Electronic Supplementary Material (ESI) for Analyst.

Molecularly imprinted polypyrrole electrochemiluminescence sensor based on a novel zinc-based metal-organic framework and chitosan for the determination of enrofloxacin

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Contents

Reagents and materials

Zinc nitrate, sodium hydroxide, potassium hydroxide, and ethanol were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Pyrrole (Py), 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA), enrofloxacin (ENR), norfloxacin (NOR), and tetracycline (TC) were purchased from Aladdin Ltd. (Shanghai, China). N, N-dimethylformamide (DMF), sodium phosphate dibasic dihydrate, and disodium hydrogen phosphate dodecahydrate were received from Lingfeng Chemical Reagent Co., Ltd. (Shanghai, China). Ciprofloxacin (CIP), potassium ferricyanide, and potassium ferrocyanide trihydrate were obtained from Sarn Chemical Technology Co., Ltd. (Shanghai, China). Chloramphenicol (CAP) was purchased from Sangon Biotech Co., Ltd. (Shanghai, China). Acetic acid was received from Shenbo Chemical Co., Ltd. (Shanghai, China). All drugs were analytical grades and the solutions were prepared in ultrapure water (>18 MΩ).

Scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) were analyzed by the JEOL scanning electron microscope (JSM-6360LA, Japan). Fourier transform infrared spectroscopy (FT-IR) was studied by the Nicolet In10 equipment (Thermo Fisher Scientific, USA). X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were respectively analyzed by the Max-2000 (Rigaku Co., Ltd., Japan) and AXIS-Ultra DLD (Shimazu, Japan). Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and differential pulse voltammetry (DPV) were carried out on a CHI 660E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd.). Electrochemiluminescence (ECL) was performed on the LK5100Plus multifunctional ECL system (Lanlike Chemical Electronic High Technology Co., Ltd., Tianjin, China). A traditional three-electrode system consisted of the modified GCE (φ = 3 mm) as the working electrode, a platinum foil as the auxiliary electrode, and an Ag/AgCl electrode as the reference electrode.

Preparation of Zn-PTC

A typical hydrothermal method was used to synthesize Zn-PTC according to the reported method and with some modifications [1,2]. As follows, 0.39 g of 3,4,9,10-perylene tetracarboxylic anhydride (PTCDA) and 0.28 g of KOH were dispersed in 5 mL of ultrapure water and stirred at 60 ° C for 10 hours. Further, the golden yellow intermediate, K_4PTC, was precipitated after 30 mL of ethanol added. Mixed the prepared K_4PTC (0.05 mmol/L) with 15 mL of $Zn(NO)_3$ aqueous solution (7 mmol/L) and stirred for 1.0 hours. The mixed suspension was subsequently transferred to the 50 mL PTFE autoclave and heated at 100 ℃ for 12 hours. The reaction products obtained were collected by successively washing in methanol and deionized water. After centrifuged under 10000 rpm, dried in a vacuum at 60 ℃ for 12 h, and ground into powder in a mortar, the orange Zn-PTC powder was obtained.

Preparation of CHIT solution

CHIT solution was prepared according to the previous work [3,4]. Briefly, 0.25 g of chitosan powder was dissolved in 1.0 wt% acetic acid solution and ultrasonically dispersed for 3 h to form a mixed CHIT solution. Subsequently, the prepared CHIT solution was stored at a low temperature for later use.

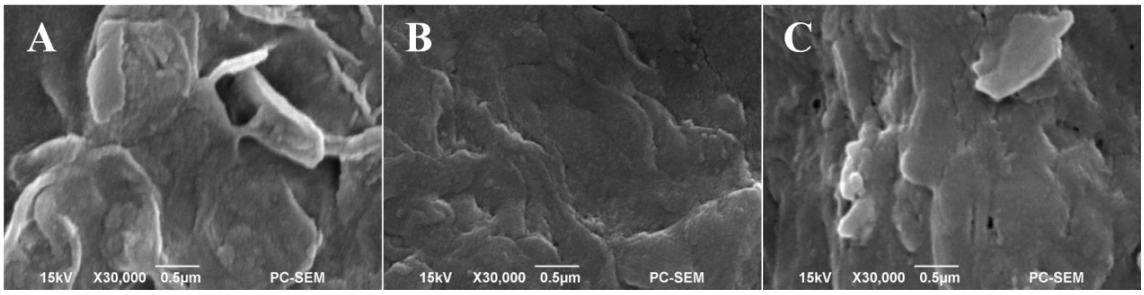

Fig. S1. The SEM morphologies of CHIT/Zn-PTC/GCE (A); Ppy-MIP-ENR/CHIT/Zn-PTC/GCE (B); Ppy-MIP/CHIT/Zn-PTC/GCE (C).

