Supporting Information

Enhancing hydrogels-based long-lasting chemiluminescence by platinum-metal organic framework and its application in array detection of pesticides and D-alanine

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Annexure S1.

Procedure for Actual Sample of Chlorpyrifos.

The pretreatment of pakchoi was as follows: pakchoi was first chopped and crushed well. Then, 1 g of each sample was mixed separately with 10 mL acetonitrile and 5 μg/mL chlorpyrifos, followed by vigorously stirring for 15 min and adding 2 mL of 1 M/L NaCl solution. Aqueous solution was discarded and the acetonitrile solution was centrifuged at 5000 rpm for 15 min. Subsequently, the supernatant was filtrated and diluted 10-fold for the subsequent experiment.

10 μL of AChE (15 mU/mL) was incubated with 10 μL of the obtained sample for 30 minutes at 37°, and 50 μL of ACh (0.075 mM), 20 μL of PBS solution and 10 μL of CHO (0.5 U/mL) were added for 1 hour at 37 °C. Then, 50 μL of the reaction solution and 20 μL of the MOF-Pt solution were added to 50 μL of the ABEI/Co^{2+}/CS hydrogels, and the chemiluminescence intensity was measured at an exposure time of 6 minutes.

Procedure in Human Serum Samples of D-Ala.

Collecting human serum from volunteers, the spiked recovery test was carried out on the blank serum. Serum was diluted 1:10 with PBS buffer solution. Three parallel samples were used in each group. 50 μL different concentrations of D-Ala, 20 μL of DAAO (2 U/mL), 10 μL serum and 20 μL PBS solution were mixed and reacted for 1 hours at 37 °C. After that, 50 μL of the above solution, 20 μL of MOF-Pt solution and 50 μL of ABEI/Co^{2+}/CS hydrogels were added into a 96-well microplate, and the CL intensity was measured at an exposure time of 3 minutes.

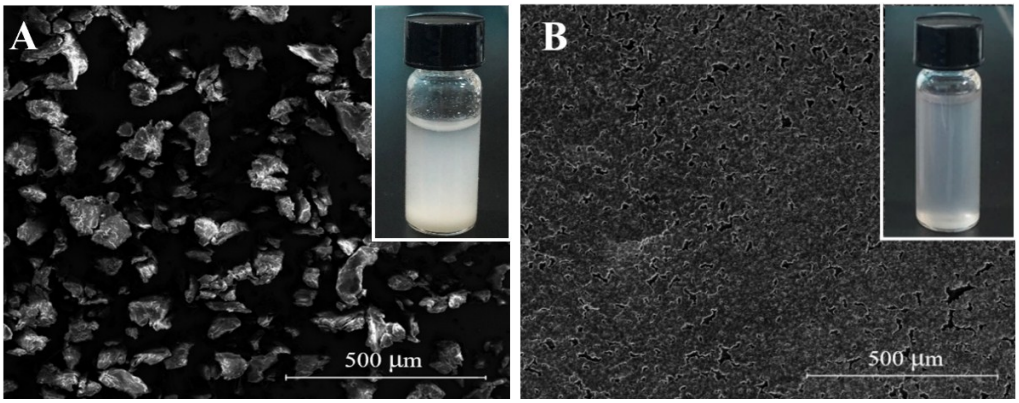

Figure S1. SEM of ABEI/Co^{2+}/CS hydrogels before (A) and after freezing and thawing (B). Before freezing and thawing, the chitosan powder was in an insoluble state. After freezing and thawing, the chitosan powder was dissolved. Insets were the corresponding actual topography image.

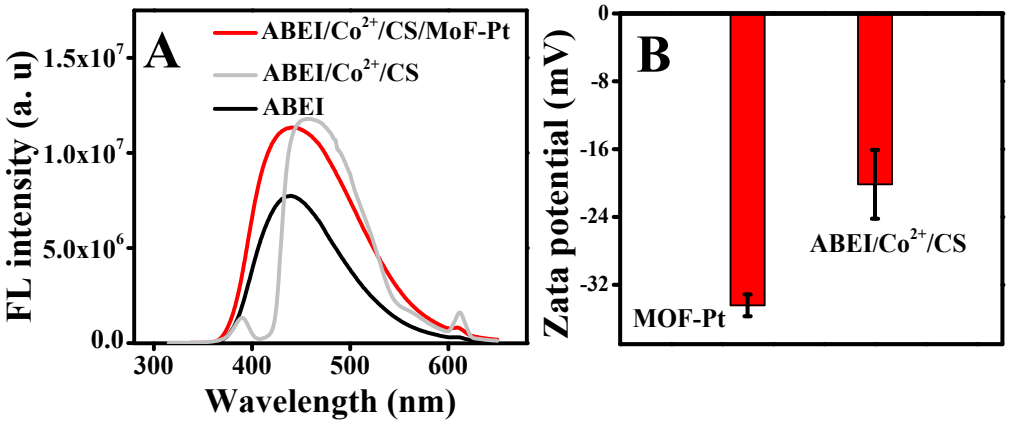

Figure S2. (A) Fluorescence emission spectra of ABEI (Black line), ABEI/Co^{2+}/CS/MOF-Pt (Red line), ABEI/Co^{2+}/CS (Gray line). (B) Zeta potentials of MOF-Pt and ABEI/Co^{2+}/CS hydrogels. The error bar represents the standard deviation of three measurements.

