SUPPLEMENTARY MATERIAL

The potential of MOF accelerator in electrochemiluminescence system for sensitivity detection of menthol enantiomers

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1. Experiment section

1.1 Reagents and Apparatus. The reagents were obtained from commercial sources and used directly without further purification. The reagents are analytical grade. $CdCl_2 \cdot 2.5H_2O$, $Na_2S \cdot 9H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, Triethylamine (TEA), 2-Methylimidazole (Hmim), L-aspartic acid (L-Asp), L-/D-menthol (L-/D-Men), L-/D-tyrosine (L-/D-Tyr), L-/D-arginine (L-/D-Arg), L-/D-tryptophan (L-/D-Trp), L-/D-glutamic acid (L-/D-Glu), L-/D-proline (L-/D-Pro), L-/D-threonine (L-/D-Thr), L-/D-histidine (L-/D-His), L-/D-serine (L-/D-Ser), L-/D-methionine (L-/D-Met), R-/S-mandelic acid (R-/S-Man), L-/D-phenylalanine (L-/D-Phe), L-/D-valine (L-/D-Val), L-/D-alanine (L-/D-Ala), L-/D-carnitine (L-/D-Car), L-/D-penicillamine (L-/D-PA), R-/S-naproxen (R-/S-Nap), potassium dihydrogen phosphate (KH_2PO_4), disodium hydrogen phosphate (Na_2HPO_4) and potassium chloride (KCl) were purchased from Sigma Aldrich (Shanghai, China). Methanol and ethanol were obtained from Tianjin Fuyu Fine Chemical Co, Ltd. All aqueous solutions were prepared with ultrapure water (DW, 18.25 MΩ.cm).

Scanning electron microscopy (SEM) images were characterized by a FEI QUANTA FEG250 transmission electron microscope at 15.0 kV. Powder X-ray patterns (PXRD) of samples were measured on a Bruker SMART APEX chargecoupled device (CCD)-based diffractometer using Cu Kα radiation (λ = 1.5418 Å) at room temperature (298 K). Fourier transform infrared (FT-IR) spectroscopy (KBr pellets) of materials was recorded on a Nicolet iS50 spectrometer. Electrochemical impedance analysis (EIS) was carried out in 0.1 M KCl aqueous solution containing $Fe(CN)_6^{3-/4-}$ as a redox marker with

scanning frequencies ranging from 1 to 10^5 Hz. ECL measurements were performed on an HYZ-3002 ECL analyzer obtained from Zhengzhou Shirui Instrument Technology Co., Ltd (Xi'an, China), and the experimental parameters were listed as follows: a photomultiplier voltage of 500 V, a scan rate of 200 mV s^{-1}, and a potential ranging from −1.6 to 0 V (vs Ag/AgCl).

1.2 Characterisation of Circular dichroism spectra. To further validate the adsorption of Men isomers by cyclodextrins, we continued to characterise the experiments with Circular dichroism (CD). Two portions of β-CD (10 mM) were taken and dissolved in water, followed by the addition of an equal amount of aqueous L-/D-Men (10 mM) solution dissolved in water, respectively, and after twenty minutes of adsorption, the β-CD was rotary distilled and washed with EtOH to remove any remnants adsorption. After drying, equal amounts of the above solid and β-CD (1 mg/mL) were dissolved in water and their CD signals were measured.

1.3 The calculation of ECL efficiency. The calculation of ECL efficiency. The ECL value refers to the ECL efficiency of $Ru(bpy)_3Cl_2/K_2S_2O_8$ using the following formula[1-3]:

$$\Phi_{ECL} = \frac{\left(\frac{\int ECL\,dt}{\int current\,dt}\right)_x}{\left(\frac{\int ECL\,dt}{\int current\,dt}\right)_{st}} \times 100\%$$

where "ECL intensity" and "current" represent the integration of ECL intensity and electrochemical current value from the cumulative ECL spectrum,

respectively, and "st" refers to the standard $Ru(bpy)_3Cl_2/K_2S_2O_8$. Specifically, Φ_{st} is the ECL efficiency of 1 mM $[Ru(bpy)_3]^{2+}$ in 0.1 M $K_2S_2O_8$/PBS, which is be regarded as a standard, taken as 5.0%. According to calculations, the calculated ECL efficiency of the β-CD/L-CdS QDs/L-His-ZIF-8 system was 34.7%.

1.4 The calculation of detection limit. An ECL measurement for blank samples was implemented with ten parallel tests, which exhibited an average ECL intensity (I_B) of 17416 with a standard deviation (S_B) of 28.2. k was a numerical factor chosen according to the signal-to-noise ratio value and a value of 3 for it in the equation was strongly recommended. Therefore, the smallest detectable signal (I_L) could be calculated as follows:

$$I_L = I_B - k^* S_B$$

After that, by substituting I_L (17430.2) into the standard curve equation, the lowest detection limit of both L-Men and D-Men can be calculated, which was 0.046 μM.

