

Electronic supplementary information

A novel colorimetric assay based on the peroxidase-like properties of amino functionalized copper metal-organic frameworks nanoparticles for ascorbic acid sensing

Zhixia Yao ^{1,2}, Zhen Li ^{1,3}, Hanmeng Liu ^{1,2}, Yaosheng Liu ^{1,2},

Yujing Sun ^{1,2,3,*}, Zhuang Li ^{1,2,3,*}

¹ *State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China*

² *University of Science and Technology of China, Hefei 230026, China*

³ *University of Chinese Academy of Sciences, Beijing 100049, China*

* *Corresponding authors. Tel/fax: +86-431-85262057*

E-mail address: yjsun@ciac.ac.cn, zli@ciac.ac.cn

Synthesis of Cu-BDC-NH₂ NPs

Typically, the precursors of $(\text{CuNO}_3)_2 \cdot 3\text{H}_2\text{O}$ (36.3 mg, 0.15 mmol) and 2-NH₂-BDC (8.15 mg, 0.045 mmol) were dissolved into 6 mL DMF, followed by adding the mixed homogeneous solution including 0.30 g PVP, 6 mL ethanol and 6 mL DMF, then the mixed solution was treated with ultrasonication for 20 min. Next, the mixture was poured into a teflon-lined autoclave for sealing and heated up to 100°C and kept for 8 h in the temperature, then cooled down to ambient temperature naturally. The obtained products were collected by centrifugal separation at 4000 rpm for 10 min. Subsequently, the precipitated products were cleaned three times using ethanol and ultrapure water separately and put into a vacuum freeze drier for 12 h.

Preparation of Cu-BDC NPs

Firstly, 0.7248 g (3 mmol) $(\text{CuNO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 0.4984 g (3mmol) H_2BDC were dissolved in 45 mL DMF, and then the mixed solution was treated with ultrasonication for 10 min. Next, the mixture was poured into a teflon-lined autoclave for sealing and heated up to 110°C and kept for 21 h in the temperature, then cooled down to ambient temperature naturally. The obtained products were collected by centrifugal separation at 6000 rpm for 20 min. Subsequently, the precipitated blue products were washed by DMF and ethanol, followed by heating at 100°C under vacuum for 12 h and stored in a desiccator.

Figure captions

Fig. S1 FT-IR spectrum of H₂BDC, Cu-BDC NPs, Cu-BDC-NH₂ NPs and 2-NH₂-BDC.

Fig. S2 Effect of the pH value on the absorbance at 655 nm of the system solution in the absence (a) and presence (b) of AA, and the ΔA (c). 100 μL of 0.2 mg mL⁻¹ Cu-BDC-NH₂ NPs, 200 μL of 5 mM TMB, 200 μL of 0.5 M H₂O₂ and 100 μL of 0.5 mM AA; room temperature; reaction time, 10 min. The error bars represent the standard deviations of three replicate measurements.

Fig. S3 Effect of the reaction time on the absorbance at 655 nm of the system solution in the absence (a) and presence (b) of AA, and the ΔA (c). 100 μL of 0.2 mg mL⁻¹ Cu-BDC-NH₂ NPs, 200 μL of 5 mM TMB, 200 μL of 0.5 M H₂O₂ and 100 μL of 0.5 mM AA; pH, 4.0; room temperature. The error bars represent the standard deviations of three replicate measurements.

Fig. S4 Effect of the concentration of Cu-BDC-NH₂ NPs on the absorbance at 655 nm of the system solution in the absence (a) and presence (b) of AA, and the ΔA (c). 100 μL of different concentrations of Cu-BDC-NH₂ NPs, 200 μL of 5 mM TMB, 200 μL of 0.5 M H₂O₂ and 100 μL of 0.5 mM AA; pH, 4.0; room temperature; reaction time, 10 min. The error bars represent the standard deviations of three replicate measurements.

Fig. S5 Effect of the concentration of H_2O_2 on the absorbance at 655 nm of the system solution in the absence (a) and presence (b) of AA, and the ΔA (c). 100 μL of 0.2 mg mL^{-1} Cu-BDC- NH_2 NPs, 200 μL of 0.5 mM TMB, 200 μL of different concentrations of H_2O_2 and 100 μL of 0.5 mM AA; pH, 4.0; room temperature; reaction time, 10 min. The error bars represent the standard deviations of three replicate measurements.

