Supplementary Information (SI) for Analyst.

Synchronous Dual-Mode Sensing Platform Based on 1D Chiral Ionic COF for Epoxiconazole Detection

Yeqian Ruan[a], Xiaodong Zheng[b], Xuan Kuang[a*] and Shusheng Li[a*]

a Key Laboratory of Interfacial Reaction & Sensing Analysis in Universities of Shandong, School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, China.

b All China Federation of Supply & Marketing Cooperatives Jinan Fruit Research Institute, Jinan, 250014, China

E-mail: chm_kuangx@ujn.edu.cn (Xuan Kuang), chm_Liss@ujn.edu.cn (Shusheng Li).

Contents

S1. Experimental section

Reagents and Apparatus. The reagents obtained from commercial sources were used directly without further purification. All of the reagents are analytical grade. 3,4,9,10-perylenetetracarboxylic dianhydride, (R)-(-)-2-Methylpiperazine, imidazole, difenoconazole, imidacloprid, propiconazole, cypermethrin, permethrin, methomyl, heptachlor, thiamethoxam, iprodione, potassium dihydrogen phosphate (KH_2PO_4), disodium hydrogen phosphate (Na_2HPO_4) and potassium chloride (KCl) were purchased from Sigma Aldrich (Shanghai, China). Phosphate buffers (PBS) of 0.1 M at different pH values were prepared using 0.1 M KH_2PO_4 and Na_2HPO_4. All aqueous solutions were prepared with ultrapure water with a resistance of 18.2 MΩ.

Instruments. The scanning electron microscope (SEM) images were characterized using a 15.0 kV Gemini300 (Germany) electron microscope produced by Zeiss. The powder X-ray patterns (PXRD) of the samples were measured at room temperature (298 K) using Cu Kα radiation ($\lambda = 1.5418$ A) on a difftometer based on Bruker SMART APEX charge-coupled device (CCD) (D8 FOCUS, Germany). This instrument is produced by BRUKER AXS GMBH. Electrochemical impedance spectroscopy (EIS) measurements were carried out on the RST5200F (Xi 'an, China) electrochemical workstation produced by Zhengzhou Shirui, in a 0.1M KCl solution containing Fe (CN) ${}_6{}^3$ (${}^{-}/{}^{4}$), with a scanning frequency range of 1 to 10 5 Hertz. ECL measurements were performed on an HYZ-3002 ECL analyzer obtained from Zhengzhou Shirui Instrument Technology Co., Ltd (Xi'an, China). The experimental parameters are as follows: a photomultiplier voltage of 550 V, a scan rate of 200 mV s^{-1}, and a potential ranging from 0 to −1.6 V (vs Ag/AgCl). The ultraviolet-visible spectral characterization was carried out using the TU-1901 (Beijing, China) double-beam ultraviolet-visible spectrophotometer produced by Beijing Puxi General Instrument Co., LTD.

Fabrication Process of the ECL Sensor. Selective determination is carried out in a three-electrode system, which has the best sensitivity and specificity. Glassy carbon electrode (GCE) with the working electrode modified by (R)-PTCDA-RMP. A 4 mm GCE was subjected to a meticulous polishing procedure using 0.05 μm α-Al_2O_3 polishing powder to achieve a mirror-like finish. Post-polishing, the electrode was meticulously cleaned through an ultrasonication process in a sequence of ultrapure water and ethanol baths, followed by gentle drying at ambient temperature. For the preparation of the modification solution, 3 mg of (R)-PTCDA-RMP covalent organic framework (COF) was accurately weighed and dispersed in N,N-dimethylformamide (DMF) to form a homogeneous solution with a concentration of 3 mg·mL^{-1}. This solution was then sonicated to ensure uniform dispersion of the COF. Subsequently, 8 μL of this well-dispersed solution was carefully cast onto the surface of the GCE, allowing it to air-dry at room temperature. Finally, the electrode was rinsed with ultrapure water to remove any non-specifically adsorbed material, ensuring a clean and well-defined sensing interface.

