Electronic Supplementary Material (ESI) for ChemComm.

Supporting information for

Synthesis of mixed valence state Ce-MOF as oxidase mimetics for colorimetric detection of biothiols

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1. Instruments and chemicals

All chemicals were at least of analytical reagent grade and used without further purification. $Ce(NO_3)_3 \cdot 6H_2O$, 1,3,5-benzenetricarboxylic acid (H_3BTC), NaOH, H_2O_2 (30 wt %) and anhydrous ethanol were purchased from Shanghai Chemical Reagents Corporation (Shanghai, China). 3,3',5,5'-tetramethylbenzidine (TMB) was purchased from TCI. Cysteine (Cys), glutathione (GSH), homocysteine (Hcy), tryptophane (Try), aspartic acid (Asp), lysine (Lys), alanine (Ala), phenylalanine(Phe), tyrosine (Tyr), histidine (His), argnine (Arg) and uric acid (UA) were purchased from Aladdin chemistry Co. Ltd. (Shanghai, China).

X-ray diffraction (XRD) patterns of the samples were recorded on a X'Pert PRO diffractometer (PANalytical, The Netherlands) with Cu Kα radiation (λ=0.15418 nm). X-ray photoelectron spectroscopy (XPS) data were obtained with a Thermo ESCALAB 250XI electron spectrometer (Thermo, USA) using 150 W Al Kα radiation. Fourier transform infrared (FT-IR) spectra (4000–400 cm^{-1}) in KBr were recorded using a PE Spectrum One FT-IR spectrometer (PE, USA). Thermogravimetric analysis (TGA) was performed with a LABSYS evo TG-DSC/DTA instrument (Setaram Instrumentation, France). Scanning electron microscope (SEM) was carried out on a FEI Quanta 200 FEG SEM (Philips, The Netherlands). UV absorption spectra were recorded on a model Cary 60 spectrophotometer (Agilent, USA). Ultrapure water was produced by a Millipore purification system (Bedford, MA, USA) and used to prepare all aqueous solutions.

2. Experimental section

2.1 Synthesis of Ce-MOF

Ce-MOF was synthesized by a simple low temperature solvothermal method.[1] In particular, 4.34 g $Ce(NO_3)_3 \cdot 6H_2O$ was dissolved in 45 mL ultrapure water (A solution); 2.10 g H_3BTC was dissolved in 10 mL water-ethanol solution (v/v=1:1) (B solution). Subsequently, the A solution was added to B solution by dropwise under vigorous magnetic stirring and kept on water bath at 60℃. After continuing the process for 1 h, the precipitate was separated from the reaction mixture by centrifugation and washed several times with ethanol and ultrapure water, finally dried in an oven at 70 °C for 12 h.

2.2 Synthesis of mixed valence state Ce-MOF (MVCM)

MVCM was synthesized by a facile and rapid *in situ* partial oxidation method. In particular, 20 mg of Ce-MOF was dispersed in 4.0 mL ultrapure water under ultrasonication for 10 min to form suspension. Then, 50 μL of fresh NaOH (9.5 mL, 2.5 M)/H_2O_2 (0.5 mL, 30 wt %) mixed solution was added to the suspension and kept shaking for 2.0 min. Subsequently, yellow product was separated via centrifugation and washed several times with ultrapure water until pH of supernatant was about 7.0, then dried in an oven at 70 °C for 12 h.

2.3 Oxidase-like activity of MVCM

The oxidase-like activity of the MVCM was investigated through the catalytic oxidation of the substrate TMB to produce a blue color reaction. Briefly, 740 μL of 0.1 M NaAc buffer (pH 4.0), 200 μL TMB solution (1.7 mM, ethanol solution) were added into 1.5 mL EP vial. Then, 60 μL of MVCM dispersion (5.0 mg mL^{-1}) was

added into the mixture. The resultant mixture was incubated at room temperature for 15 min and UV-vis absorbance spectroscopy at wavelength 655 nm.

