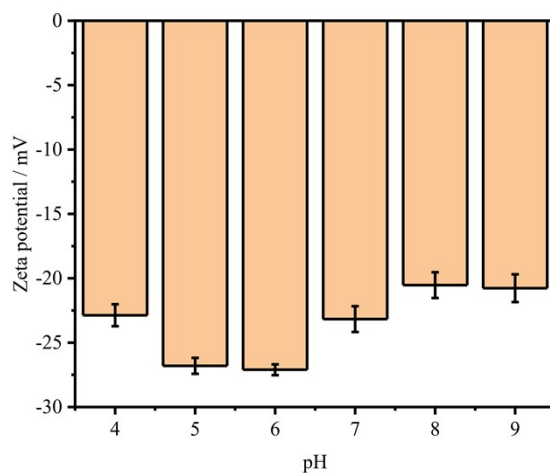


Figure S3. Zeta potential of WP6@Fc-MOL at different pH values.

Table S1. ICP-OES results of different samples.

Sample	Element	Content (wt%)
MOL	Zr	20.30 ± 0.200
FC-MOL	Zr	19.69 ± 0.094
WP6@FC-MOL	Zr	19.17 ± 0.022
FC-MOL	Fe	3.61 ± 0.100
WP6@FC-MOL	Fe	3.18 ± 0.026

3. Host-guest interaction between WP6 and tryptophan

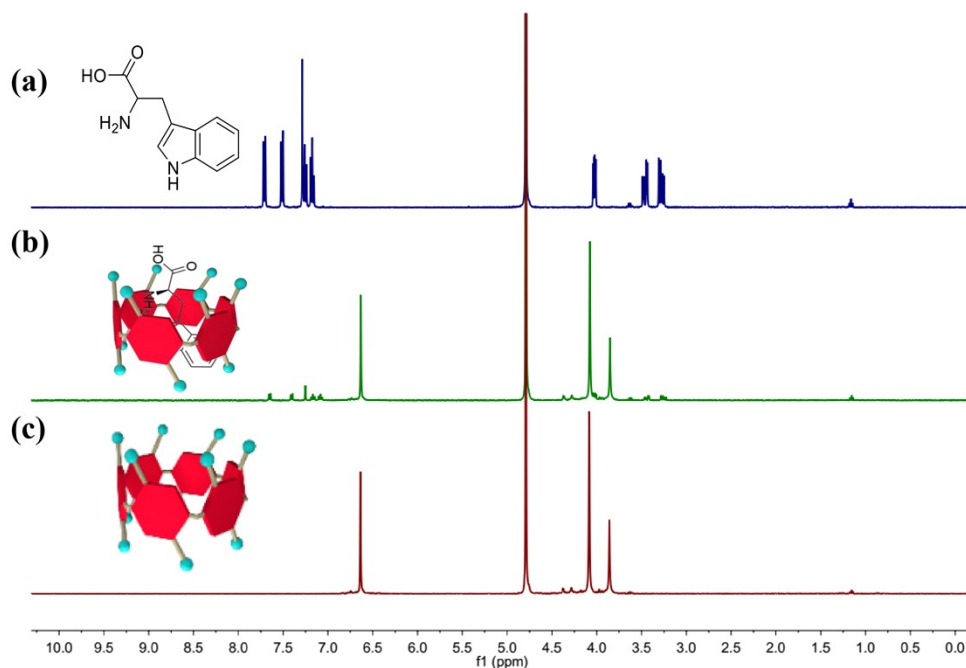


Figure S4. (a) ^1H NMR spectrum (400 MHz, D_2O) of 4.5 mM Trp , (b) 4.5 mM Trp + 4.5 mM WP6 and (c) 4.5 mM WP6.