ECL Agricultural Residue Detection. Selective determination is carried out in a three-electrode system, which has the best sensitivity and specificity. The working electrode is (R)-PTCDA-RMP modified GCE, and the preparation method is described above. The silver chloride electrode was used as the reference electrode, and the platinum wire electrode was used as the auxiliary electrode. The electrochemical measurements were performed in optimized electrolyte systems: for ECL measurements, 0.1 M phosphate-buffered saline (PBS, pH 8.04) containing 0.1 M potassium persulfate ($K_2S_2O_8$) as a coreactant was employed, while DPV measurements utilized 0.1 M PBS (pH 7.38) with 0.1 M KCl as supporting electrolyte. Before each measurement, the modified working electrode was evenly coated with 5 μL of fluocyclozole solution with a certain concentration, and then evaporates naturally and is fixed on the electrode surface. ECL measurements are carried out under standardized conditions, with photomultiplier tubes operating at a high voltage of 550 V, with a potential sweep range of 0 to -1.6 V and a scan rate set to 0.2 mV/s and the DPV measurements were conducted under optimized parameters with an applied potential range from 0.25 to -1.25 V, employing a pulse amplitude of 50 mV and a potential increment of 4 mV to ensure consistency and repeatability of results.

S2. UV-Vis spectrum.

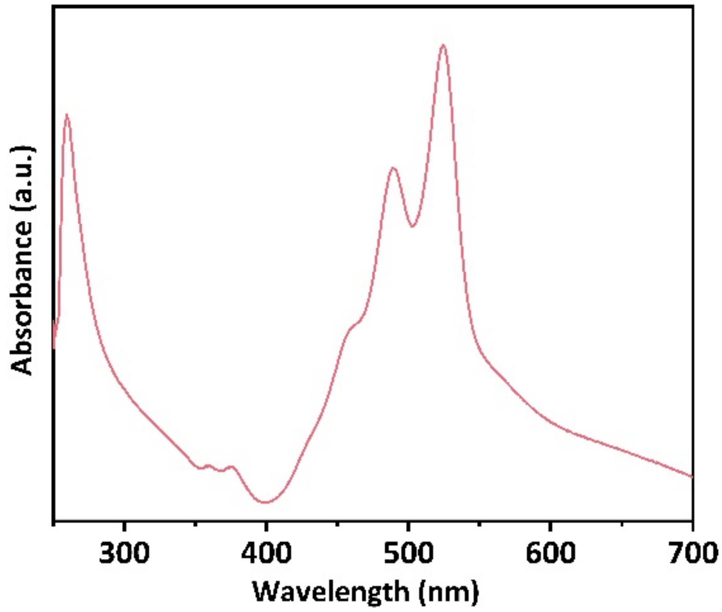

Fig S1. UV-Vis spectrum of (R)-PTCDA-RMP.

S3. CVs and EISs of different modified electrodes.