2.4 Detection of biothiols

The colorimetric assay was performed as follows: (a) preparation of oxTMB, 1480 μL of 0.1 M NaAc buffer (pH 4.0), 400 μL TMB solution (1.7 mM, ethanol solution) were added into 4.0 mL EP vial. Then, 120 μL of MVCM dispersion (5.0 mg mL^{-1}) was added into the mixture. The resultant mixture was incubated at room temperature for 15 min and the blue color oxTMB supernatant was collected by filtering through a 0.25 μm nylon membrane filter. The oxTMB solution was stored in the dark at 4°C until use. (b) detection of biothiols, 200 μL oxTMB solution was added into 1.0 mL EP vial. Then, 200 μL of different concentrations Cys solution or serum was added. The resultant mixture was incubated at room temperature for 25 min and UV-vis absorbance spectroscopy at wavelength 655 nm.

References

1. K. Liu, H. You, G. Jia, Y. Zheng, Y. Huang, Y. Song, M. Yang, L. Zhang and H. Zhang, *Cryst Growth Des*, 2010, **10**, 790-797.

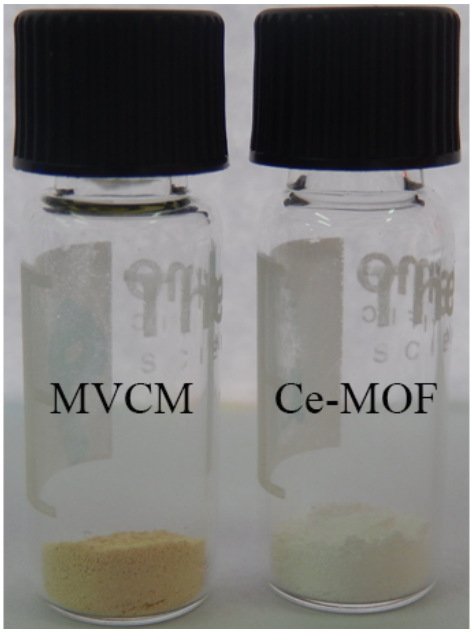

Fig. S1 Photograph of MVMC and Ce-MOF

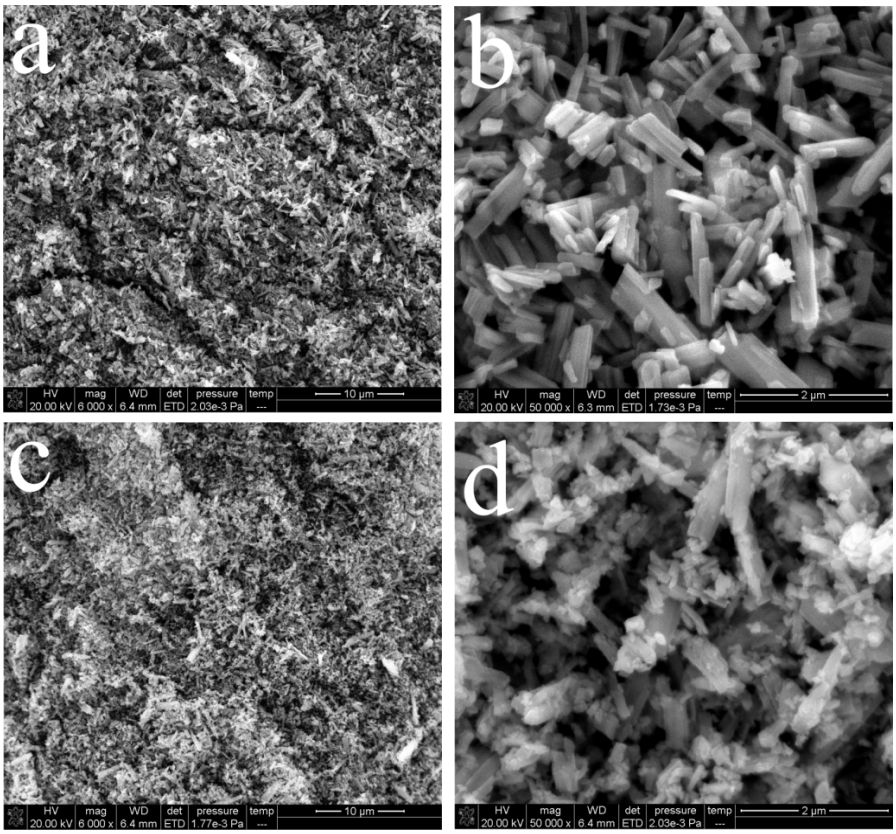

Fig. S2 SEM images of MVCM (a, b) and Ce-MOF (c, d)