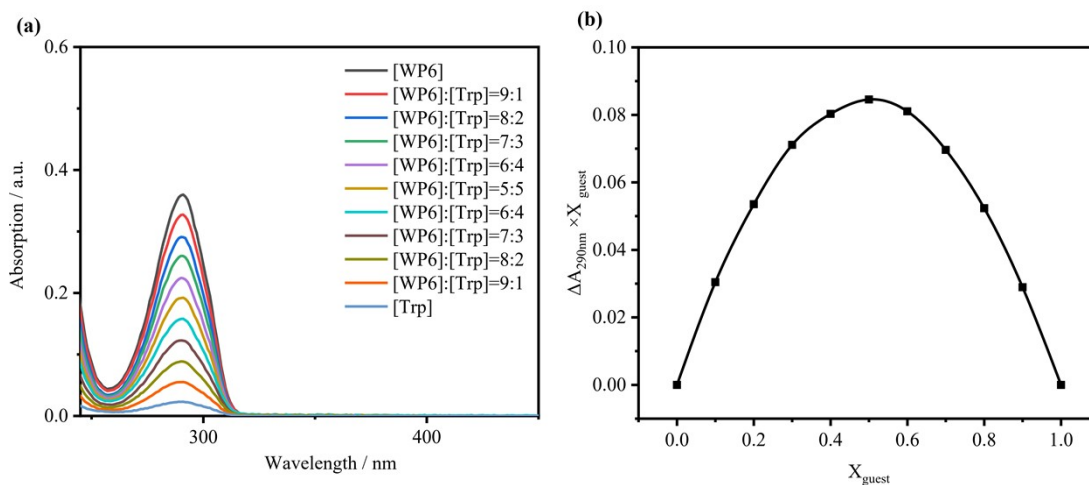


Figure S5. (a) UV-Vis absorption of WP6 and Trp in water at different molar ratios while $[\text{WP6}] + [\text{Trp}] = 1.0 \times 10^{-5} \text{ M}$. (b) Job plot showing the 1:1 stoichiometry of the complex between WP6 and Trp by plotting the difference in absorption at 290 nm (a characteristic absorption peak of WP6) against the mole fraction of Trp at an invariant total concentration of $1.0 \times 10^{-5} \text{ M}$ in aqueous solution.

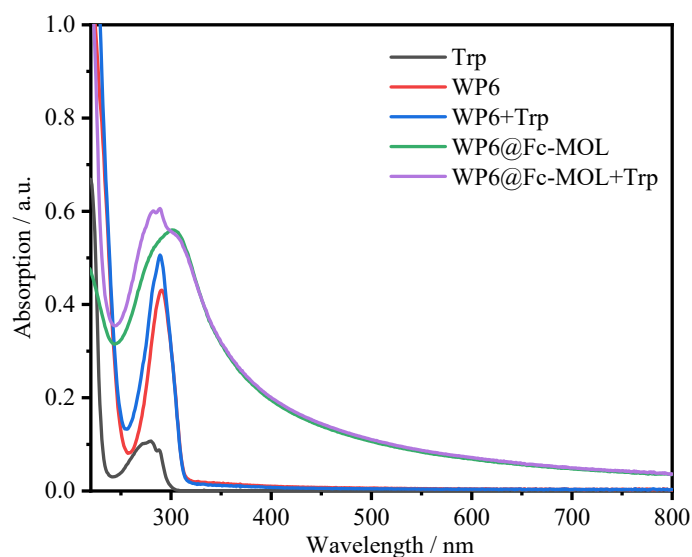


Figure S6. UV-vis spectra of Trp , WP6 ,WP6 + Trp ,WP6@Fc-MOL and WP6@Fc-MOL + Trp.

4. Preparation of electrodes

The bare GCE was initially polished with 1.0, 0.3 and 0.05 μm alumina slurries, followed by ultrasonication in deionized water and ethanol . Subsequently, after the polished GCE mirror surface was dried at room temperature, 7 μL WP6@Fc-MOL was dropped onto the surface of GCE. After drying at room temperature, 2 μL Nafion solution 0.05 wt% was added as a adhesive drops on the surface of the coated electrode, drying at room temperature. For comparison, other modified electrodes Nafion/Fc-MOL/GCE, Nafion/MOL/GCE, Nafion/GCE were obtained by the same method.

5. Electrochemical measurements

0.1 M phosphate-buffered saline (PBS, pH=6.0) was prepared by using Na_2HPO_4 and KH_2PO_4 , which was used in all electrochemical measurements. Square wave voltammetry (SWV) measurements were performed with the following parameters: potential scan from 0.1 to 1.0 V, increment = 0.004 V, Amplitude = 0.025 V,

Frequency = 15 Hz and quiet time = 60 s. Before measurement, the solution was thoroughly deaerated with nitrogen. The electrochemical properties of bare GCE and different modified electrode were analyzed by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) methods in 5 mM $K_3[Fe(CN)_6]$ solution containing 0.1 M KCl. The scan range of CV was from -0.2 to 0.6 V with a scan rate of 50 mVs^{-1} . CV measurements were performed at different scan rates in PBS (0.1 M, pH 6.0). EIS plots were recorded at a bias potential of 0.18 V vs SCE and 5 mV amplitude in the frequency ranging from 0.01 Hz to 100 kHz.

