Electronic Supplementary Information for

Enhanced oxidase-mimicking activity of Ce^{4+} by complexing with nucleotides and its tunable activity for colorimetric detection of Fe^{2+}

Jiaojiao Liu, Ying Cao, Xinyue Zhu, Lina Zou, Gaiping Li* and Baoxian Ye

College of Chemistry, Zhengzhou University, Zhengzhou, 450001, PR China.

Experimental

Materials and reagents

Adenosine-5'-monophosphate (AMP), reduced glutathione (GSH) and L-Ascorbic acid (AA) were obtained from Sangon Biotech Co., Ltd. (Shanghai, China). 3,3',5,5'-tetramethylbenzidine (TMB), N-2-hydroxyethylpiperazine-N'-ethanesulfonic acid (HEPES), ammonium ceric nitrate (Ce(NH$_4$)$_2$(NO$_3$)$_6$), ferrous sulfate heptahydrate (Fe$_2$SO$_4$·7H$_2$O), acetic acid (HAc), sodium acetate (NaAc), cysteine (Cys) and other metal salts were purchased from Aladin Co., Ltd. (Shanghai, China). All the reagents were used directly without any purification. Solutions were made from ultrapure water with a conductivity of 18.2 MΩ cm^{-1} (Thermo Fisher Scientific Co. Ltd., Shanghai, China). HEPES buffer (0.1 M, pH 7.4) and HAc-NaAc buffer (0.2 M, pH 4.0) was used through this study.

Instruments

Scanning electron microscopy (SEM, Sigma 500, Gemini, Japan) was used to characterized the morphologies. UV-vis absorption spectra were collected with Lambda 35 UV-vis spectrometer (Pgeneral Instrument, Beijing, China) using silica cuvette (3.0 mL, 1 cm light path). X-ray photoelectron spectroscopy (XPS) characterizations were measured by AXIS Ultra DLD electron spectrometer (Kratos). Fourier transform infrared (FT-IR) spectra were obtained using NEXUS 470 FT-IR

College of Chemistry, Zhengzhou University, Zhengzhou, 450001, PR China.

E-mail: lgpingzy@zzu.edu.cn; Fax: +86 0371 67763654; Tel: +86 0371 67781757

spectrometer.

Preparation of AMP-Ce^{4+} ICPs

AMP-Ce^{4+} ICPs were synthesized according to the previous report.[1] In brief, Ce(NH$_4$)$_2$(NO$_3$)$_6$ aqueous solution (10 mM, 4.5 mL) was mixed with HEPES buffer (0.1 M, 4.5 mL, pH, 7.4) containing AMP (10 mM), and then the mixture was stirred at room temperature for 30 min to obtain a turbid suspension. The product was obtained by centrifugation (10000 rpm, 10 min) and purified by washing for three times with ultrapure water. Finally, the purified product was re-dispersed into HEPES buffer (0.1 M, 9 mL, pH, 7.4) to form AMP-Ce^{4+} ICPs suspension and stored at 4 ℃ for use.

Oxidase mimicking activity of AMP-Ce^{4+} ICPs

The oxidase mimicking activity of AMP-Ce^{4+} ICPs was investigated by the blue color reaction of catalyzing TMB oxidation without H$_2$O$_2$. Briefly, AMP-Ce^{4+} ICPs stock solution (5 mM, 30 μL) and TMB solution (5 mM, 20 μL, dissolved in ethanol) were added into HAc-NaAc buffer (0.2 M, 450 μL, pH 4.0). The mixture was incubated under the room temperature, and the time-dependent UV-vis spectra were measured accordingly.

Colorimetric detection of Fe^{2+}

Fe^{2+} detection was performed as follows: firstly, 30 μL of AMP-Ce^{4+} ICPs stock solution and 100 mM of Fe^{2+} with various volume were incubated at room temperature for 10 min; secondly, 20 μL of 5 mM TMB solution and HAc-NaAc buffer (0.2 M, pH 4.0) were added into the above solution to bring the final total volume to 500 μL; finally, the UV-vis spectra of each reaction solution were measured after 15 min.