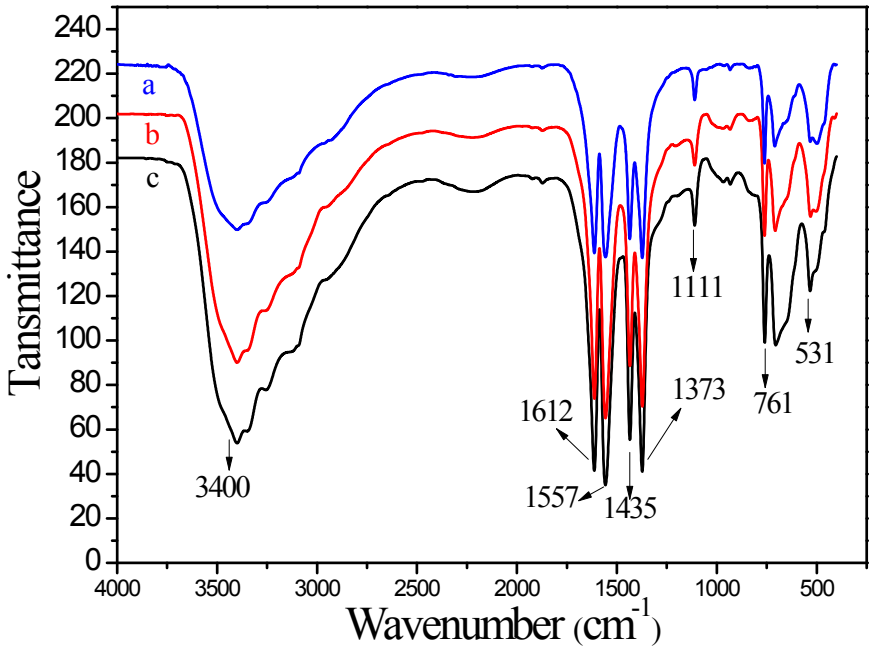

Fig. S3 FT-IR spectrum of MVCM (a) after, (b) before catalytic reaction and (c)Ce-MOF.

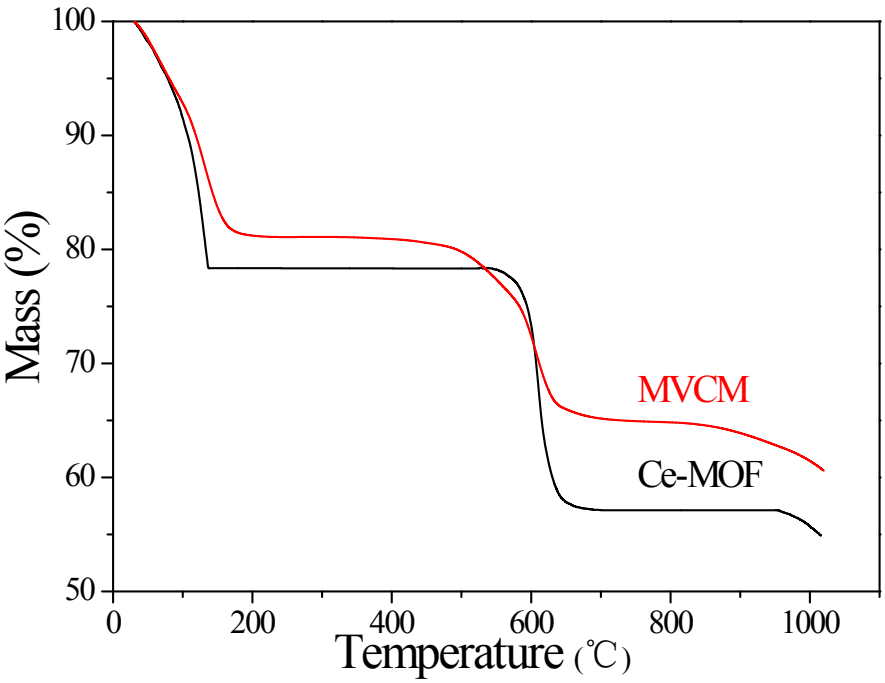

Fig. S4 TGA curves of MVCM and Ce-MOF.