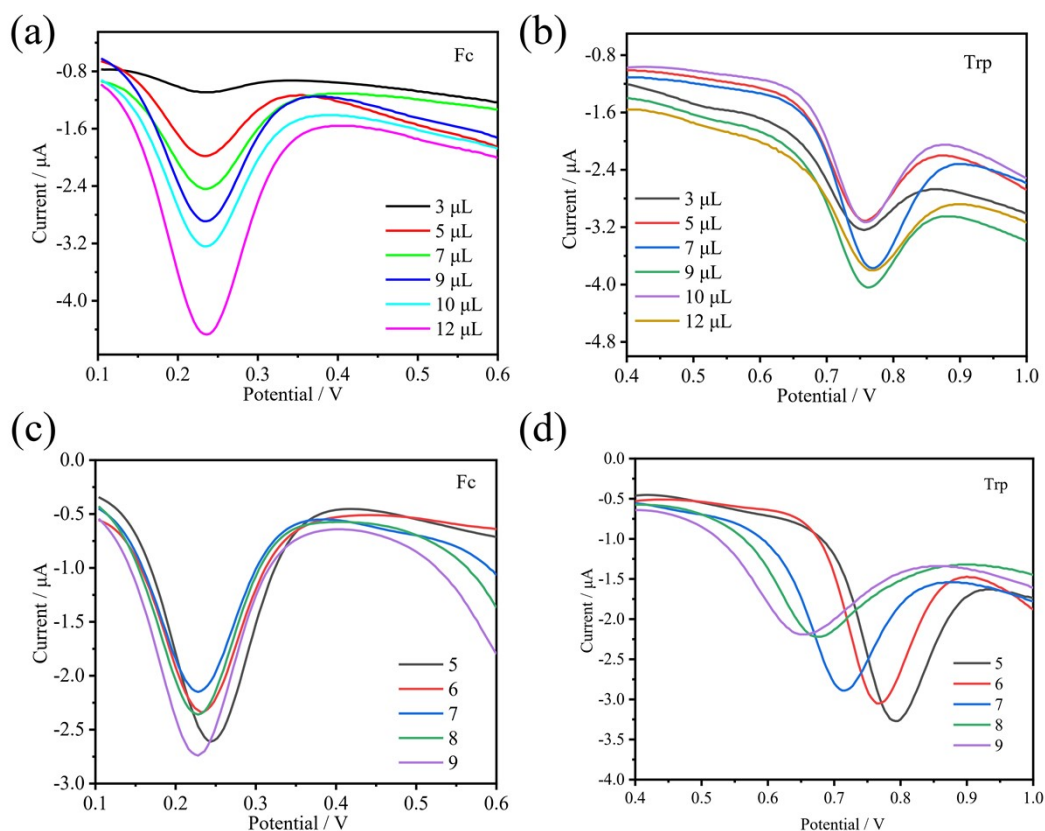


Figure S7. (a, b) Signal responses of Nafion/WP6@Fc-MOL/GCE for Fc and Trp in 0.1 M PBS (pH=6.0) upon different drip coating levels. (c, d) SWV responses of Nafion/WP6@Fc-MOL/GCE for Fc and Trp in 0.1 M PBS under different pH conditions.

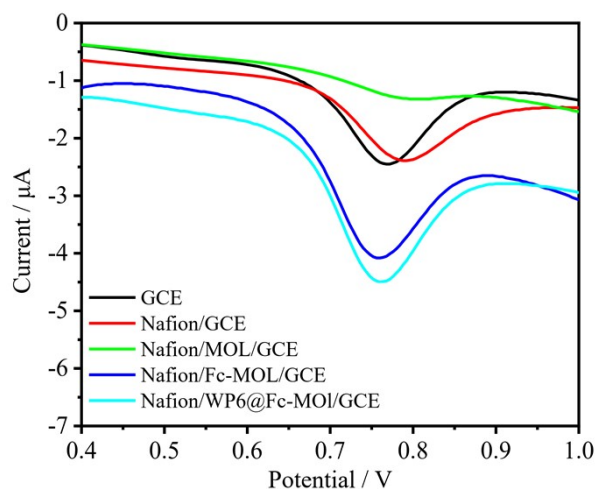


Figure S8. SWV responses of different electrodes in 0.1 M PBS (pH=6.0) containing 50 μM Trp.