Fig. S6 Effect of the concentration of TMB on the absorbance at 655 nm of the system solution in the absence (a) and presence (b) of AA, and the ΔA (c). 100 μL of 0.2 mg mL^{-1} Cu-BDC- NH_2 NPs, 200 μL of different concentrations of TMB, 200 μL of 0.5 M H_2O_2 and 100 μL of 0.5 mM AA; pH, 4.0; room temperature; reaction time, 10 min. The error bars represent the standard deviations of three replicate measurements.

Table S1 Analytical results of the detection of AA in pharmaceutical vitamin C tablets.

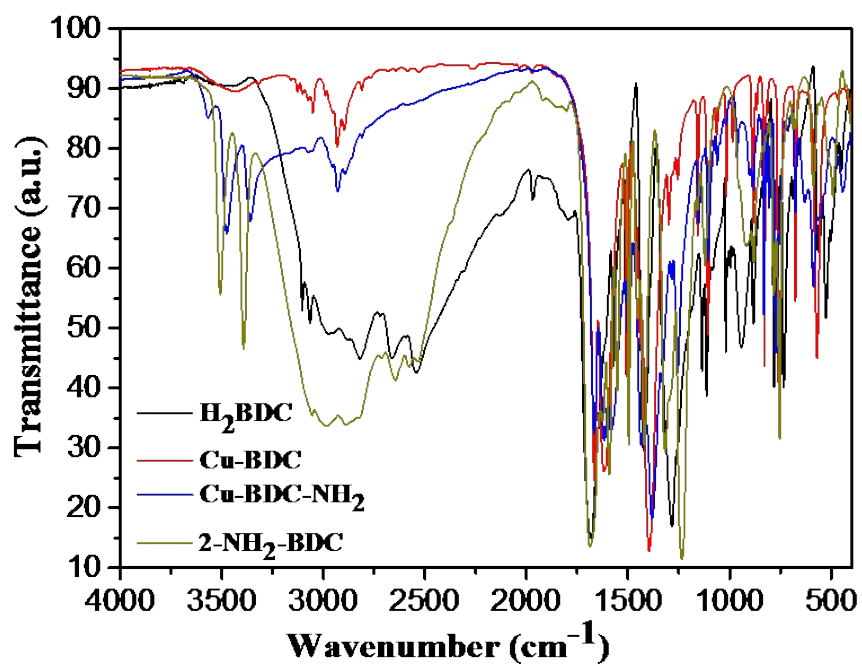


Fig. S1 FT-IR spectrum of H₂BDC, Cu-BDC NPs, Cu-BDC-NH₂ NPs and 2-NH₂-BDC.

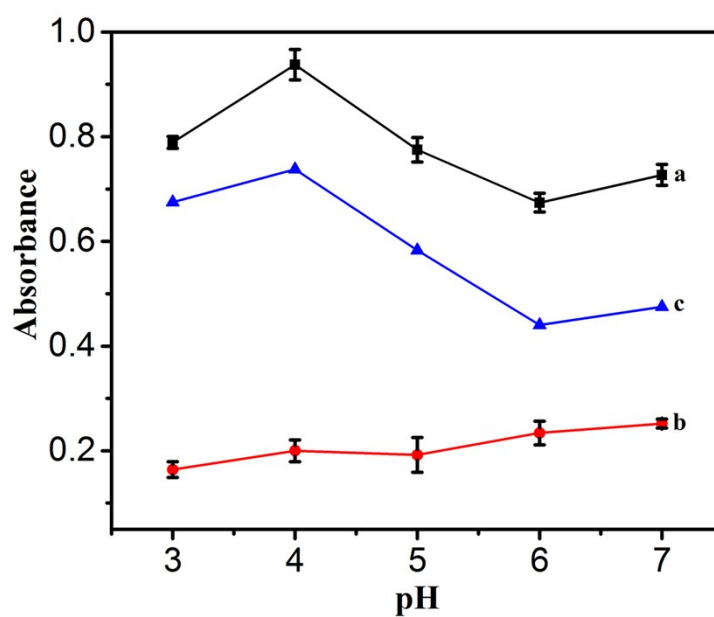


Fig. S2 Effect of the pH value on the absorbance at 655 nm of the system solution in the absence (a) and presence (b) of AA, and the ΔA (c). 100 μL of 0.2 mg mL^{-1} Cu-BDC-NH₂ NPs, 200 μL of 5 mM TMB, 200 μL of 0.5 M H₂O₂ and 100 μL of 0.5 mM AA; room temperature; reaction time, 10 min. The error bars represent the standard deviations of three replicate measurements.