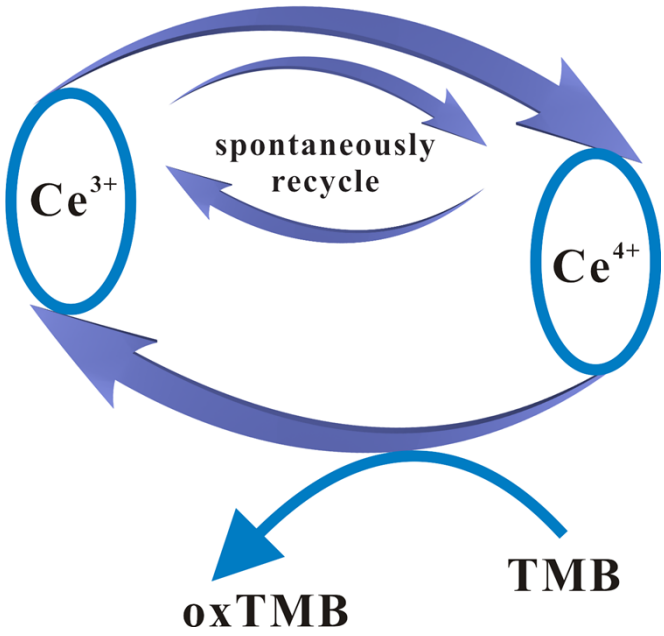

Fig. S5 Probable mechanism of the oxidase-like activity of MVCM toward TMB.

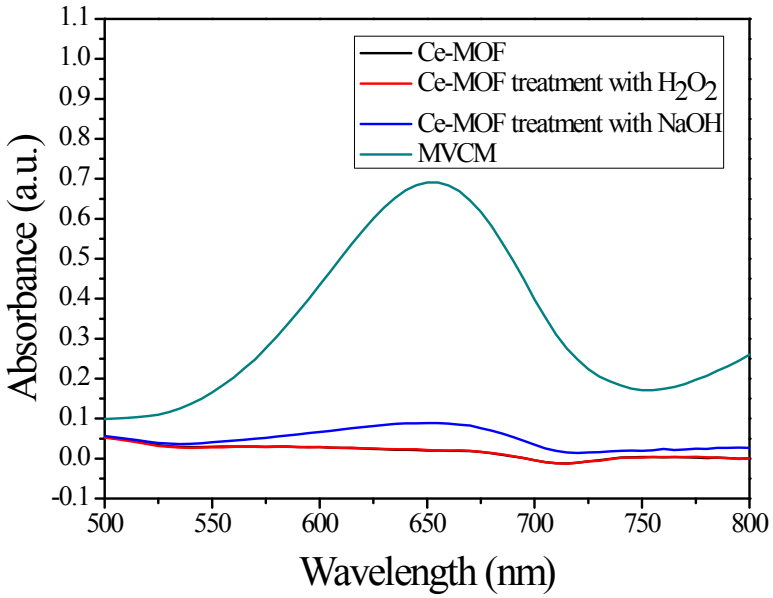

Fig. S6 Catalytic activity of different oxidase mimetic.