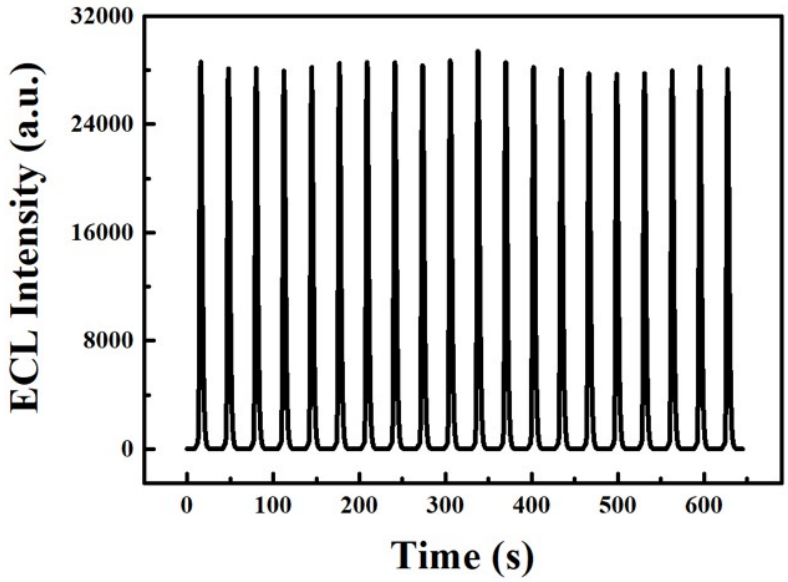

Fig. S2. The ECL stability of CHIT/Zn-PTC/GCE under continuous scanning for 20 cycles at a potential range of -1.7~0 V.

The CHIT was used to immobilize the modified electrodes owing to the film-making capability. In addition, due to the positive charges of chitosan, the electrode surface could attract more peroxydisulfate to amplify the ECL signal [5]. The ECL signal of the Ppy-MIP/CHIT/Zn-PTC/GCE and Ppy-MIP/Zn-PTC/GCE were explored under continuous scanning for 10 cycles at a potential range of - 1.7 ~ 0 V, the results were shown in Fig.S3. Thanks to the film-making capability of CHIT, the Ppy-MIP/CHIT/Zn-PTC/GCE represents more stable and higher ECL signal.

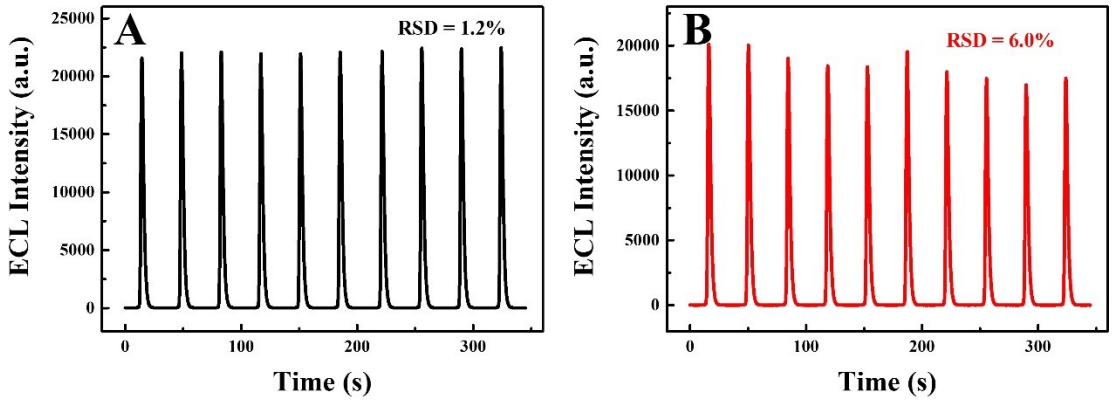

Fig. S3 ECL signal of the Ppy-MIP/CHIT/Zn-PTC/GCE (black) and Ppy-MIP/Zn-PTC/GCE (red) under continuous scanning for 10 cycles at a potential range of - 1.7 ~ 0 V.

