Electronic Supplementary Material (ESI) for Analyst.

Supplementary materials

Highly Enhanced Electrochemiluminescence Luminophore Generated by Metal Organic Frameworks Linked perylene derivative and Its Application for Ractopamine Assay

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Experimental section

1. Chemicals and materials

The following chemicals were used as analytical grade without any purification. Ractopamine (RAC) hydrochloride was purchased from Inokai Biotech Co. Ltd. Copper nitrate trihydrate (Cu $(NO_3)_2 \cdot 3H_2O$), Trimesic acid ($C_9H_6O_6$), Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA), Ethylene imine polymer (PEI) were purchased from aladdin (Shanghai, China). N, N-dimethylformamide (DMF), hydrochloric acid (HCl), sodium hydroxide (NaOH), potassium persulfate ($K_2S_2O_8$), dimethyl sulfoxide (DMSO), N-(3-dimethylaminopropyl)-N'-ethylcarbodiimidehydrochloride (EDC), N-hydroxysuccinimide (NHS), were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The synthetic RAC aptamer was provided by Shanghai Sangon Biotech Co. Ltd. (Shanghai, China), was treated with Tris-HCl buffer solution and storied in 4°C for further use. The sequence of the RAC aptamer was designed as: 5'-NH_2-AAAAGTGCGGGCAAA-3'. The 0.1 M phosphate buffer solution containing $K_2S_2O_8$ (pH 7.4, NaH_2PO_4-Na_2HPO_4, PBS) was used for ECL detection. All chemical reagents were analytical grade. All aqueous solutions of the whole experiment were prepared with ultra-pure water (>18 MΩ). All chemical reagents were analytical grade.

2. Apparatus and methods

The field emission scanning electron microscope (SEM) and energy-dispersed spectrum (EDS) were received by a SUPRA-55 SEM instrument (Zeiss, Germany), respectively. Fourier transform infrared spectroscopy (FT-IR) characterization was analyzed by a Nicolet In10 (Thermo Fisher Scientific, USA). Electrochemical characterizations including cyclic voltammetry (CV) and Electrochemical impedance spectroscopy (EIS) were studied by CHI660D electrochemical workstation (Shanghai CH Instrument Co., Ltd., China) and ZENNIUM electrochemical workstation (Zahner Instruments, Germany), respectively. The fluorescence spectrum and X-ray photoelectron spectroscopy (XPS) data were tested by a Hitachi F-4500 fluorescence spectrophotometer (Tokyo, Japan) and Thermo Fisher Nexsa, respectively. ECL measurements were performed on MPI-B multifunctional ECL system (Xi'an Ruimai Analytical Instrument Co., Ltd.), with three-electrode system, which chose glassy carbon electrode (GCE) as a working electrode, platinum wire as a counter electrode and Ag/AgCl as a reference electrode for ECL detection.

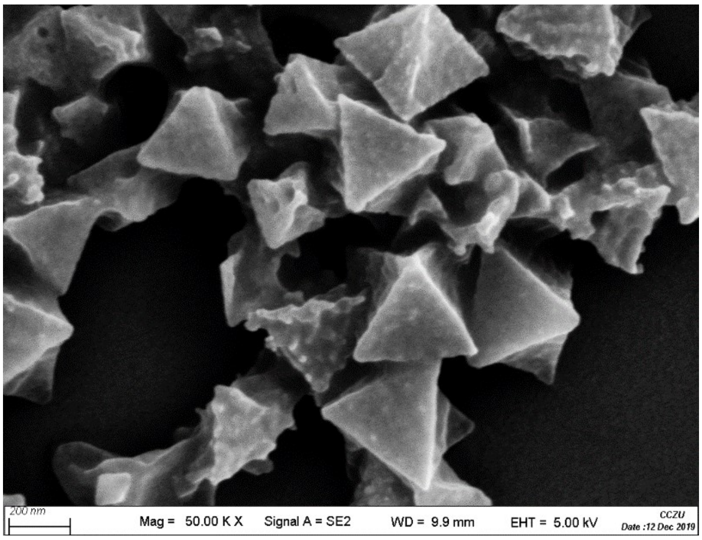

Fig. S1. The SEM of HKUST-1(including cross-linking agent)