For Fe^{2+} determination in tap water, different volumes of Fe^{2+} stock solution (10 mM) was diluted with tap water for the measurement. The detection procedure was

same to the above description.
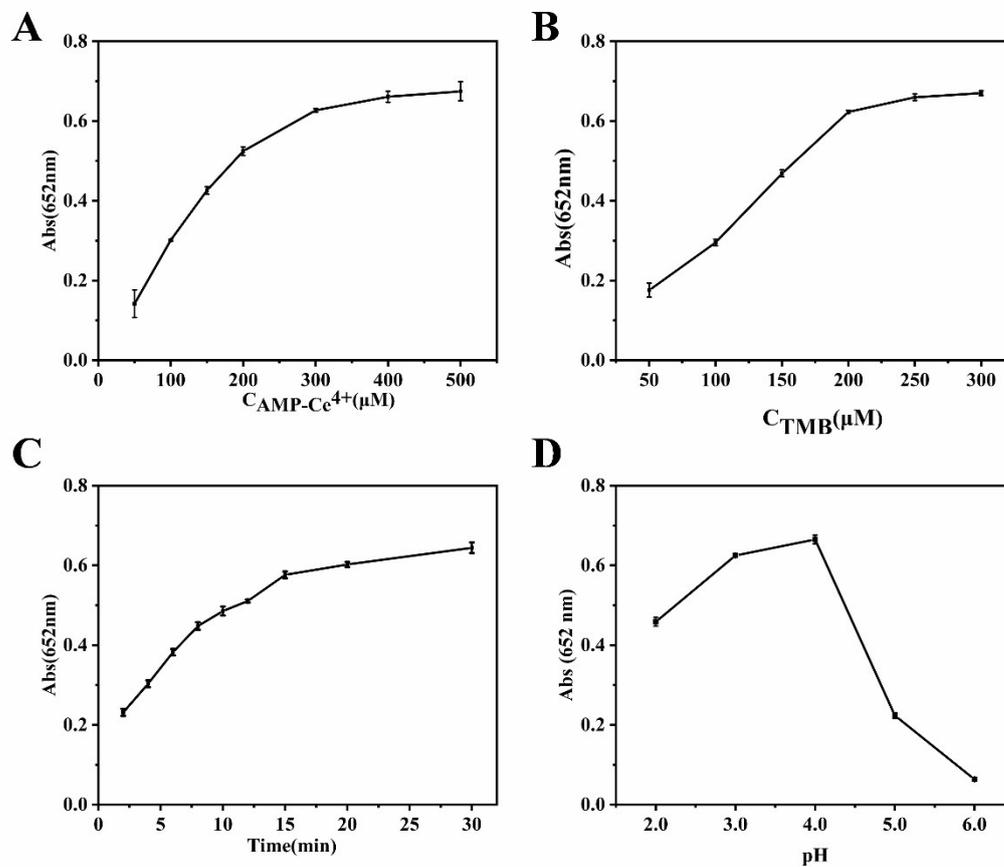
Fig. S1. Dependency of the relative activity of AMP-Ce^{4+} ICPs on (A) concentration of AMP-Ce^{4+} ICPs, (B) concentration of TMB, (C) reaction time and (D) buffer pH.
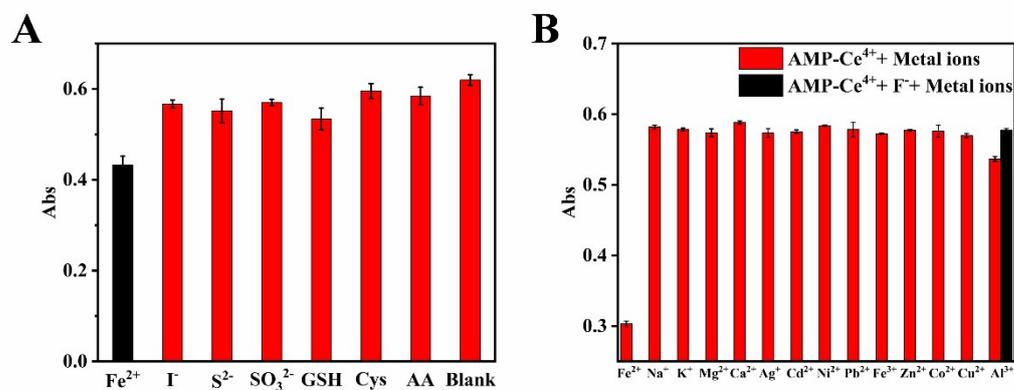
Fig. S2. (A) Selectivity of this colorimetric sensor for Fe^{2+} detection against common