2. Figure and Table

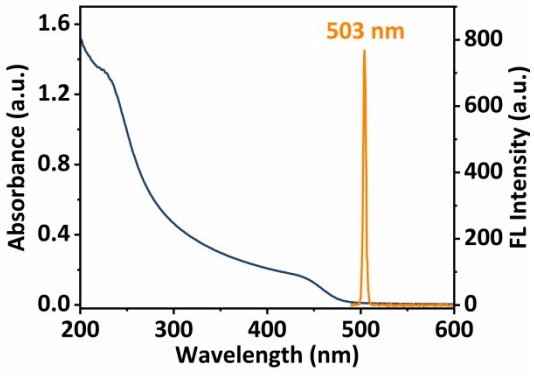

Figure S1. UV-vis absorption (blue) and FL emission spectrum (orange) of L-CdS QDs.

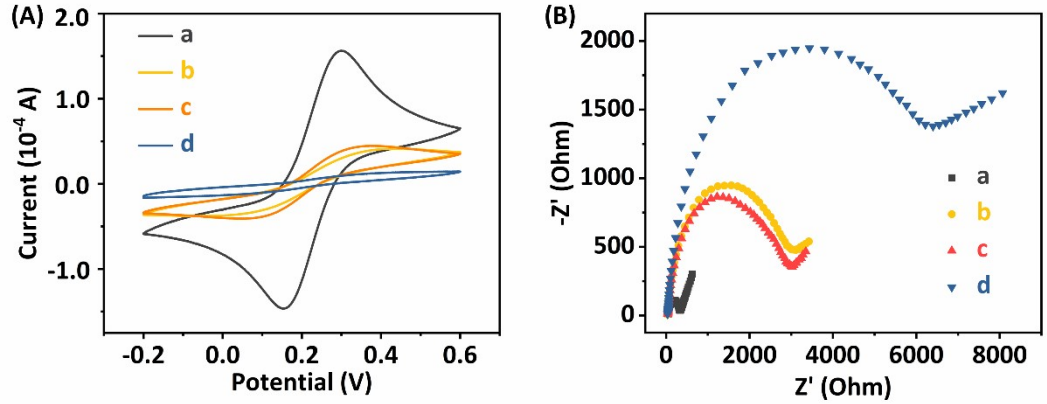

Figure S2. (A) Cyclic voltammograms and (B) Nyquist plots of (curve a) bare GCE, (curve b) β-CD/GCE, (curve c) β-CD/L-CdS QDs/GCE and (curve d) β-CD/L-CdS QDs/L-His-ZIF-8/GCE in 0.1 M KCl containing 5 mM $[Fe(CN)_6]^{4-/3-}$.

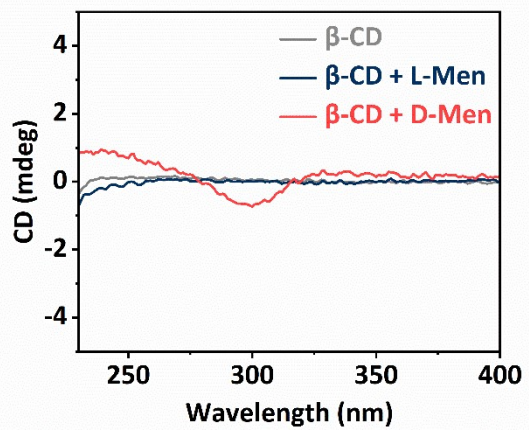

Figure S3. Circular dichroism of β-CD (grey), β-CD + L-Men (blue) and β-CD + D-Men (red).

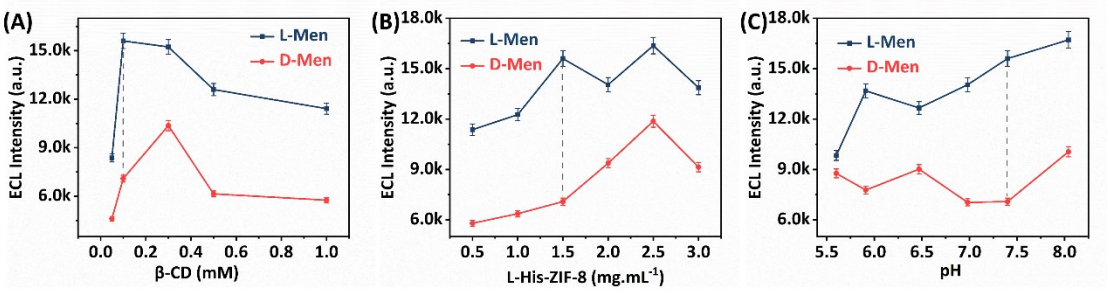

Figure S4. Influence of (A) the concentration of β-CD, (B) the concentration of L-His-ZIF-8 and (C) pH on the ECL signals. Error bars are RSD (n = 3).