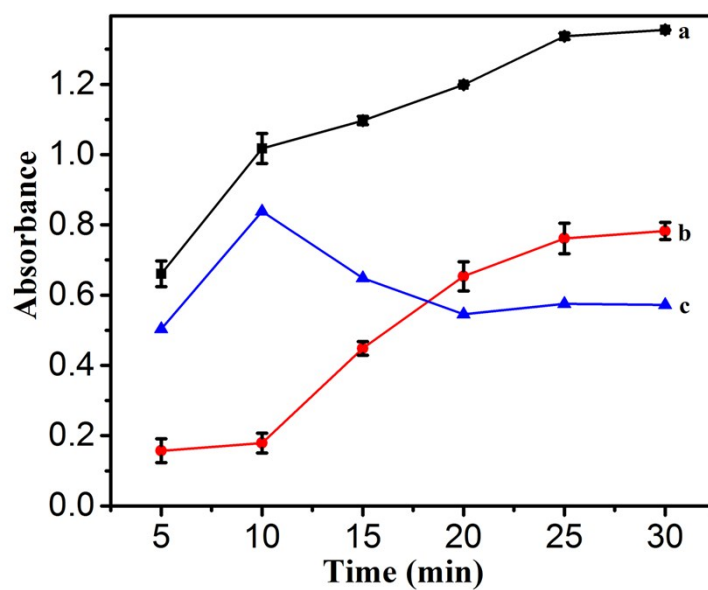


Fig. S3 Effect of the reaction time on the absorbance at 655 nm of the system solution in the absence (a) and presence (b) of AA, and the ΔA (c). 100 μL of 0.2 mg mL^{-1} Cu-BDC-NH₂ NPs, 200 μL of 5 mM TMB, 200 μL of 0.5 M H₂O₂ and 100 μL of 0.5 mM AA; pH, 4.0; room temperature. The error bars represent the standard deviations of three replicate measurements.

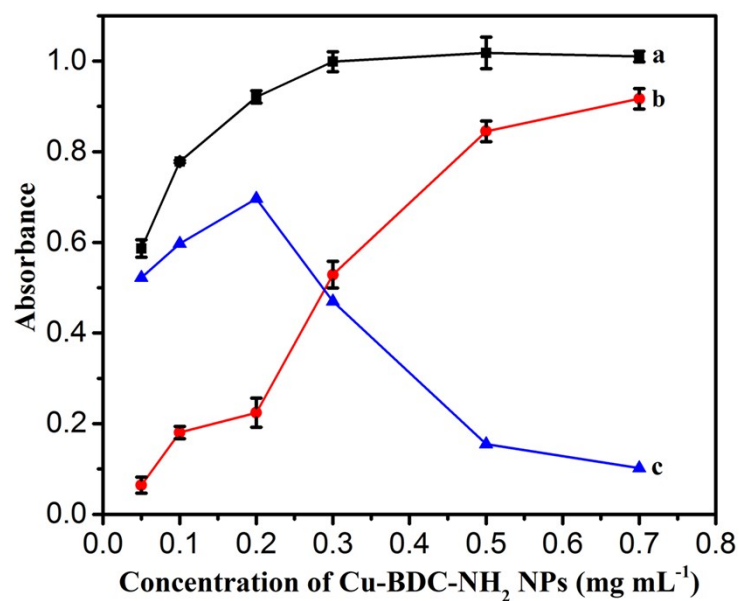


Fig. S4 Effect of the concentration of Cu-BDC-NH₂ NPs on the absorbance at 655 nm of the system solution in the absence (a) and presence (b) of AA, and the ΔA (c). 100 μL of different concentrations of Cu-BDC-NH₂ NPs, 200 μL of 5 mM TMB, 200 μL of 0.5 M H₂O₂ and 100 μL of 0.5 mM AA; pH, 4.0; room temperature; reaction time, 10 min. The error bars represent the standard deviations of three replicate measurements.

