Supplementary Information for

Three hidden talents in one framework: a terephthalic acid-coordinated cupric metal-organic framework with cascade cysteine oxidase- and peroxidase-mimicking activities and stimulus-responsive fluorescence for cysteine sensing

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Experimental Section

1. Chemicals and reagents

Copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), terephthalic acid (TA), hydrogen peroxide (H_2O_2), isopropanol, and N,N-dimethylformamide (DMF) were purchased from Sinopharm Chemical Regent Co., Ltd. Alanine (Ala), arginine (Arg), aspartic acid (Asp), asparagine (Asn), cysteine (Cys), glutamine (Gln), glutamic acid (Glu), glycine (Gly), histidine (His), isoleucine (Ile), leucine (Leu), lysine (Lys), methionine (Met), phenylalanine (Phe), proline (Pro), serine (Ser), threonine (Thr), tryptophan (Trp), tyrosine (Tyr), and valine (Val) were provided by Shanghai Aladdin Biochemical Technology Co., Ltd. All other chemicals were of analytical grade and used without further purification. Deionized water was utilized throughout the study.

2. Preparation and characterization of CuBDC

The proposed CuBDC was synthesized as follows: 0.97 g $Cu(NO_3)_2 \cdot 3H_2O$ and 0.67 g TA were first dissolved in 20 mL DMF; The resulting solution was then transferred into a 50 mL Teflon-lined stainless steel autoclave for reaction at 150℃ for 3 h; After reaction, the formed aquamarine blue crystals were collected by centrifugation and rinsed with adequate ethanol and deionized water alternately.

X-ray diffraction (XRD) measurements were carried out on a 6100 XRD instrument (Shimadzu) with a Cu Kα radiation. The morphology of the obtained CuBDC was observed with a 6700 scanning electron microscope (SEM, JEOL). Fourier transform infrared spectra (FT-IR) were detected by a Nicolet Nexus 470 instrument (USA Nicolet Co., Ltd.).

3. Fluorescence detection of Cys using the three-in-one CuBDC probe

All fluorescence measurements were performed on a Cary Eclipse fluorescence spectrophotometer (Australian Varian Co., Ltd.) at room temperature. Typically, 720 μL CuBDC suspension (500 μg L^{-1}) was first added into 3.28 mL NaAc-HAc solution (0.2 M, pH 7.0) containing different concentrations of Cys. The mixture was then incubated at room temperature for 30 min. Last, the emission fluorescence spectra of corresponding solutions were recorded with an excitation wavelength of 312 nm. The human serum sample provided by the Affiliated Hospital of Jiangsu University was first diluted 100 times with deionized water and then analyzed by our assay. The urine sample from the same provider was measured directly.

Supplementary Figures

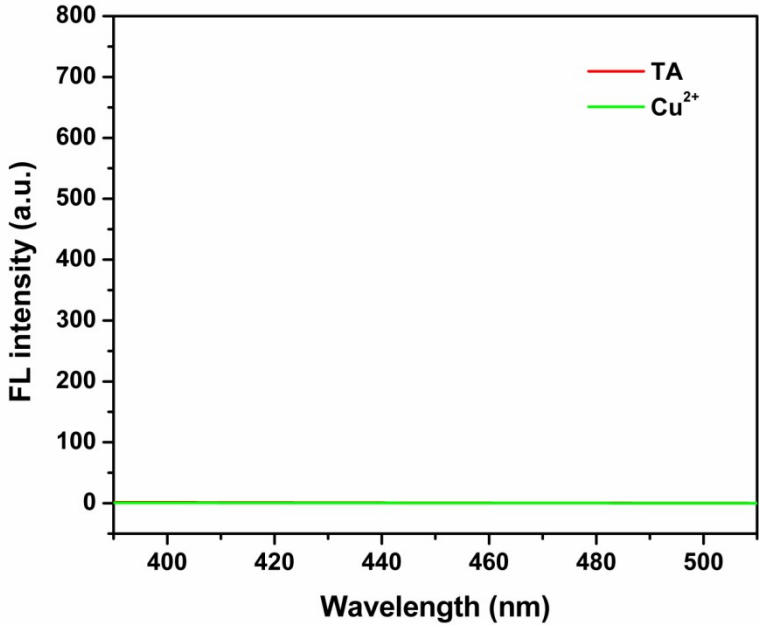

Figure S1. Fluorescence spectra of the TA and Cu^{2+} precursors.