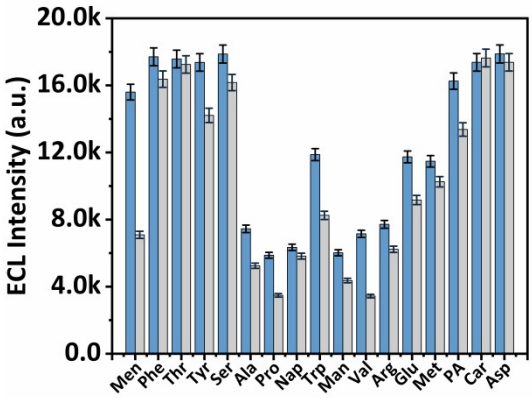

Figure S5. Comparison of enantioselectivity of enantiomers (0.1 mM) on the β-CD/L-CdS QDs/L-His-ZIF-8/GCE + different amino acid enantiomers in PBS (pH 7.4). Among them, the blue bar chart shows L-enantiomers, and the gray bar chart shows D-enantiomers (except for Nap and Man, where the blue and gray bar charts correspond to R and S enantiomers, respectively). Error bars are RSD (n = 3).

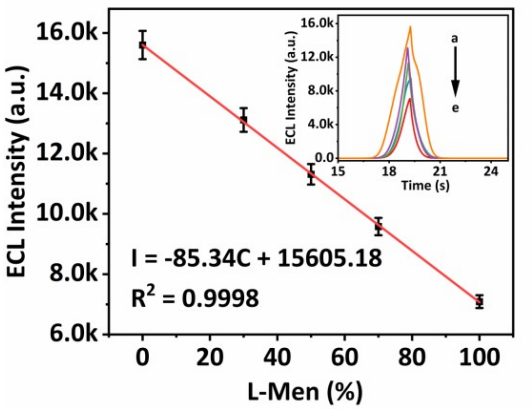

Figure S6. The linear relationship between ECL signals and L-Men%. Inset: ECL of 0.1 mM Men mixture containing different content of L-Men in the mixture (0, 30, 50, 70 and 100%, corresponding to curves a to e) on β-CD/L-CdS QDs/L-His-ZIF-8/GCE. Error bars are RSD (n = 3).

Table S1. Comparison of the performance of the proposed and referenced ECL chiral sensors for enantiomers detection.

Anaiyte	Methods	Linear range	LOD	Reference
Glu	ECL	0.005-5.0 mM	1.6 μM	4
Pro	ECL	0.001-1 mM	0.33 μM	5
PA	ECL	2-12 mM	0.3 mM	6
Pen	ECL	0.1-5.0 mM	33 μM	7
DAAO	ECL	0-10.0 mM	0.03 mM	8
Men	ECL	0.050-100 μM	0.046 μM	This work

3. References

1. J. Wang, Z. Han, T. Shang, Y. Feng, R. Liu and X. Lu, Artemisinin: a novel chiral electrochemiluminescence luminophore-assisted enantiospecific recognition and mechanism identification, *Chemical Science*, 2024, **15**, 5581-5588.

2. Y. Fang, Z. Zhou, Y. Hou, C. Wang, X. Cao, S. Liu, Y. Shen and Y. Zhang, Highly Efficient Wavelength-Resolved Electrochemiluminescence of Carbon Nitride Films for Ultrasensitive Multiplex MicroRNA Detection, *Analytical Chemistry*, 2023, **95**, 6620-6628.

3. J. Fang, L. Dai, R. Feng, D. Wu, X. Ren, W. Cao, H. Ma and Q. Wei, High-Performance Electrochemiluminescence of a Coordination-Driven J-Aggregate K-PTC MOF Regulated by Metal–Phenolic Nanoparticles for Biomarker Analysis, *Analytical Chemistry*, 2023, **95**, 1287-1293.

4. S. Zhu, X. Lin, P. Ran, F. Mo, Q. Xia and Y. Fu, A glassy carbon electrode modified with C-dots and silver nanoparticles for enzymatic electrochemiluminescent detection of glutamate enantiomers, *Microchimica Acta*, 2017, **184**, 4679-4684.

5. S. Zhu, P. Ran, J. Wu, M. Chen and Y. Fu, An Electrochemiluminesence Chiral Sensor for Propranolol Enantiomers Based on Functionalized Graphite-like Carbon Nitride Nanosheets, *Electroanalysis*, 2020, **32**, 185-190.

6. L. Lan, X. Song, X. Kuang, X. Sun and R. Kuang, Chiral Discrimination of Penicillamine Enantiomers: The Role of Aggregation-Caused Quenching in Achieving High Selectivity, *Analytical Chemistry*, 2023, **95**, 14659-14664.

7. X. Lin, S. Zhu, Q. Wang, Q. Xia, P. Ran and Y. Fu, Chiral recognition of penicillamine enantiomers using hemoglobin and gold nanoparticles functionalized graphite-like carbon nitride nanosheets via electrochemiluminescence, *Colloids and Surfaces B: Biointerfaces*, 2016, **148**, 371-376.

8. Q. Zhao, W. Zhu, W. Cai, J. Li, D. Wu and Y. Kong, TiO2 Nanotubes Decorated with CdSe Quantum Dots: A Bifunctional Electrochemiluminescent Platform for Chiral Discrimination and Chiral Sensing, *Analytical Chemistry*, 2022, **94**, 9399-9406.