Supplementary Material (ESI) for Analyst

Indicator approach to develop a chemosensor for the colorimetric sensing of thiol-containing in water and its application for the thiol detection in plasma

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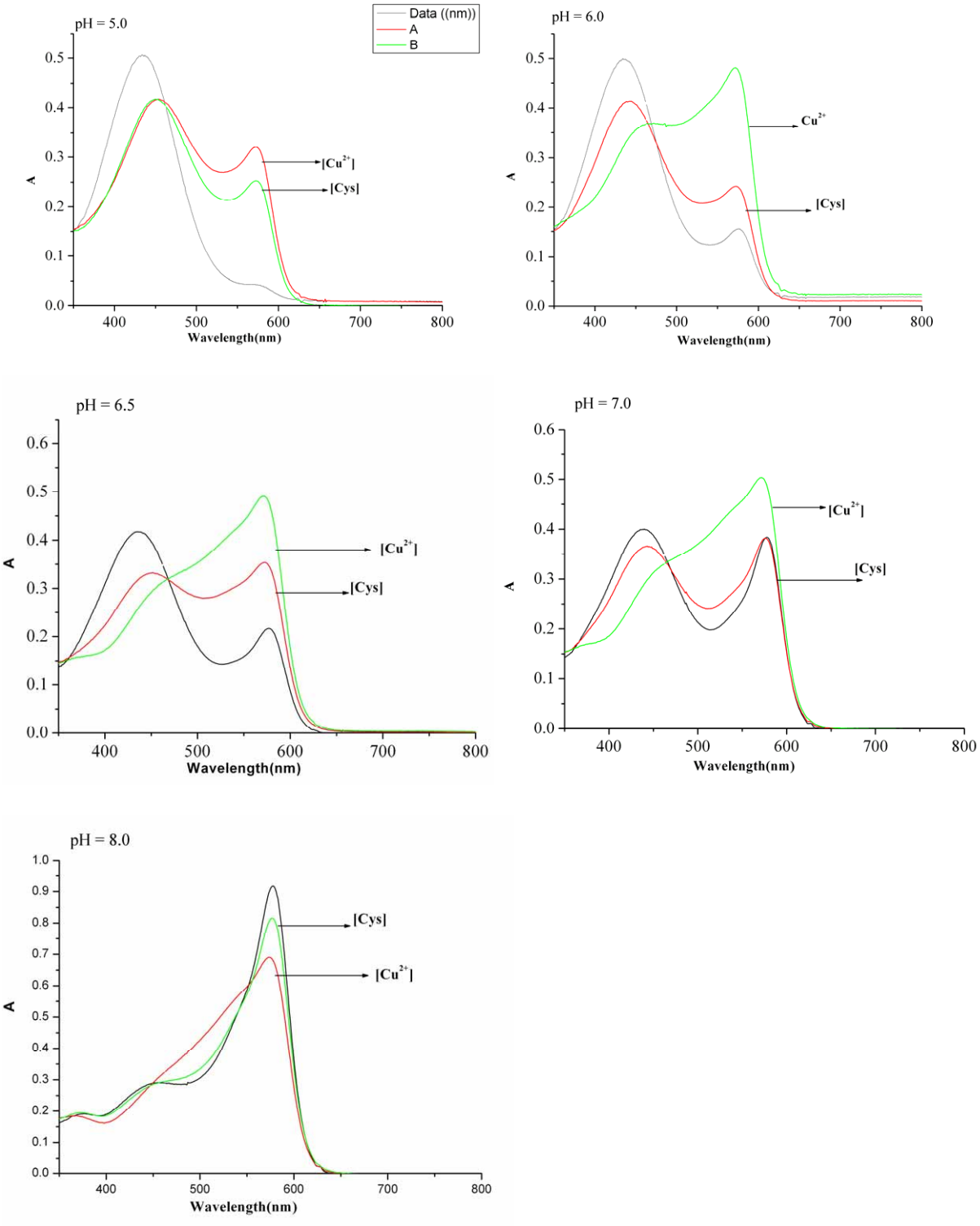
Figure S1 Choice of pH-range for the Measurement.