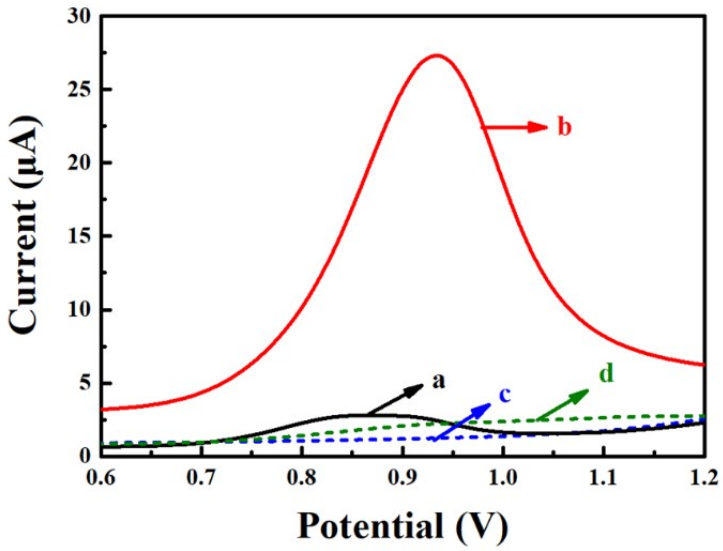

Fig. S4. DPV curves of bare GCE (a), and Ppy-MIP/CHIT/Zn-PTC/GCE (b) detected in 0.05 mol/L PBS containing 1×10^{-4} mol/L ENR, DPV curves of bare GCE (c) and Ppy-MIP-ENR/CHIT/Zn-PTC/GCE (d) detected in 0.05 mol/L blank PBS.

Controlling the thickness of the polymer film is one of the biggest advantages of electropolymerization. The imprinting cavities formed on the electrode surface are too few under lower scan cycles. The polymer film is too thick and the imprinted molecules are difficult to elute under higher scan cycles. For this reason, different scanning numbers from 5 to 30 were explored to ensure the optimal electropolymerization cycles (Fig. S5A). The generated Ppy film is unstable when the scanning cycles are lower than 15 and the ΔECL reaches its maximum at 15 cycles. Therefore, the optimal electropolymerization cycle is 15.

The pH value of the electropolymerization solution not only affects the polymerization of Py but also affects the interaction between Py and ENR molecules. the ΔECL intensity of the sensor was investigated with a pH value in the range of 4.0~9.0. As shown in Fig. S5B, the ΔECL intensity increases gradually and reaches its maximum as the pH changes from 4.0 to 7.0. Therefore, the optimal pH value for the electropolymerization solution is 7.0.

The extraction time of ENR is critical because it ensures the sufficient elution of ENR molecules away from the electrode surface. So, the elution procedure of the Ppy-MIP/CHIT/Zn-TC/GCE in the eluent was investigated from 5 to 25 minutes. As shown in Fig. S5C, the ΔECL intensity reached its maximum value when the elution time was set to 10 minutes. Subsequently, the ΔECL value decreased gradually with the elution time increased. This phenomenon could be due to the alkaline eluent breaking the structure of the specific imprinted cavities. Therefore, the optimal elution time of ENR is 10 minutes.

To promote the full adsorption of the target molecule on the electrode surface, the rebinding time of the ENR was optimized. As shown in Fig. S5D, the ΔECL value increased gradually and reached its maximum at 15 minutes, owing to the charge transfer between $K_2S_2O_8$ in the solution and the luminous body on the sensing interface was inhibited with the ENR molecules reoccupying the specific ENR cavities. Therefore, the optimal rebinding time of ENR is 15 minutes.