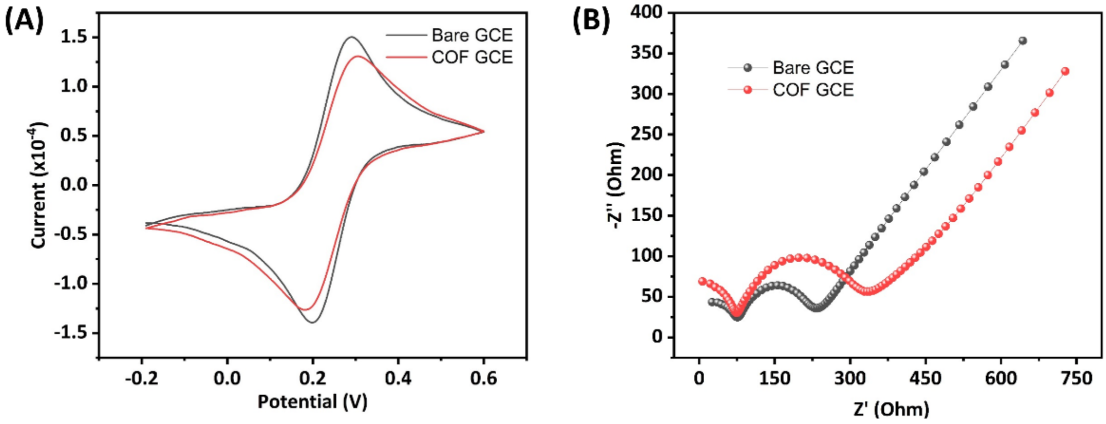

Fig S2. (A) CVs of bare GCE, COF-GCE. (B) EIS of bare GCE and COF-GCE.

S4. (R)-PTCDA-RMP GCE at varied scan rates.

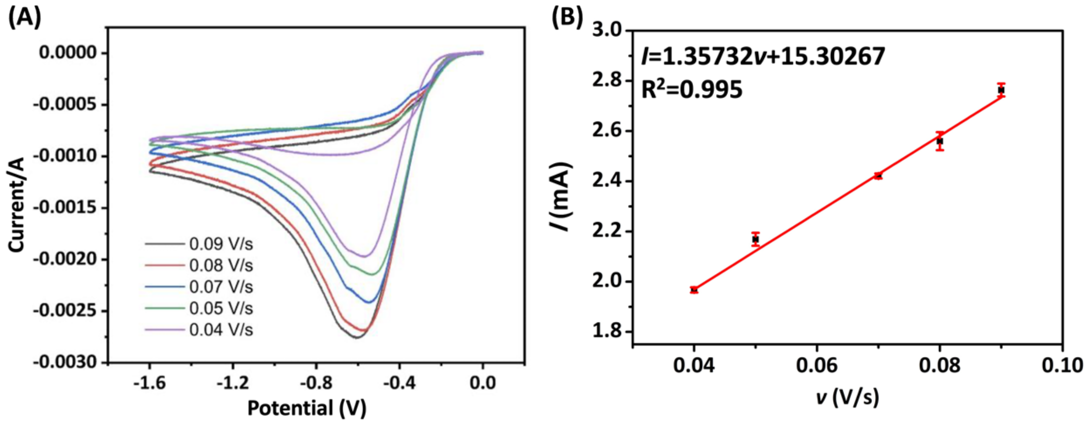

Fig S3. CV curves of (R)-PTCDA-RMP GCE at varied scan rates (A). Linear regression equation plot of (R)-PTCDA-RMP (B). (5 mM $[Fe(CN)_6]^{4-/3-}$, error bars = SD, n = 3).

S5. Experimental condition optimization.

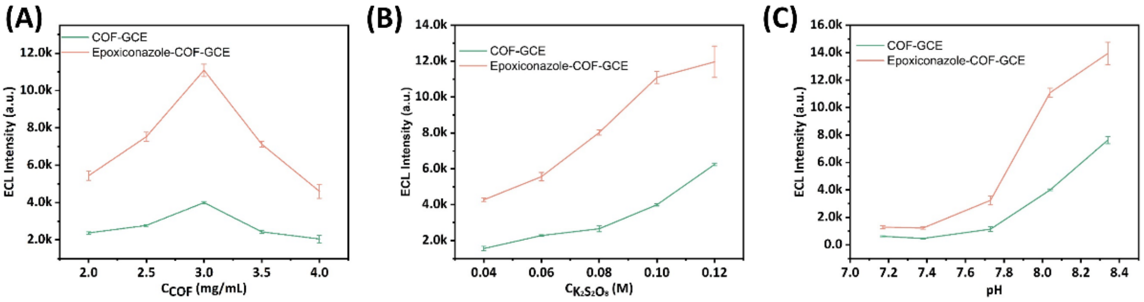

Fig S4. Influence of the concentration of (R)-PTCDA-RMP (A), concentration of $K_2S_2O_8$ (B) and pH (C).