The absorbance under various pH values. These black lines represent the absorbance of XO (25 μM), red ones are the absorbance of [Cu(XO] (25 μM, XO + 25 μM $CuCl_2$), and the green ones the absorbance of the ensemble when 80 μM Cys was added into the solution of [Cu(XO] (25 μM). The pH (5.0-8.0) of the buffers (10 mM HEPES) was adjusted with 5 M NaOH or 6 M HCl.

Figure S2 The experiments of UV-vis spectrophotometer titration for Cu^{2+}: XO

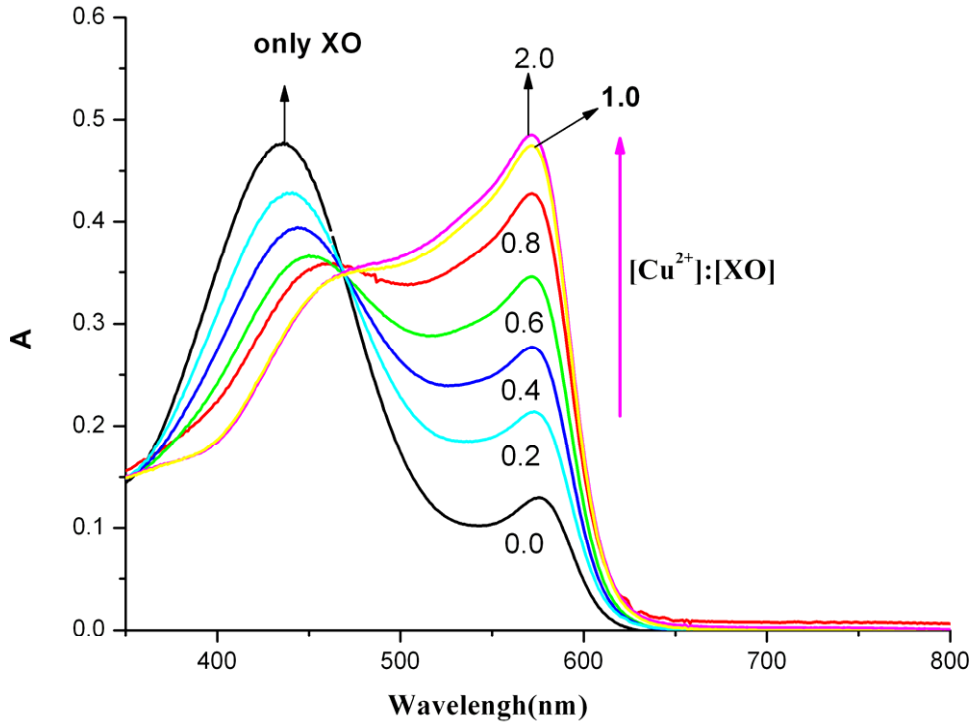


Figure S3 To determine the coordination ratio of Cu^{2+} to Cys. Cys was added to the solution of Cu^{2+}-XO (25 μM) in HEPES (10 mM) buffer.

