Supporting Information

Zirconium–Metalloporphyrin Frameworks as a Three-in-One Platform Possessing Oxygen Nanocage, Electron Media, and Bonding Site for Electrochemiluminescence Protein Kinase Activity Assay

Guang-Yao Zhang,[†] Chang Cai,[†] Serge Cosnier,[‡] Hai-Bo Zeng,[§]

Xue-Ji Zhang,[†] Dan Shan*[†]

[†]Sino-French Laboratory of Biomaterials and Bioanalytical Chemistry, School of Environmental and Biological Engineering, Nanjing University of Science and Technology, Nanjing 210094, China
[‡] Univ. Grenoble Alpes DCM UMR 5250, F 38000, Grenoble, France
[¢] CNRS, DCM UMR 5250, F-38000 Grenoble, France
[§]Institute of Optoelectronics & Nanomaterials, Jiangsu Key Laboratory of Advanced Micro & Nano Materials and Technology, College of Material Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, China Figure S1 FT-IR spectra of ZnTCPP (a) and MOF-525-Zn (b).

Figure S2 (A) Effects of different buffer solutions on the ECL peak intensity of GCE/MOF-525-Zn/TOAB in the O₂-saturated condition. (B) Effect of pH on the ECL peak intensity of GCE/MOF-525-Zn/TOAB in the O₂-saturated HEPES buffer solutions.

Figure S3 ECL-time response of the biosensor at PKA concentration of 0.1 U mL⁻¹ under continuous potential scan with a scan rate of 100 mV s⁻¹ in the O_2 -saturated pH 7.4 HEPES solution.

Figure S1



Figure S2



Figure S3



Analytical method	Linear range	Detection limit	Reference
Ag nanoclusters-based	$0.001-2 \text{ U } \mu\text{L}^{-1}$	$0.5 \text{ mU } \mu L^{-1}$	1
fluorescence assay			
Synthetic phosphorylated receptor	5-50 U mL ⁻¹	0.1 U mL ⁻¹	2
probebased electrochemical assay			
DNA-Au NPs network-based	0.1–40 U mL ⁻¹	0.03 U/mL	3
electrochemical assay			
Gold nanoparticles amplification-	0.07–32 U mL ⁻¹	0.07 U mL ⁻¹	4
based ECL assay			
Graphite-like carbon nitride-based	0.05–100 U mL ⁻¹	0.015 U mL ⁻¹	5
photoelectrochemical assay			
Dual-potential ECL ratiometric	0.01–10 U mL ⁻¹	0.005 U mL ⁻¹	6
strategy			
Semisynthetic GFP-based	$2.5-125 \text{ mU } \mu \text{L}^{-1}$	$0.5 \text{ mU } \mu \text{L}^{-1}$	7
fluorescent assay			
Zirconium-(zinc)porphyrin	0.01 to 20 U mL ⁻¹	0.005 U mL ⁻¹	This work
frameworks-based ECL assay			

Table S1 Comparison of the performance of our proposed sensor with other published PKA sensors.

Samples	Add (U mL ⁻¹)	Found (U mL ⁻¹)	Recovery (%)	RSD (%)
1	0.1	0.093	93	2.1
2	1.0	1.02	102	2.3
3	10.0	10.5	105	2.6

Table S2 PKA activity measured in human serum with the proposed ECL biosensor

References

1 C. Shen, X. Xia, S. Hu, M. Yang and J. Wang, *Anal. Chem.* 2014, **87**, 693-698.

I. S. Shin, R. Chand, S. W. Lee, H. W. Rhee, Y. S. Kim and J. I. Hong, *Anal. Chem.*2014, 86, 10992-10995.

3 Z. Wang, N. Sun, Y. He, Y. Liu and J. Li, Anal. Chem. 2014, 86, 6153-6159.

4 S. Xu, Y. Liu, T. Wang and J. Li, *Anal. Chem.* 2010, **82**, 9566-9572.

5 H. Yin, B. Sun, L. Dong, B. Li, Y. Zhou and S. Ai, *Biosens. Bioelectron.* 2015, **64**, 462-468.

6 H. F. Zhao, R. P. Liang, J. W. Wang and J. D. Qiu, *Chem. Commun.* 2015, **51**, 12669-12672.

7 C. Yin, M. Wang, C. Lei, Z. Wang, P. Li, Y. Li, W. Li, Y. Huang, Z. Nie and S. Yao, *Anal. Chem.* 2015, **87**, 6311-6318.