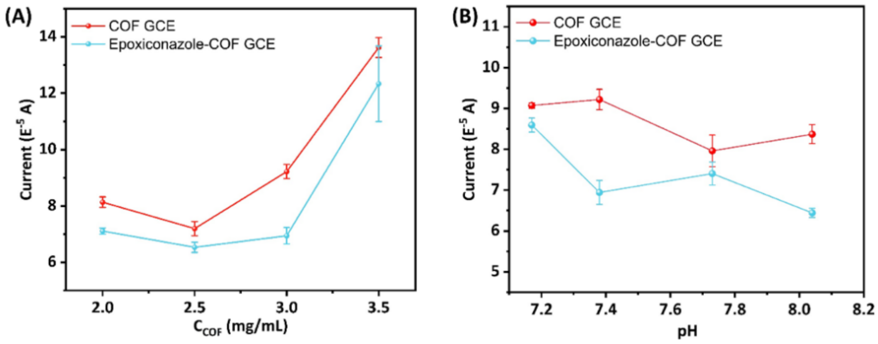

Fig S5. Influence of the concentration of (R)-PTCDA-RMP (A) and pH (B).

S6. Mechanisms of DPV-ECL interaction in the (R)-PTCDA-RMP sensor.

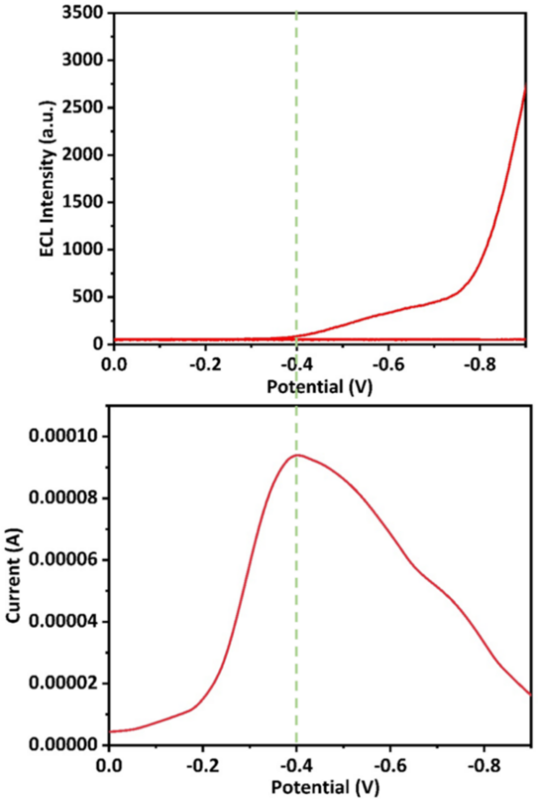

Fig S6. Mechanisms of DPV-ECL interaction in the (R)-PTCDA-RMP sensor.

S7. Specific recognition and detection.