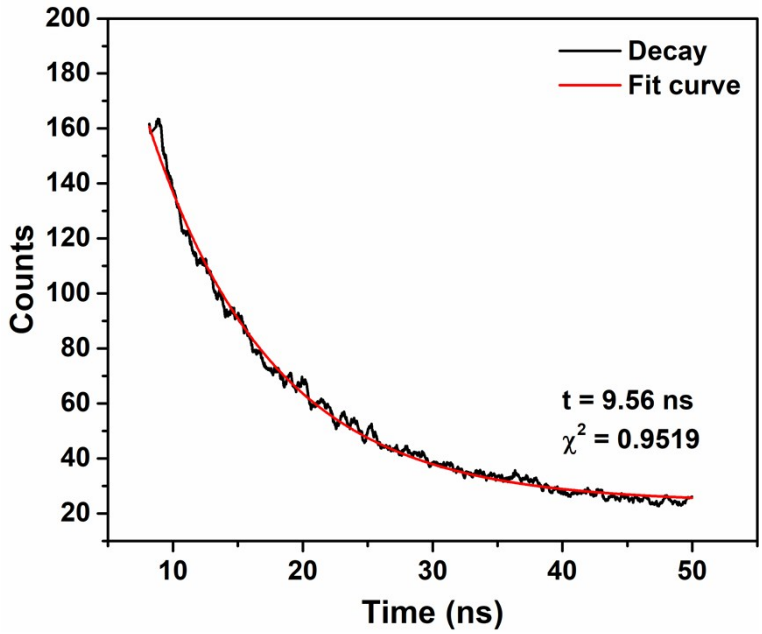

Figure S2. Fluorescence life-time of the Cu^{2+}+Cys system.

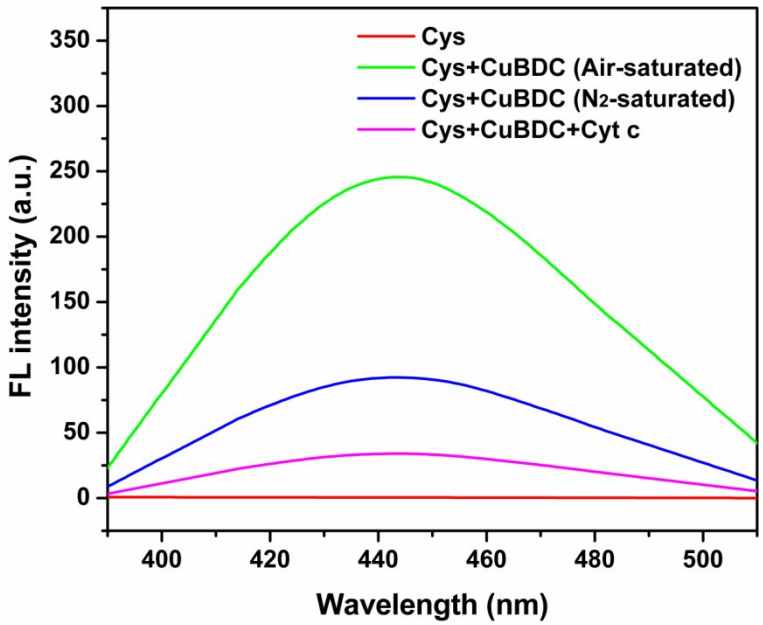

Figure S3. Fluorescence spectra of different reaction systems.