reductive substance. The concentration of these substance is 10 μM. (B) Selectivity of this colorimetric sensor for Fe^{2+} detection against common metal ions. Except the concentration of Fe^{2+} is 20 μM, the concentration of other interfering ions is 200 μM. The concentration of F⁻ is 600 μM.、

Table S1 Comparison of apparent kinetic parameters of AMP-Ce^{4+} and Ce^{4+} toward TMB.

Oxidase mimics	K_m (mM)	V_{max} (10^{-8} Ms⁻¹)
AMP-Ce^{4+} ICPs	0.090	14.8
Ce^{4+}	0.345	12.96

Table S2. XPS data of AMP-Ce^{4+} before and after addition of Fe^{2+}.

Samples	Binding energy (eV)		Relative proportion	
	Ce^{4+}	Ce^{3+}	Ce^{4+}	Ce^{3+}
AMP-Ce^{4+}	882.44, 888.10, 898.25	885.54	94.94%	5.06%
	901.41, 907.87, 916.81	904.16		

AMP-Ce^{4+} + Fe^{2+}	882.22, 888.44, 898.04	885.69	73.73%	26.27%
	901.22, 907.84, 916.50	903.88		

Table S3. Comparison with the performance of the AMP-Ce^{4+} sensor with the referenced methods for colorimetric detection of Fe^{2+}.

Material	Linear range (µM)	LOD (µM)	Ref.
HPHN	1-18	0.77	2
EAR-AuNPs	10-500	1.5	3
Phenylene-acetylene	0-6	0.02	4
Carbon nanotubes	1-100	0.22	5
MoS$_2$/H$_2$O$_2$/OPD	0.01-0.8	0.007	6
2,6-bis((2-(((pyridine-2-yl)methylamino)methyl)phenol)ethylamido)pyridine)	0-60	2.94	7
Electrospun nanofiber	1.76-62.5	1.82	8
AMP-Ce^{4+}	1-25	0.089	This work

Table S4. Recovery test results of Fe^{2+} in tap water samples

Sample	Fe^{2+} added (μM)	Fe^{2+} founded (μM)	Recovery (%)	RSD (%)
1	2	1.95	97.5	2.2
2	10	9.56	95.6	3.0
3	20	20.63	103.2	2.2

References

1. Z. Zhang, Y. Wu, S. He, Y. Xu, G. Li and B. Ye, *Anal. Chim. Acta*, 2018, **1014**,85-90.

2. M. Yang, S. C. Lee, M. Kim, M. H. Lim and C. Kim, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, 2021, **245**, 118899.

3. X. Chen, J. Ji, G. Shi, Z. Xue, X. Zhou, L. Zhao and S. Feng, *RSC Adv.*, 2020, **10**, 32897-32905.

4. Y. Zhang, X. Chen, X. Liu, M. Wang, J. Liu, G. Gao, X. Zhang, R. Sun, S. Hou and H. Wang, *Sens. Actuators B Chem.*, 2018, **273**, 1077-1084.

5. C. Wang, Q. Wang and R. Tan, ***Analyst***, 2018, 143, 4118-4127.

6. Y. Wang, J. Hu, Q. Zhuang and Y. Ni, *Biosens. Bioelectron.*, 2016, **80**, 111-117.

7. H. Kim, Y. J. Na, E. J. Song, K. B. Kim, J. M. Bae and C. Kim, *RSC Adv.*, 2014, **4**, 22463-22469.

8. D. A. Ondigo, Z. R. Tshentu and N. Torto, *Anal. Chim. Acta*, 2013, **804**, 228-234.