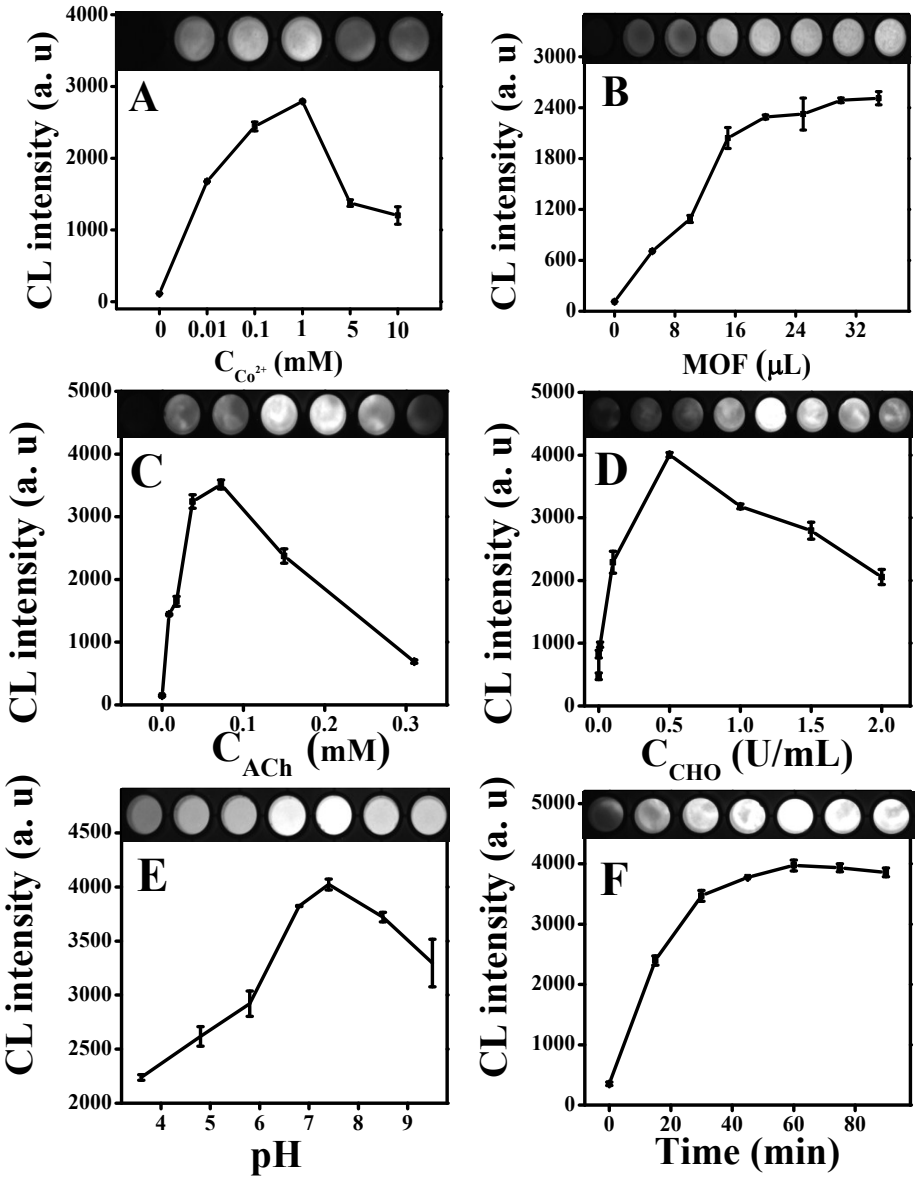

Figure S3. Optimize the detection conditions for OPs. (A) Concentration of Co^{2+} in hydrogels. (B) Concentration of MOF-Pt. (C) Concentration of ACh. (D) Concentration of CHO. (E) PH of PBS-buffer. (F) Reaction time (0-90 min). The insets were CL images measured at exposure time of 6 minutes.