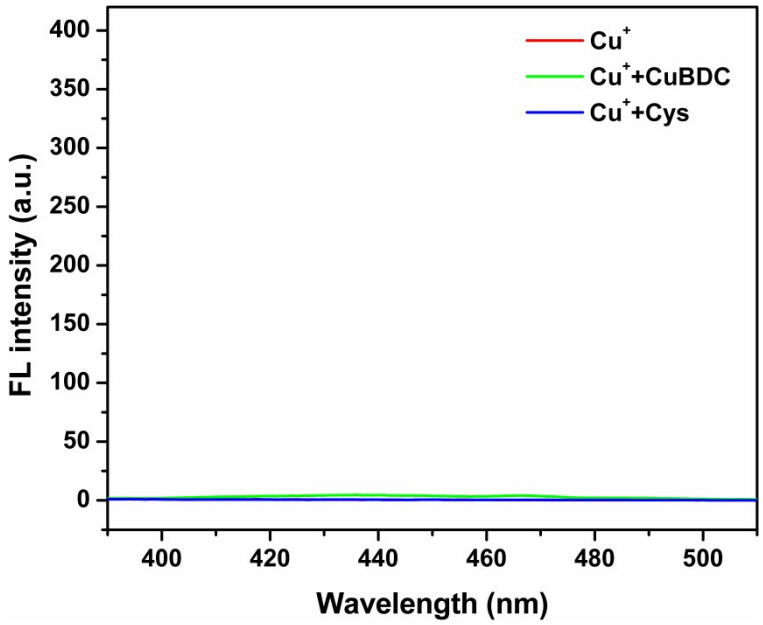

Figure S4. Fluorescence spectra of the Cu^{+} intermediate in different systems.

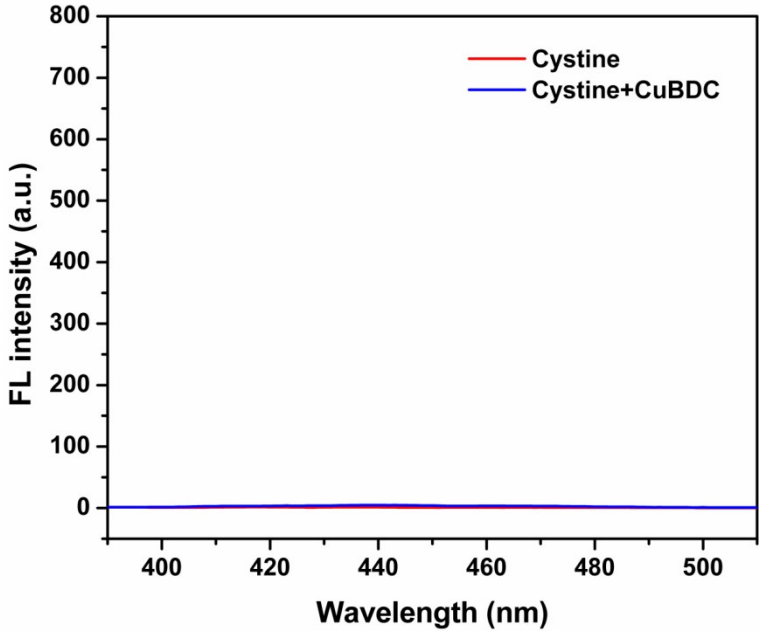

Figure S5. Fluorescence spectra of the cystine product in different systems.

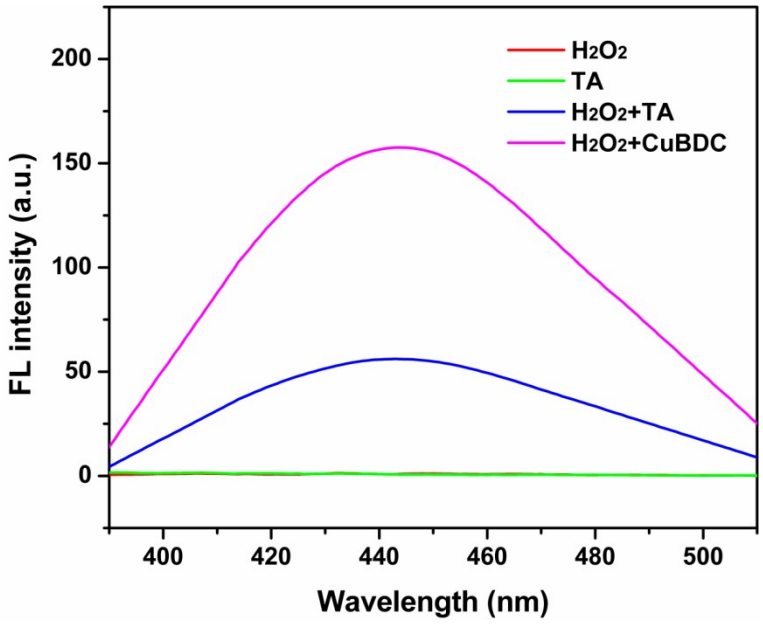

Figure S6. Fluorescence spectra for the peroxidase-mimicking activity of CuBDC.