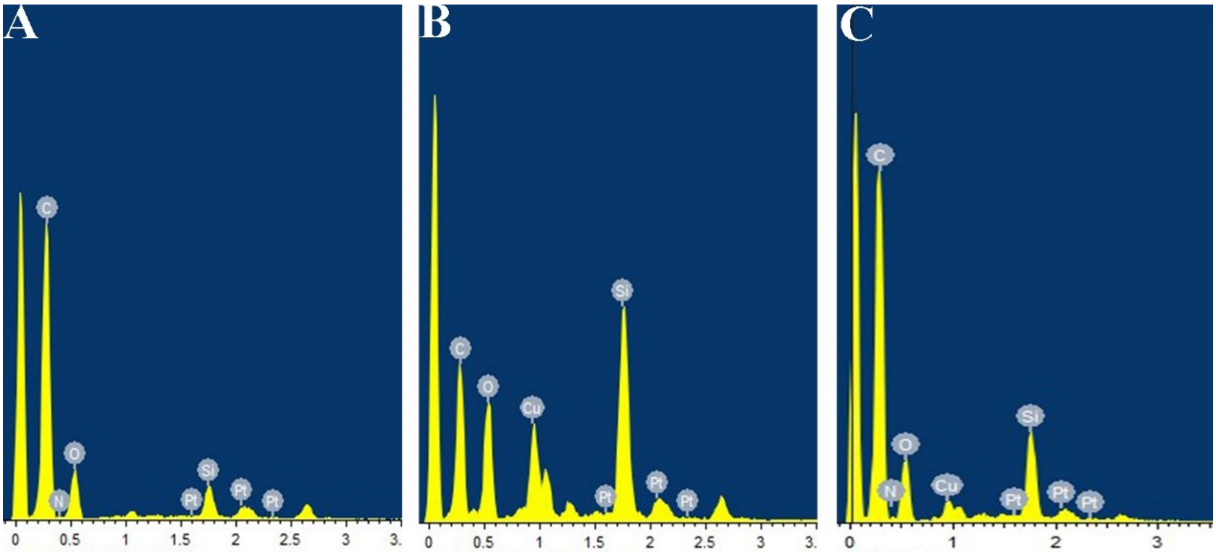

Fig. S2. The EDS of PTC-PEI (A), HKUST-1(B) and HKUST-1/PTC-PEI (C).