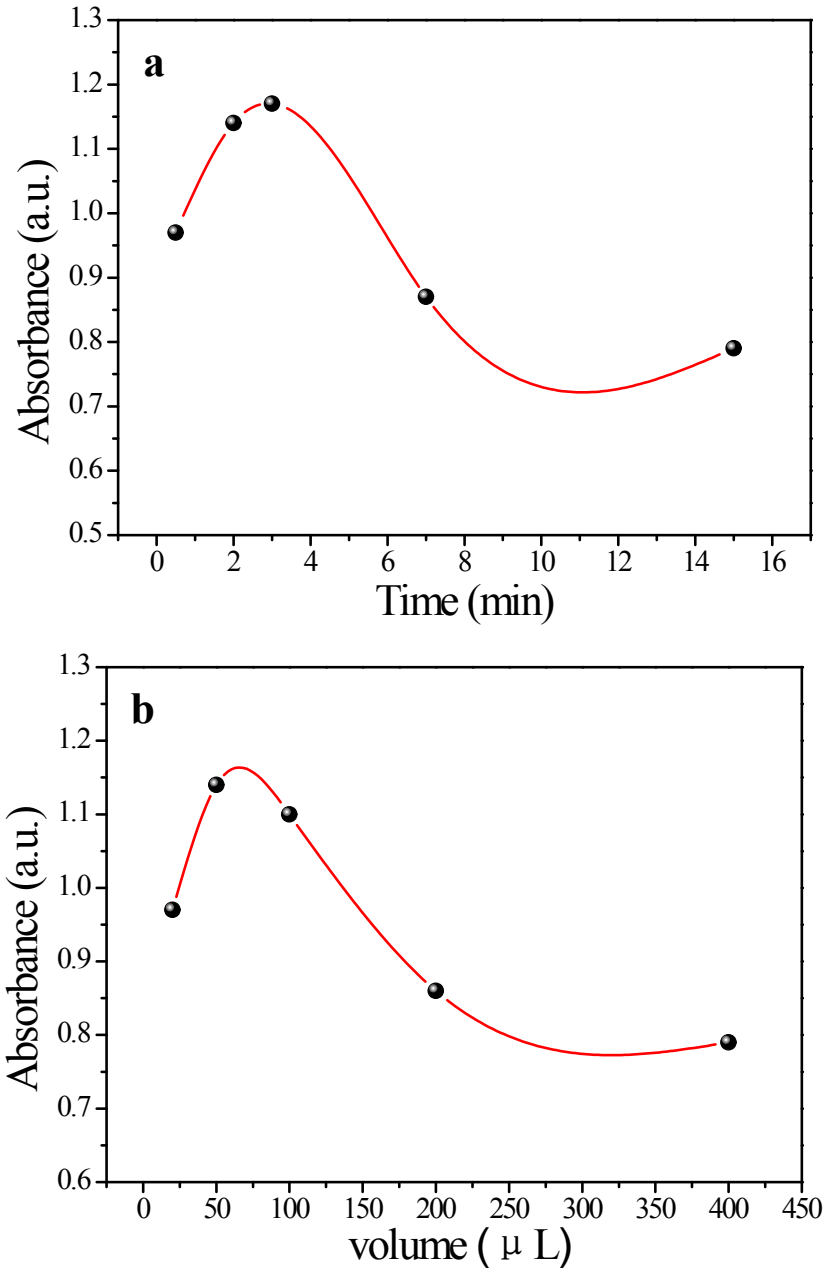

Fig. S7 Effects of catalytic activities of MVCM at different synthetic conditions

(a) the reaction time (b) the volume of NaOH /H_2O_2 mixed solution.

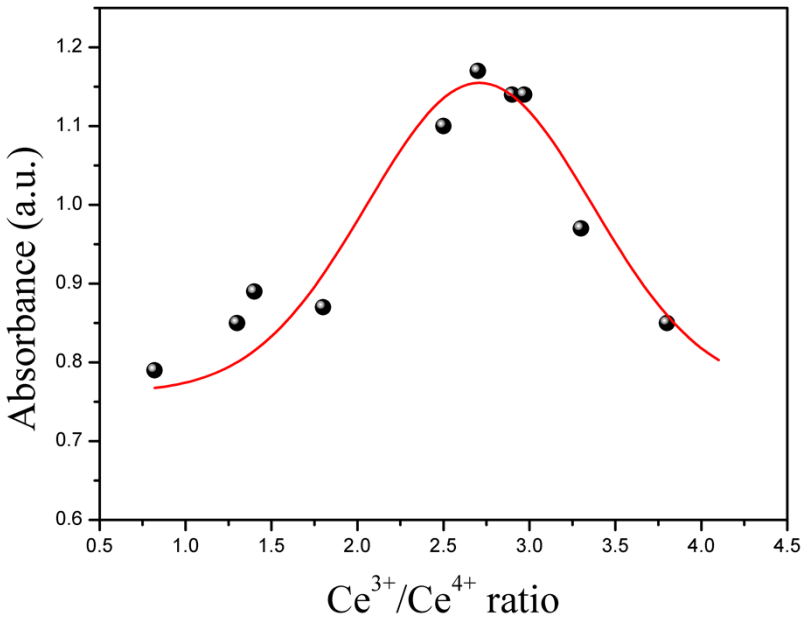

Fig. S8 The catalytic activities of MVCM at different Ce^{3+}/Ce^{4+} ratios.