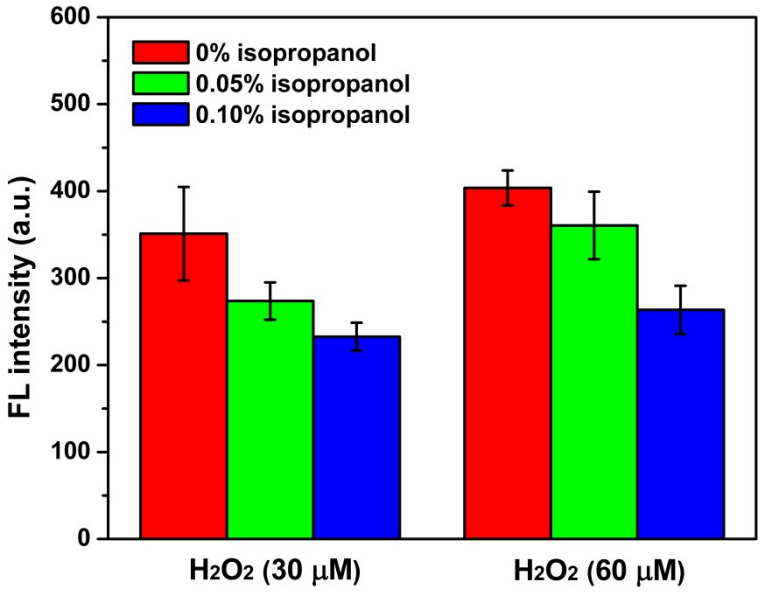

Figure S7. Catalytic oxidation of CuBDC by H_2O_2 with the presence of different concentrations of isopropanol.

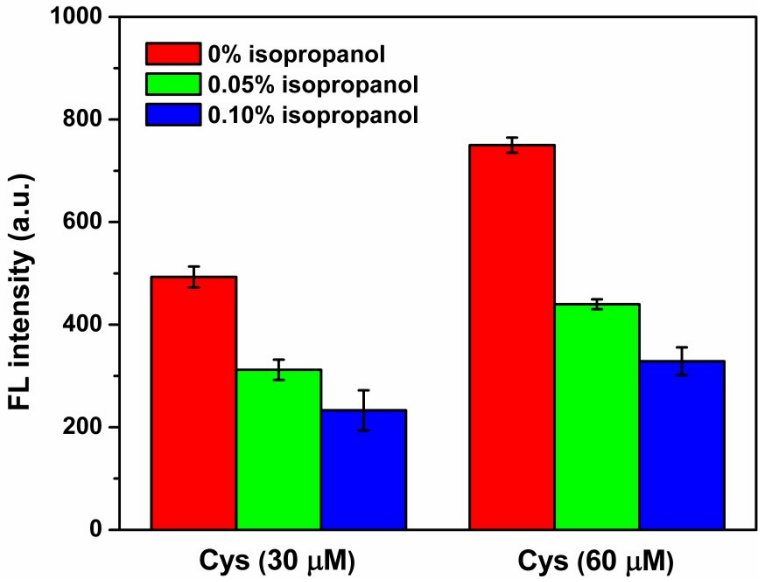

Figure S8. Catalytic oxidation of CuBDC by Cys with the presence of different concentrations of isopropanol.

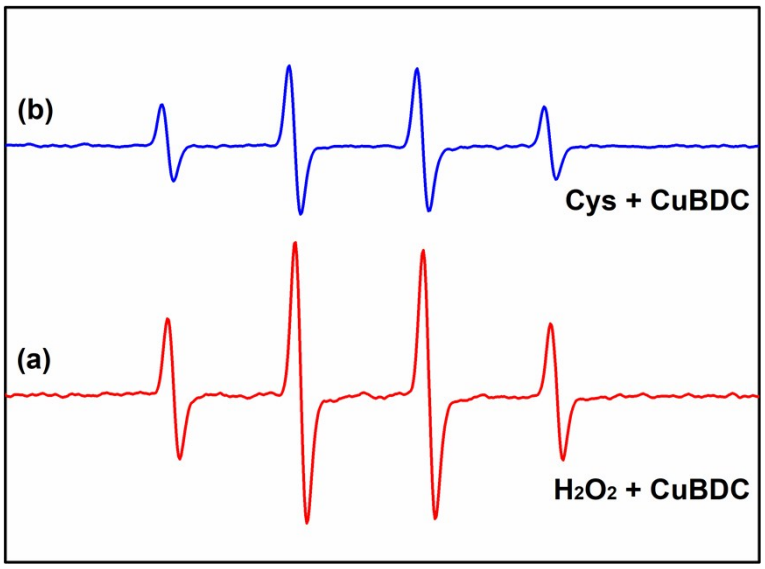

Figure S9. ESR spectra for different systems.