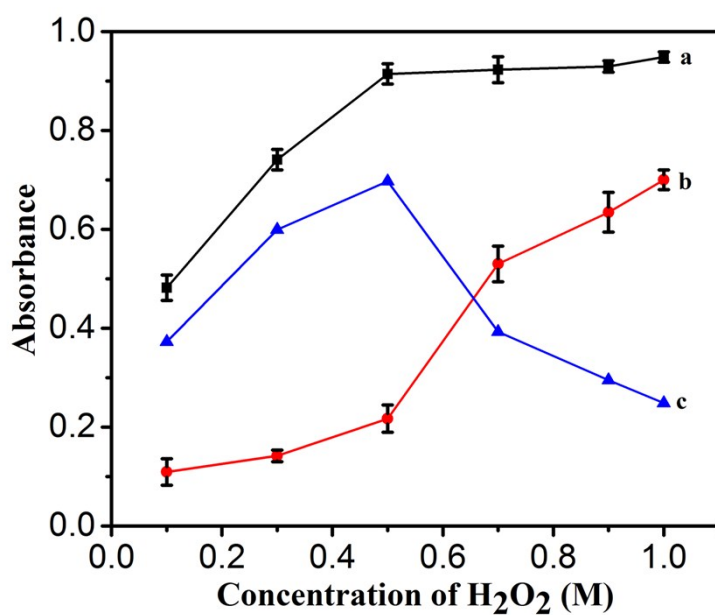


Fig. S5 Effect of the concentration of H₂O₂ on the absorbance at 655 nm of the system solution in the absence (a) and presence (b) of AA, and the ΔA (c). 100 μL of 0.2 mg mL⁻¹ Cu-BDC-NH₂ NPs, 200 μL of 0.5 mM TMB, 200 μL of different concentrations of H₂O₂ and 100 μL of 0.5 mM AA; pH, 4.0; room temperature; reaction time, 10 min. The error bars represent the standard deviations of three replicate measurements.

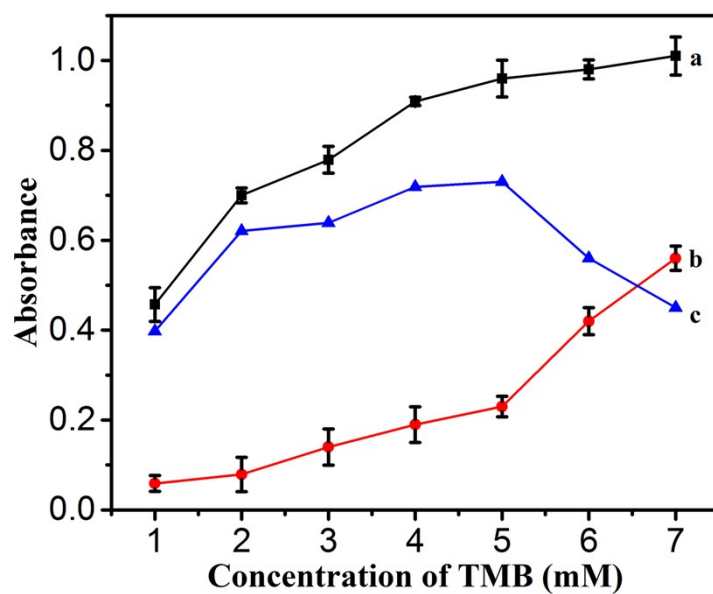


Fig. S6 Effect of the concentration of TMB on the absorbance at 655 nm of the system solution in the absence (a) and presence (b) of AA, and the ΔA (c). 100 μL of 0.2 $\text{mg}_{\text{Cu}}\text{mL}^{-1}$ Cu-BDC-NH₂ NPs, 200 μL of different concentrations of TMB, 200 μL of 0.5 M H₂O₂ and 100 μL of 0.5 mM AA; pH, 4.0; room temperature; reaction time, 10 min. The error bars represent the standard deviations of three replicate measurements.

Table S1 Analytical results of the detection of AA in pharmaceutical vitamin C tablets.

Sample	Labeled (μ M)	Found ^a (μ M)	Recovery (%)	RSD (%)
1	50	52.12 \pm 0.85	104.24	1.63
2	50	52.83 \pm 1.15	105.66	2.18
3	50	52.25 \pm 1.28	104.50	2.45

^a Average of three determinations \pm standard deviation.