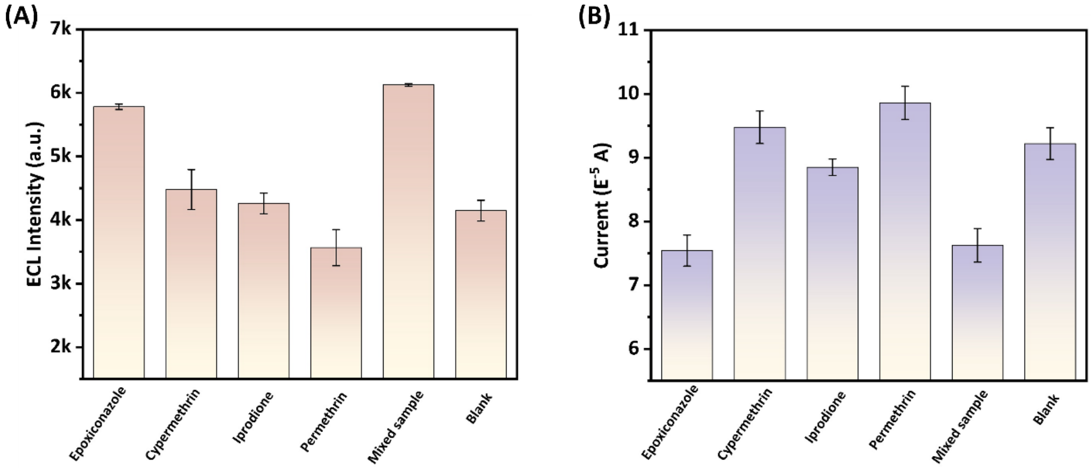

Fig S7. (A) ECL intensity and (B) DPV intensity with Epoxiconazole for (20 µg/L), (b) Cypermethrin (20 µg/L), Iprodione (20 µg/L), Permethrin (20 µg/L), Mixtures and blank.

S8. Consistency between DPV and ECL response.

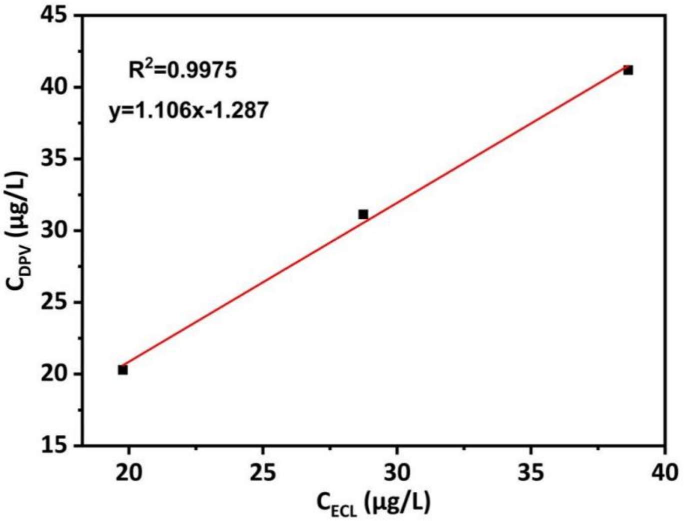

Fig S8. Consistency between DPV and ECL response in the (R)-PTCDA-RMP sensor.

Table S1. Comparison of detection methods.

Methods	Recovery (%)	Linear range (μM/L)	LOD (nM)
DPV	96-99.7	5-80	746[1]
DPV	-	0.08-50	27[2]
DPV	100.9-105.5	0.1-35	38[3]
DPV	94.92-104.73	3.0-120	240[4]
ECL	94.21-99.63	$3.03\text{x}10^{-5}$-3.03	6.71[5]
ECL-DPV	95.3-101.45、103-103.8	0.05-1 mM	0.6、16.4 (This work)

Reference

[1] L. Lan, B. Li, X. M. Chen, Y. K. Gao, X. Kuang, *ChemNanoMat*, 2023, 9(6):n/a-n/a.

[2] Y. Zhou, Y. Li, P. Han, Y. Dang, M. Zhu, Q. Li, *New J. Chem*. 2019, 43, 14009-14019.

[3] R. Cui, D. Xu, X. Xie, Y. Yi, Y. Quan, M. Zhou, J. Gong, Z. Han, G. Zhang, *Food Chemistry* 2017, 221, 457-463.

[4] X. Gao, Y. Gao, C. Bian, H. Ma, H. Liu, *Electrochimica Acta*, 2019, 310, 78-85.

[5] Z. Yu, C. Li, J. Sun, X. Sun, G.Hu, *Foods*, 2023, 12(23): 4363.