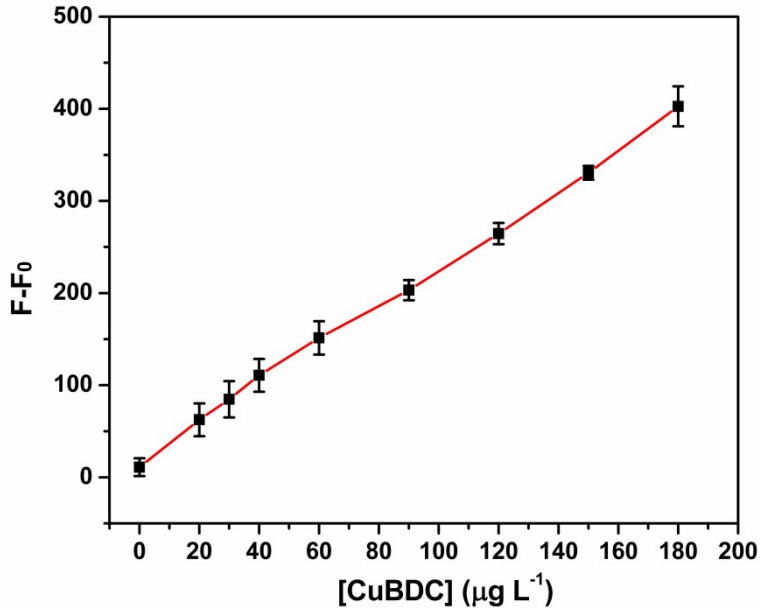

Figure S10. Effect of the CuBDC concentration on the fluorescence intensity of the CuBDC+Cys system.

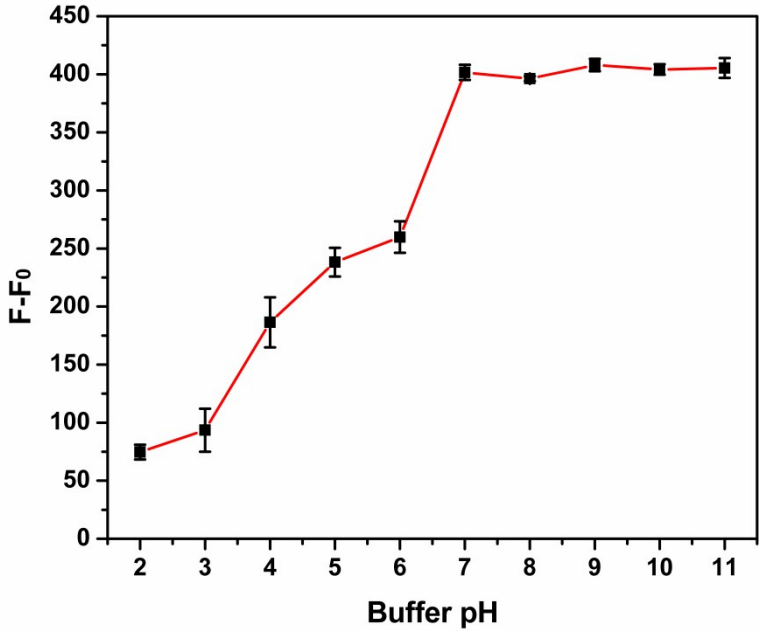

Figure S11. Effect of the buffer pH on the fluorescence intensity of the CuBDC+Cys system.