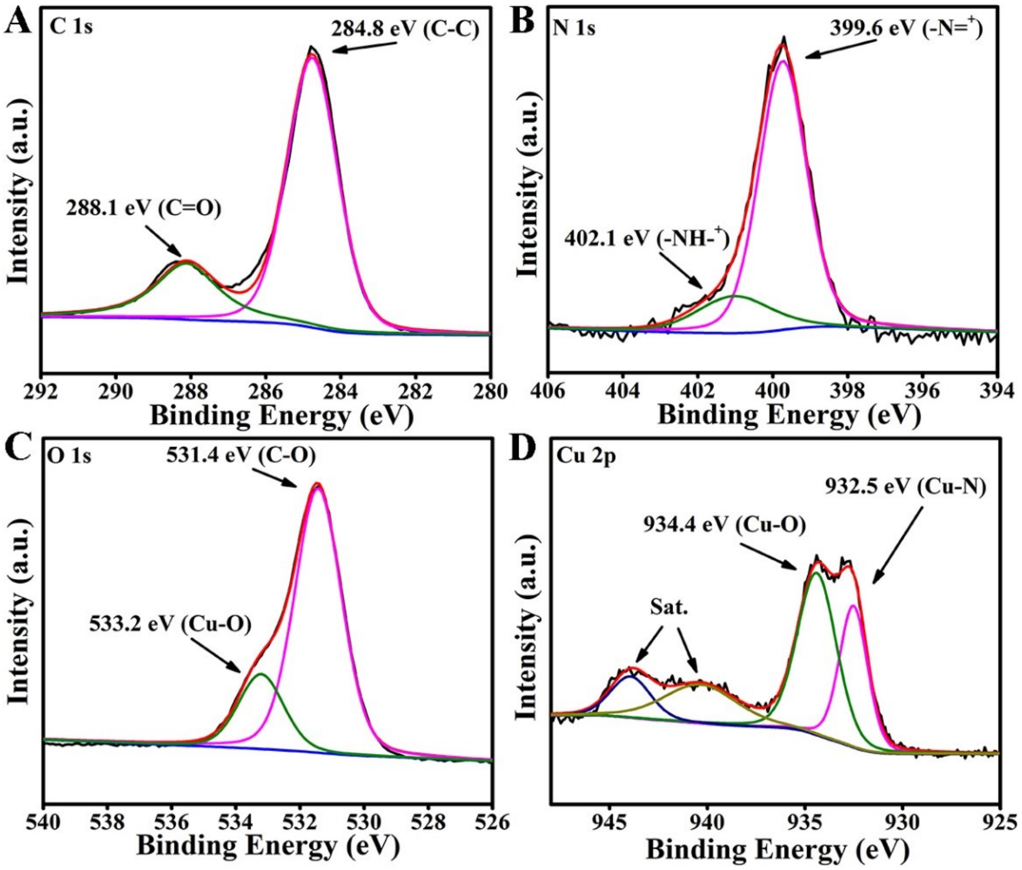

Fig. S3. Survey of the sample, C 1s(A), N 1s (B), O 1s (C) and Cu 2p(D).

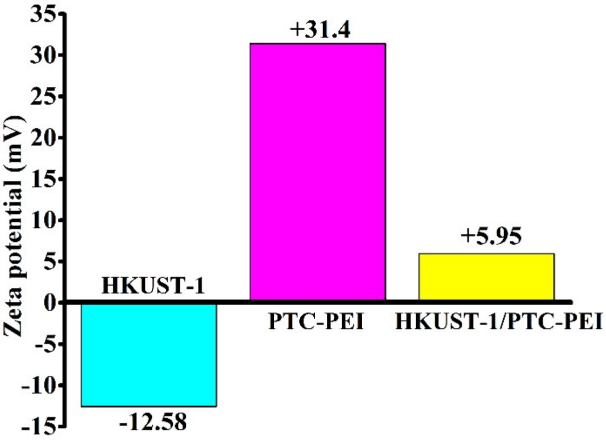

Fig. S4. The zeta potential of HKUST-1, PTC-PEI and HKUST-1/PTC-PEI.

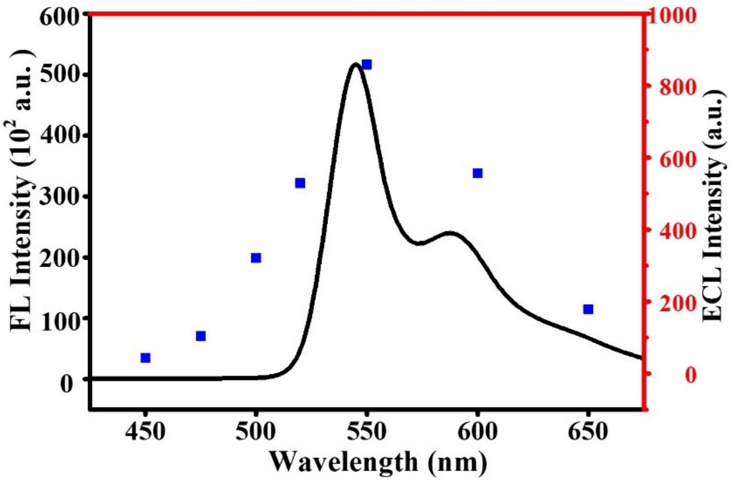

Fig. S5. The FL and ECL spectra of PTC-PEI.