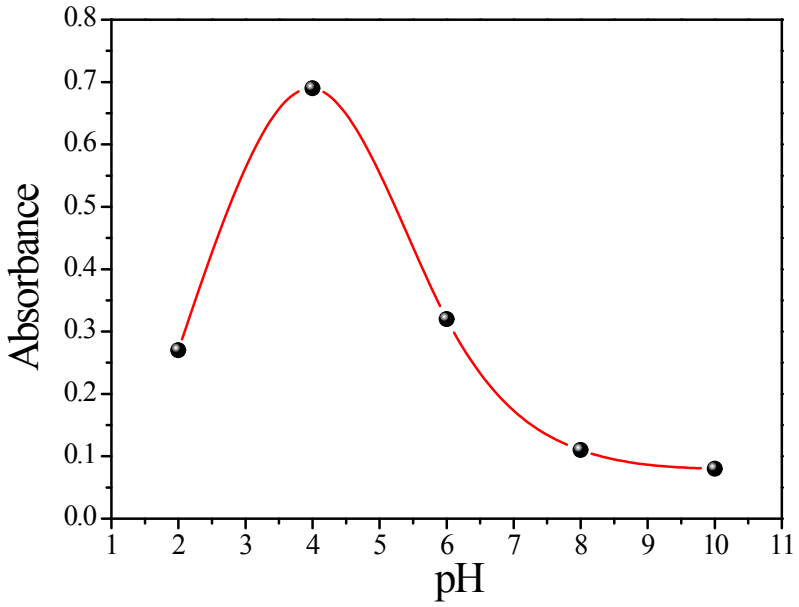

Fig. S9 The catalytic activity of MVCM at different pH values of solution.

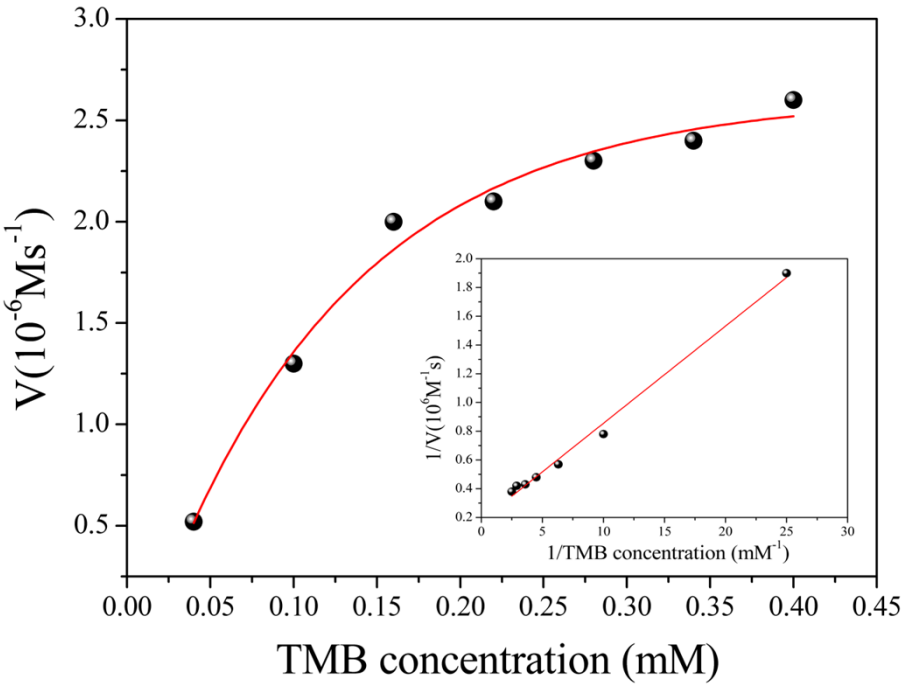

Fig. S10 Steady-state kinetic assays of the MVCM. Insets: Lineweaver–Burk plots of the double reciprocal of the Michaelis–Menten equation. TMB was used as substrate.