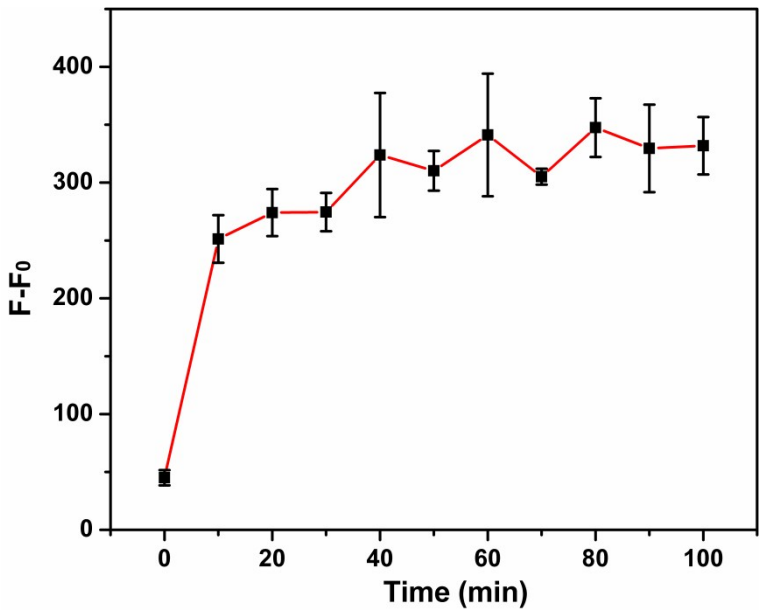

Figure S12. Effect of the reaction time on the fluorescence intensity of the CuBDC+Cys system.

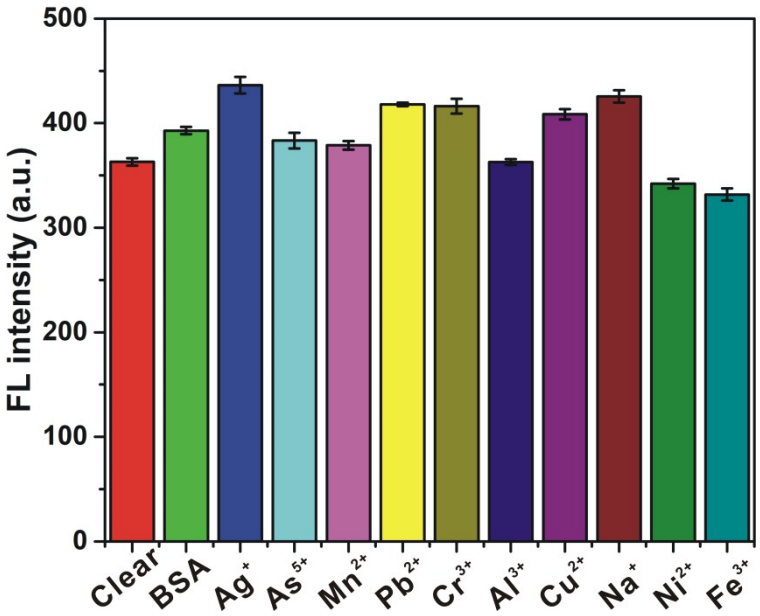

Figure S13. Possible effects of BSA and a number of common metal ions (Ag^{+}, As^{5+}, Mn^{2+}, Pb^{2+}, Cr^{3+}, Al^{3+}, Cu^{2+}, Na^{+}, Ni^{2+}, and Fe^{3+}) on the selective detection of Cys.

Supplementary Tables

Table S1. Comparison of our CuBDC probe with previously reported methods for Cys detection.

Material	Method	Linear range	LOD	Ref.
CNFs	Electrochemical	0.15~64 μM	0.1 μM	1
DNA-AuNPs	Colorimetric	0.05~10 μM	100 nM	2
MB/Hg^{2+}	Fluorometric	4~200 nM	4.2 nM	3
PBI-Hg^{2+}	Fluorometric	0.05~0.3 μM	9.6 nM	4
PMAA-Ag^{+}	Fluorometric	0.025~6.0 μM	20 nM	5
CuBDC	Fluorometric	0.75~150 μM	0.67 μM	Our work

Table S2. Performance of our probe for the determination of Cys in real matrices.

Sample	Measured[a] (μM)	Spiked (μM)	Measured[b] (μM)	Recovery (%)
Serum	3.5±0.7	75	76.0±0.9	96.7
Urine	11.2±0.8	75	85.1±0.4	98.5
Tap water	—	75	76.7±0.5	102.3

[a] The Cys level in original samples

[b] The Cys level in spiked samples

Supplementary References

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