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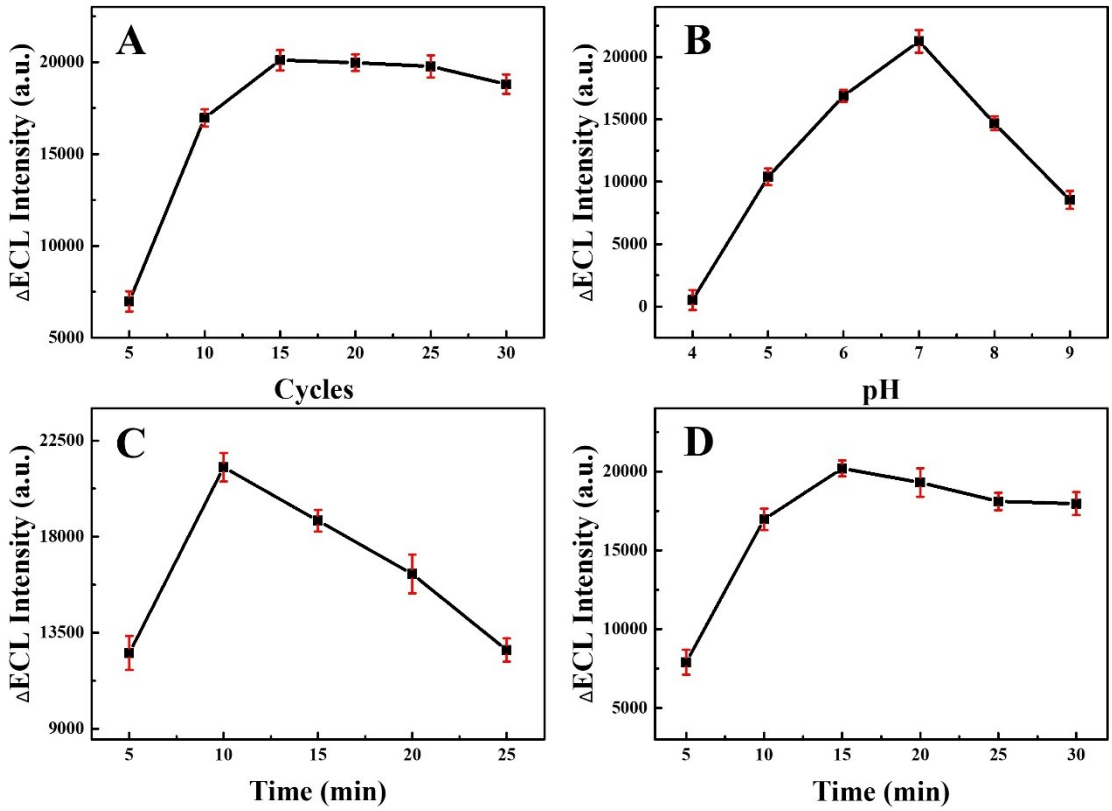

Fig. S5. The optimization of experimental conditions: the electropolymerization cycles (A); the pH of the electropolymerization solution (B); the extraction of ENR (C); and the rebinding time of ENR (D).

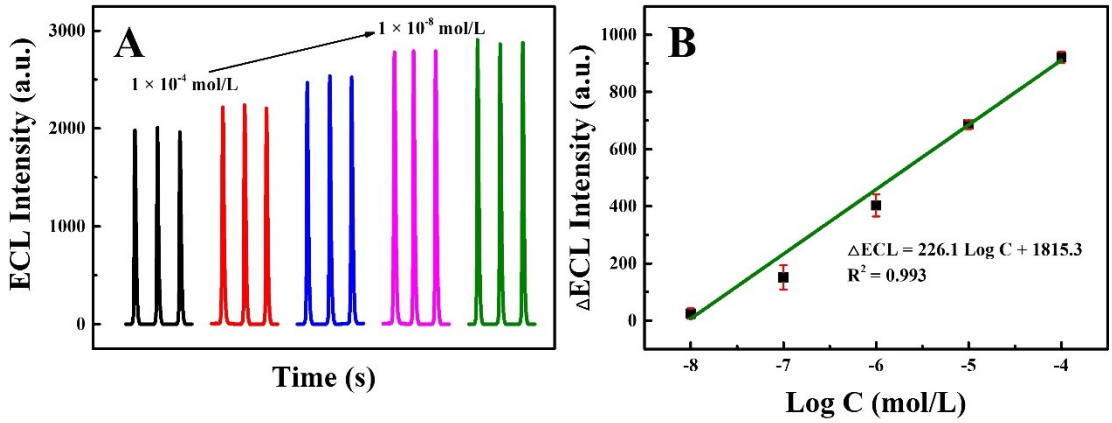

Fig. S6 (A) ECL-Time curve diagram of Ppy-NIP/CHIT/Zn-PTC/GCE and (B) Linear relationship between the ECL responses of Ppy-NIP/CHIT/Zn-PTC/GCE and the different concentrations of ENR (from 1.0×10^{-8} to 1.0×10^{-4} mol/L). Error bars, n = 3.

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