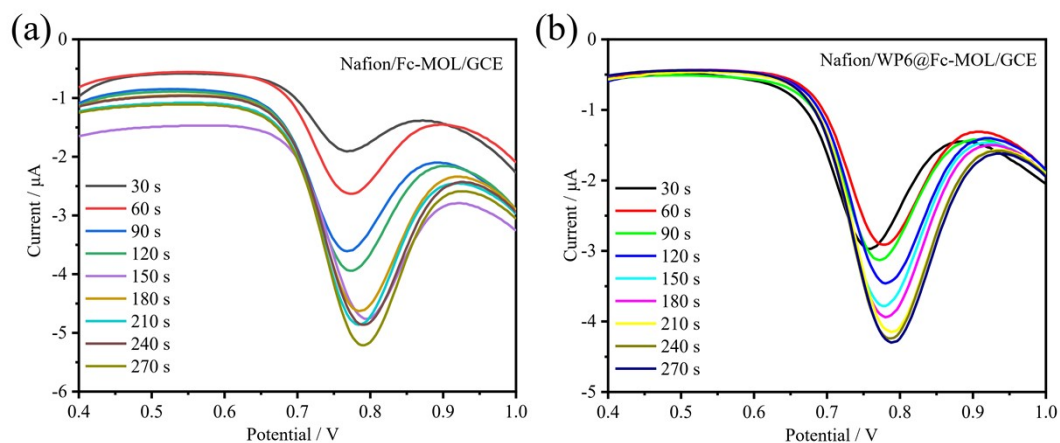


Figure S9. SWV responses of (a) Nafion /FC-MOL/GCE and (b) Nafion/WP6@Fc-MOL/GCE in 0.1 M PBS (pH=6.0) after the addition of 50 μM Trp for different time points.

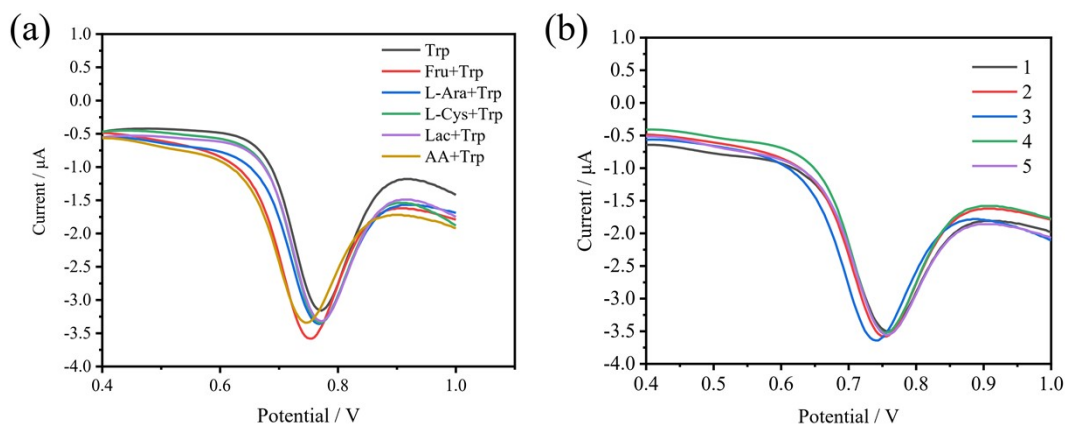


Figure S10 (a) SWV responses of 50 μM Trp and Trp containing excess other potential interfering biomolecules (Lac: Lactose; L-Cys: L-Cysteine; Ara: Arabinose; Fru: Fructose; AA: Ascorbic acid) at Nafion/WP6@Fc-MOL/GCE; (b) Current responses of 5 independent Nafion/WP6@Fc-MOL/GCEs in 0.1 M PBS (pH 6.0) containing 50 μM Trp. RSD=2.88% (n=5).

6. Real samples analysis

The real samples analysis was carried out by examining the SWV of Trp in the milk samples. The milk was purchased from a local market. The milk samples were diluted 500 times with PBS and then were used for the detailed measured.

7. References

S1. G. Yu, M. Xue, Z. Zhang, J. Li, C. Han and F. Huang, *Journal of the American Chemical Society*, 2012, **134**, 13248-13251.

S2. Z. Wang, Y. Liu, Z. Wang, L. Cao, Y. Zhao, C. Wang and W. Lin, *Chemical Communications*, 2017, **53**, 9356-9359.