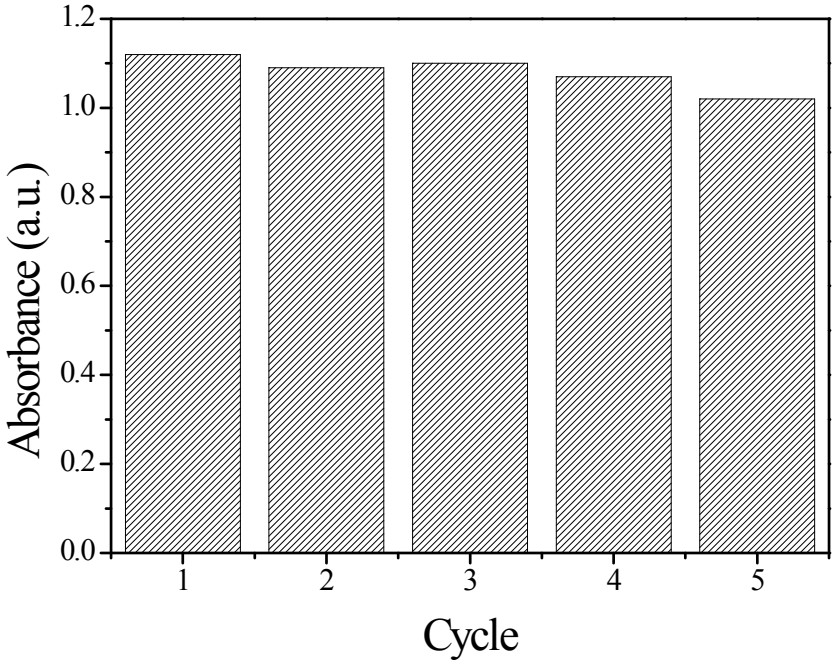

Fig. S11 Five consecutive catalysis cycles of MVCM.