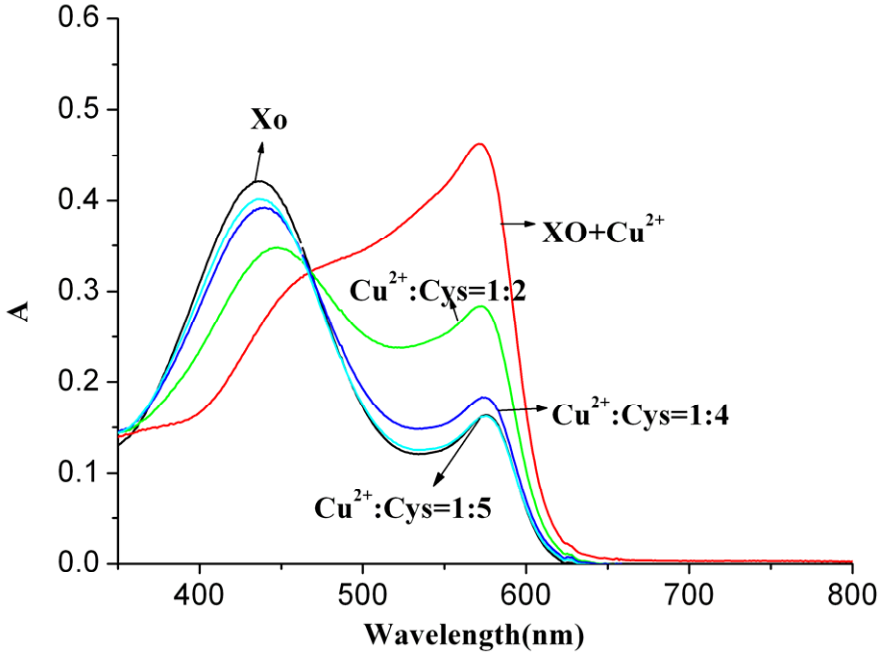


Figure S4 Dada of Absorbance for the Ensemble of Cu^{2+}-XO-Cys

The working curve for Cys measurement (**Figure S4**) was plotted with the absorbance value against various concentrations of Cys (12, 24, 48, 96, 192 μM) (**Table S1**). The average of ε is 6350 $L \cdot mol^{-1} \cdot cm^{-1}$. Base a hypothetic equation: **A=K*c*+B.** These data was analyzed using the software OriginPro 7.0.

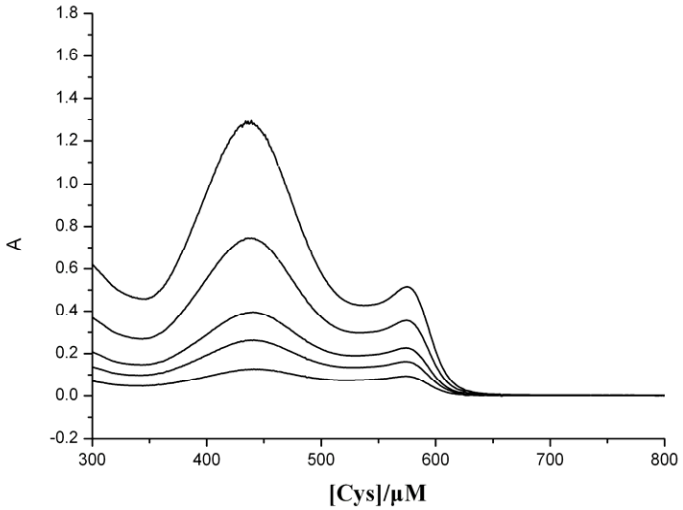
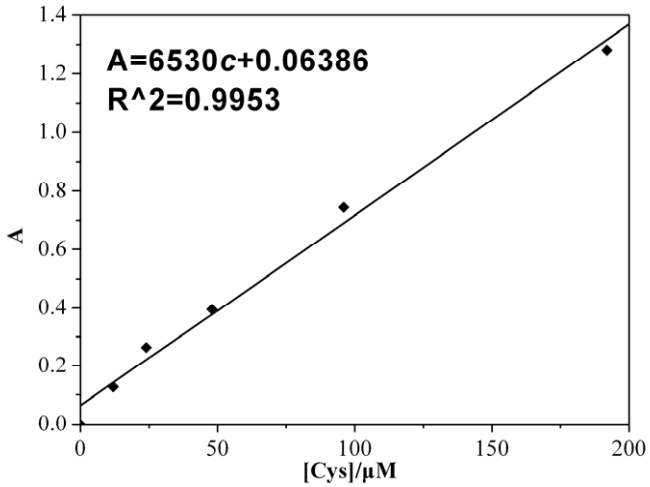


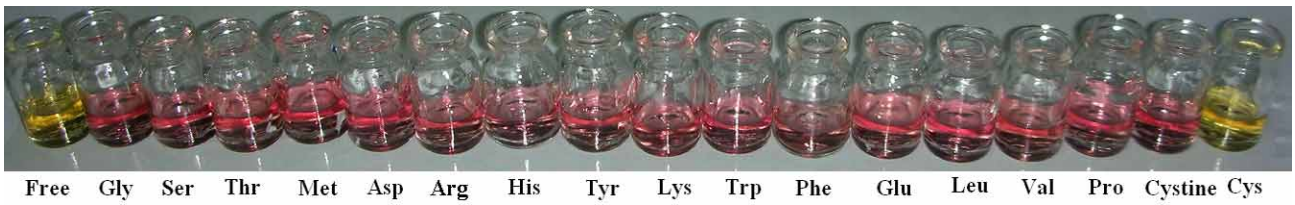
Table S1

Conc. of Cys / μM	Absorbance
12.0	0.1274
24.0	0.2634
48.0	0.3952
96.0	0.7436
192.0	1.2811