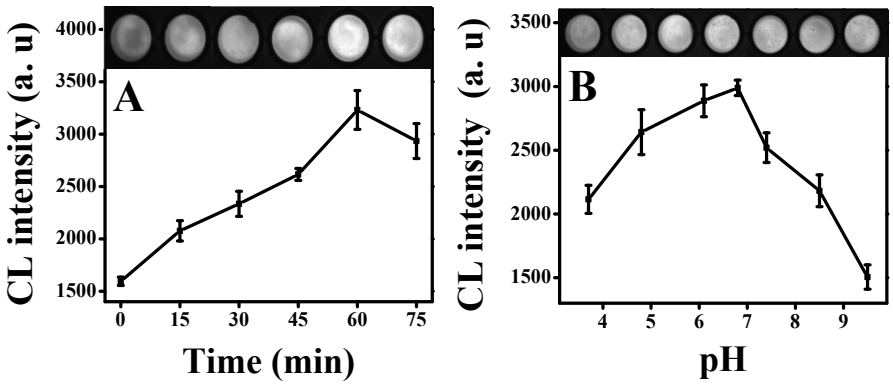

Figure S4. Optimizing the detection conditions for D-Ala. (A) Reaction time (0-75 min). (B) pH (3.8-9.4). Insets were CL images measured at exposure time of 3 minutes.

Probe	Method	LOD (μg/L)	Linear range (μg/L)	Analyte	Ref.
Dinuclear Ir (III)	fluorescence	0.37	0.5-25	aldicarb	Lu et al., 2018
MIPs@$CsPbBr_3$ QDs	fluorescence	18.8	50-400	omethoate	Huang et al., 2018
MnO_2 nanoflowers	colorimetric	0.033	0.1−50	chlorpyrifos	Ouyang et al., 2018
TMB-H_2O_2	colorimetric	4.0	10-10000	Paraoxon	Han et al., 2018
MoS_2	electrochemical	0.13	1.0- 1000	Paraoxon	Zhao et al., 2018
MB	electrochemical	2.1	10- 10000	omethoate	Liu et al., 2017
I-BiOCl/N-GQD	PEC	0.01	0.3−80	chlorpyrifos	Wang et al., 2018
ABEI/Co^{2+}/CS/MOF/Pt	CL	0.21	0.5-1000	chlorpyrifos	This work

Table S1. Comparison of analytical performance on OPs of various methods.

Method	System	Linear range	LOD	Ref
Fluorescence	DNA/silver nanocluster	1.0 μM-1.0 mM	0.1 μM	Zhang et al., 2018
FIA	D-AAOx/PyOx	0.1 mM-1.0 mM	0.05 mM	Inaba et al., 2018
Electrochemistry	Screen-printed amperometric biosensor	50-200 μM	16.6 nM	Sarkar et al., 2018
ECL	DAAO/Au-PtNW/rGO-H-Cys	1.0 nM-5.0 mM	0.33 nM	Lata et al., 2018
CV	DAAO/Pin5-COOH/ ZnSNPs/Au	1.0 μM-2.0 mM	1.0 nM	Takano et al., 2018
CE	CuNPs/PANI/c-MWCNT/AuE	1.0 μM-0.7 mM	0.2 μM	Carlavilla et al., 2018
Chemiluminescence	ABEI/Co^{2+}/CS hydrogels	1.0 μM-10 mM	0.12μM	This work

Table S2. Comparison of analytical performance on D-Ala of various methods.

References

Lu, L.H., Su, H.J., Liu, Q.Y., Li, F., 2018. Anal. Chem. 90(19), 11716-11722.

Huang, S.Y., Guo, M.L., Tan, J.A., Geng, Y.Y., Wu, J.Y., Tang, Y.W., Su, C.C., Lin, C.C.; Liang, Y. 2018. ACS Appl. Mater. Inter. 10(45), 39056-39063.

Ouyang, H., Lu, Q., Wang, W.W., Song, Y., Tu, X. M., Zhu, C.Z., Smith, J.N., Du, D., Fu, Z. F., Lin, Y. H., 2018. Anal. Chem. 90(8), 5147-5152.

Han, T., Wang, G. J., Mater. Chem. B. 2019, 7.

Zhao, F.N., Yao, Y., Liu, X.J., Lan, L.Y., Jiang, C.M., Ping, J.F., 2018. Anal. Chem. 90(19), 11658-11664.

Liu, X.J., Song, M.M., Hou, T., Li, F., 2017. ACS Sensors. 2(4), 562-568.

Wang, H., Zhang, B.H., Zhao, F.Q., Zeng, B.Z., 2018. ACS Appl. Mater. Inter. 10(41), 35281-35288.

Zhang, Z.K., Liu, Y., Liu, P.F., Jiang, X.Y., Lou, D., Yang, D.Y., 2017. Nanoscale 9(48), 19367-19373.

Inaba, Y., Mizukami, K., Hamada-Sato, N., Kobayashi, T., Imada, C., Watanabe, E., 2003. Biosens. Bioelectron. 19(5), 423-431.

Sarkar, P., Tothill, I.E., Setford, S.J., Turner, A.P.F., 1999. Analyst 124(6), 865-870.

Lata, S., Batra, B., Kumar, P., Pundir, C.S., 2013. Anal. Biochem 437(1), 1-9.

Takano, Y., Chikaraishi, Y., Ogawa, N.O., Kitazato, H., Ohkouchi, N., 2009. Anal Chem 81(1), 394-9.

Carlavilla, D., Moreno-Arribas, M.V., Fanali, S., Cifuentes, A., 2006. Electrophoresis 27(13), 2551-2557.