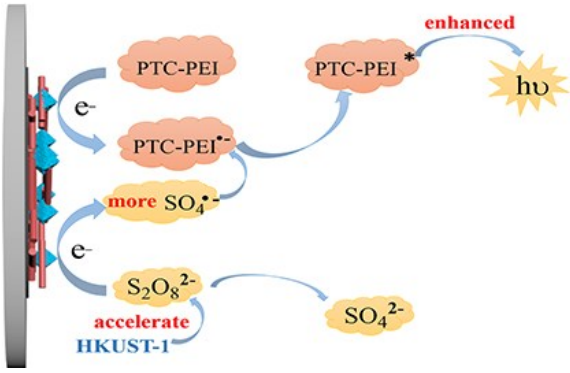

Fig. S6. The mechanism of the system

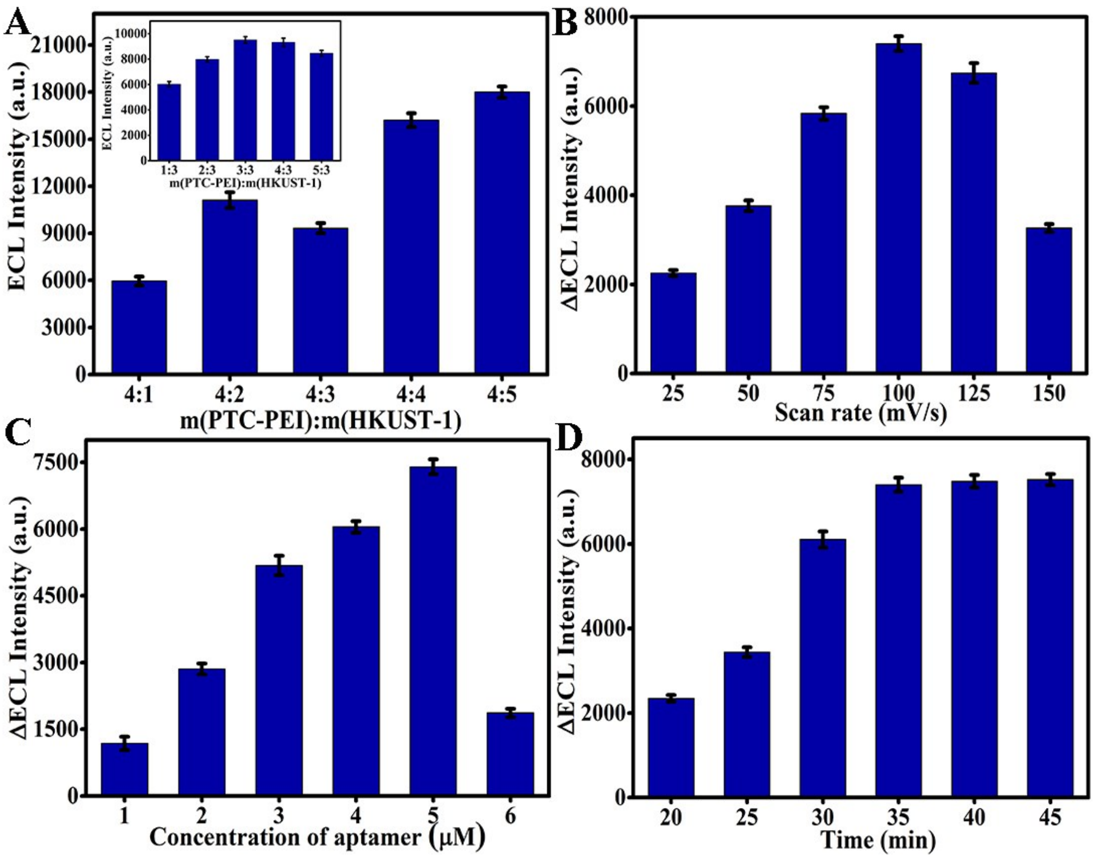

Fig. S7. Optimization of (A) the ratio of PTC-PEI and HKUST-1(Inset); (B)Scan rate; (C) incubated concentration of RAC aptamer and (D) incubation time of ECL aptamer-sensor in 1.0×10^{-9} M RAC solution.

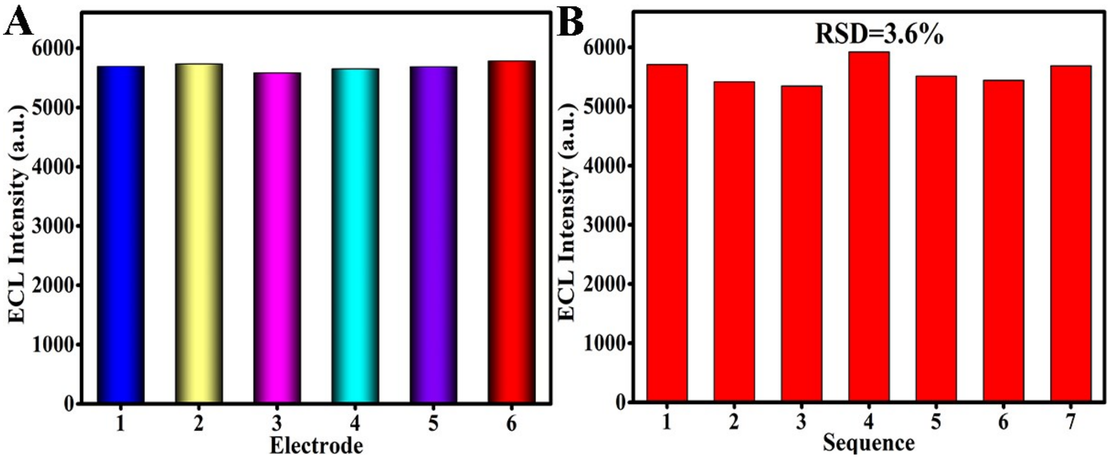

Fig. S8. (A)Repeatability of RAC detection by 6 parallel measurements; (B) Stability of RAC detection in seven times. The concentration of RAC was 10^{-8}M.

Table S1. The comparison of different method to determine RAC

Methods	**Linear range（M）**	**LOD（M）**	**Reference**
Visual detection	3.0×10^{-8}~1.2×10^{-6}	3.0×10^{-8}	1
EC sensor	1.0×10^{-6}~2.8×10^{-5}	1.5×10^{-7}	2
[a] DPV	1.48×10^{-7}~5.92×10^{-6}	5.9×10^{-8}	3
HPLC-MS/MS	1.5×10^{-9}~1.5×10^{-7}	3.0×10^{-11}	4
ECL	2.9×10^{-11}~ 2.9×10^{-7}	7.7×10^{-12}	5
MIP-ECL	1.0×10^{-10}~ 5.0×10^{-8}	3.5×10^{-12}	6
ECL aptamer-sensor	1.0×10^{-12}~ 1.0×10^{-6}	6.17×10^{-13}	This work

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

Table S2. Analytical data of RAC in the pork sample with the as-developed approach (n = 3)**.**

Sample	**Analyte**	**Added （nM）**	**Found (nM)**	**Recovery (%)**	**RSD (%)**
Pork	Ractopamine	0	None	0	0
		1	0.97	97	2.65
			1.02	102	
			1.01	101	
		10	10.04	100.4	4.73
			9.97	99.7	
			9.95	99.5	

References

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