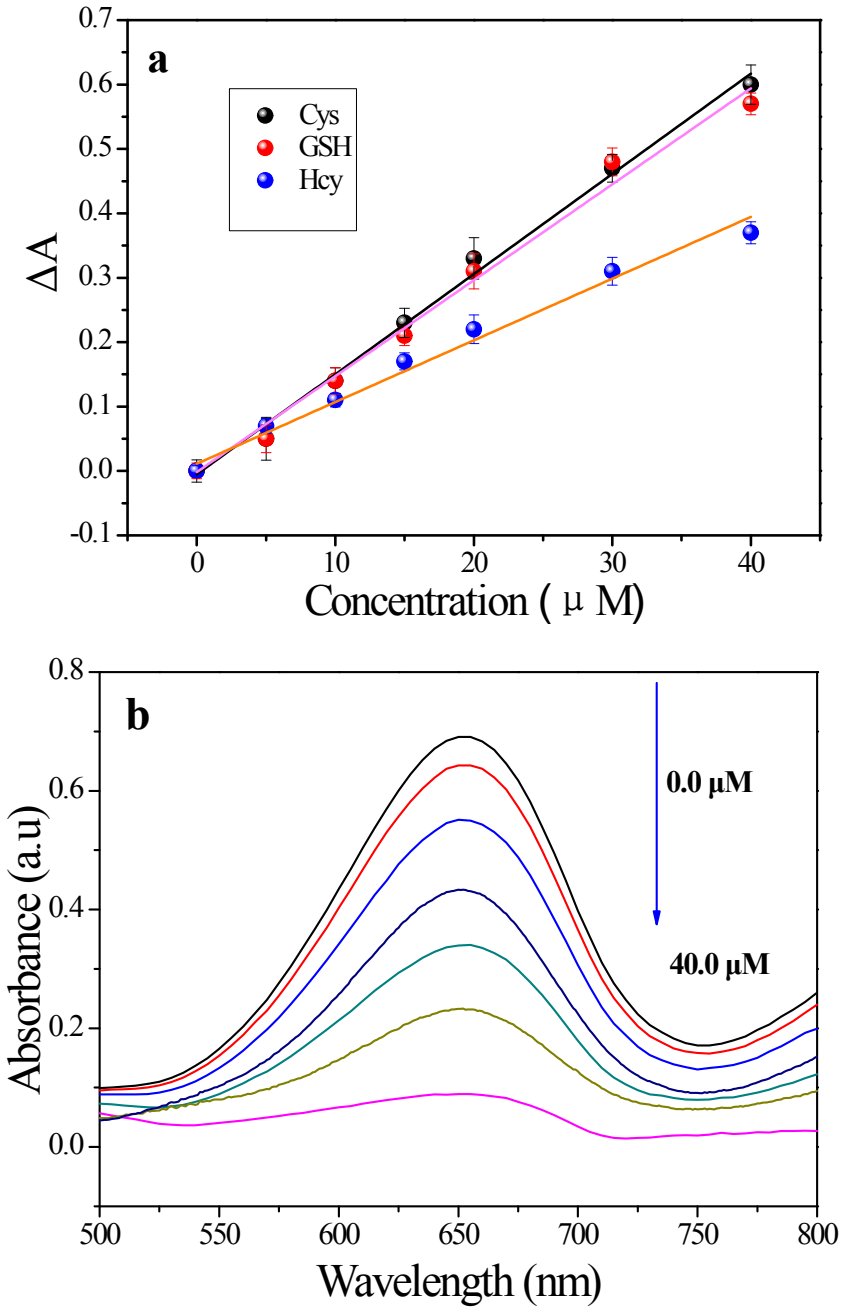

Fig. S12 Calibration plot for detection biothiols (a) and Cys UV/vis spectra (b)

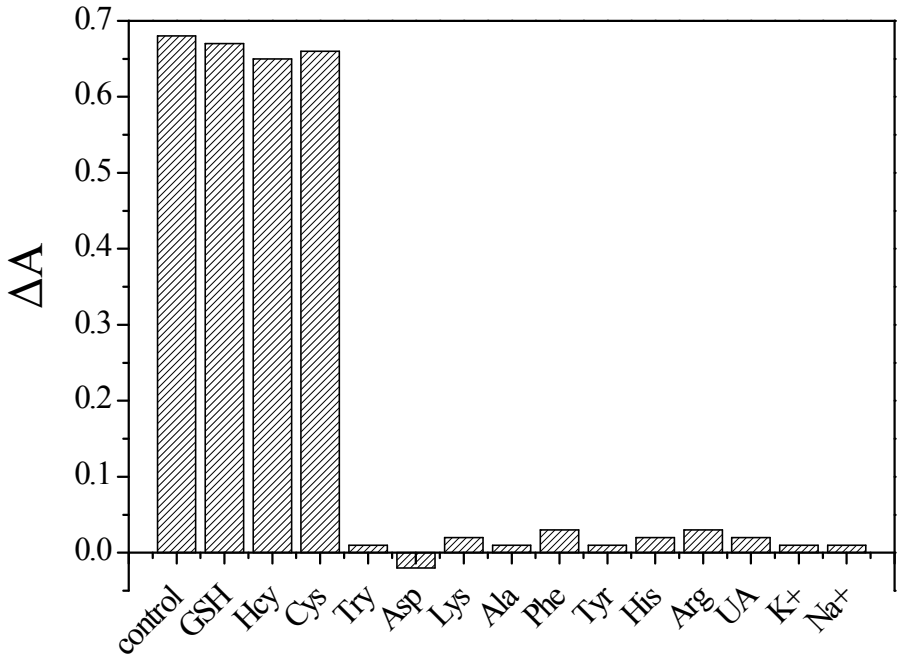

Fig. S13 Colorimetric response of the system toward biothiols and other biomolecules.

Table S1. Quantitative analyses of Cys, GSH and Hcy through this colorimetric method.

Analyte	Linear range (μM)	Regression equation	Correlation coefficient (R)	Detection limits (μM)
Cys	0-40	A=0.016c	0.997	0.135
GSH	0-40	A=0.015c	0.991	0.129
Hcy	0-40	A=0.011c	0.989	0.143

Table S2. Results of recovery studies of the analysis of Cys in human blood.

Sample	Original amount (μM)	Added (μM)	Found (μM)	Recovery (%)	RSD (%)
Sample1	12.5	5.0	4.9	98.0	2.1
		10.0	10.3	103.0	1.4
		20.0	20.2	96.4	1.1
Sample2	25.2	10.0	9.8	98.0	2.3
		20.0	19.9	99.5	1.7
		50.0	50.1	100.2	1.3
Sample3	46.9	20.0	20.3	101.5	1.8
		50.0	49.0	98.0	1.3
		80.0	80.2	100.3	0.8