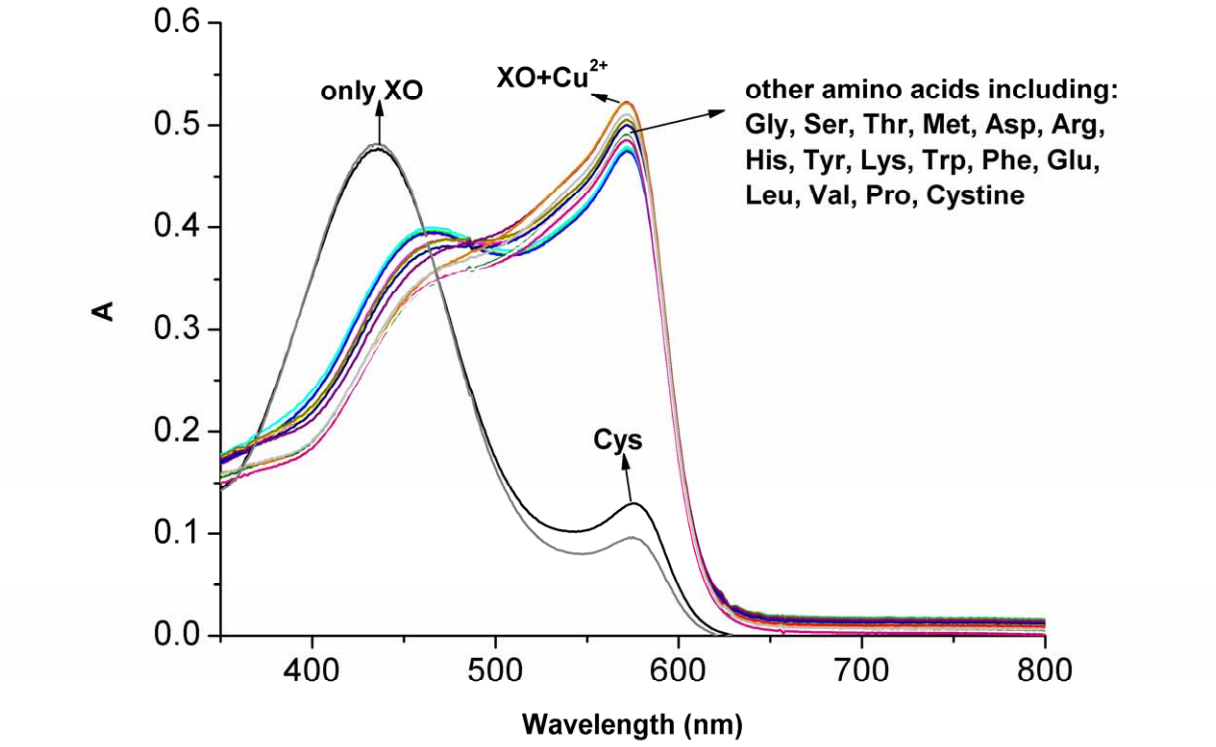
Plot the absorbance value against total concentrations of Cys. Dots are experiments data, the curve is best fit with linear regression R^2=0.9953

Figure S5 A color change photograph for Cys and other amino acids



Only cysteine causes the color change from violet-red to yellow. **Concentrations:** Cu^{2+}-XO (25 μM); [Cys]=100 μM; [other amino acids] = 5000 μM**.**

Figure S6 Other amino acids do not affect Cys.



UV/Vis spectra of the [Cu(XO)] mixture (25 μM in a pH 6.0, 10 mM HEPES buffer solution) was added with various other amino acids 5000 μM and Cys 100 μM in final concentration.

Figure S7 Excluded various anions interfering to determination of Cys

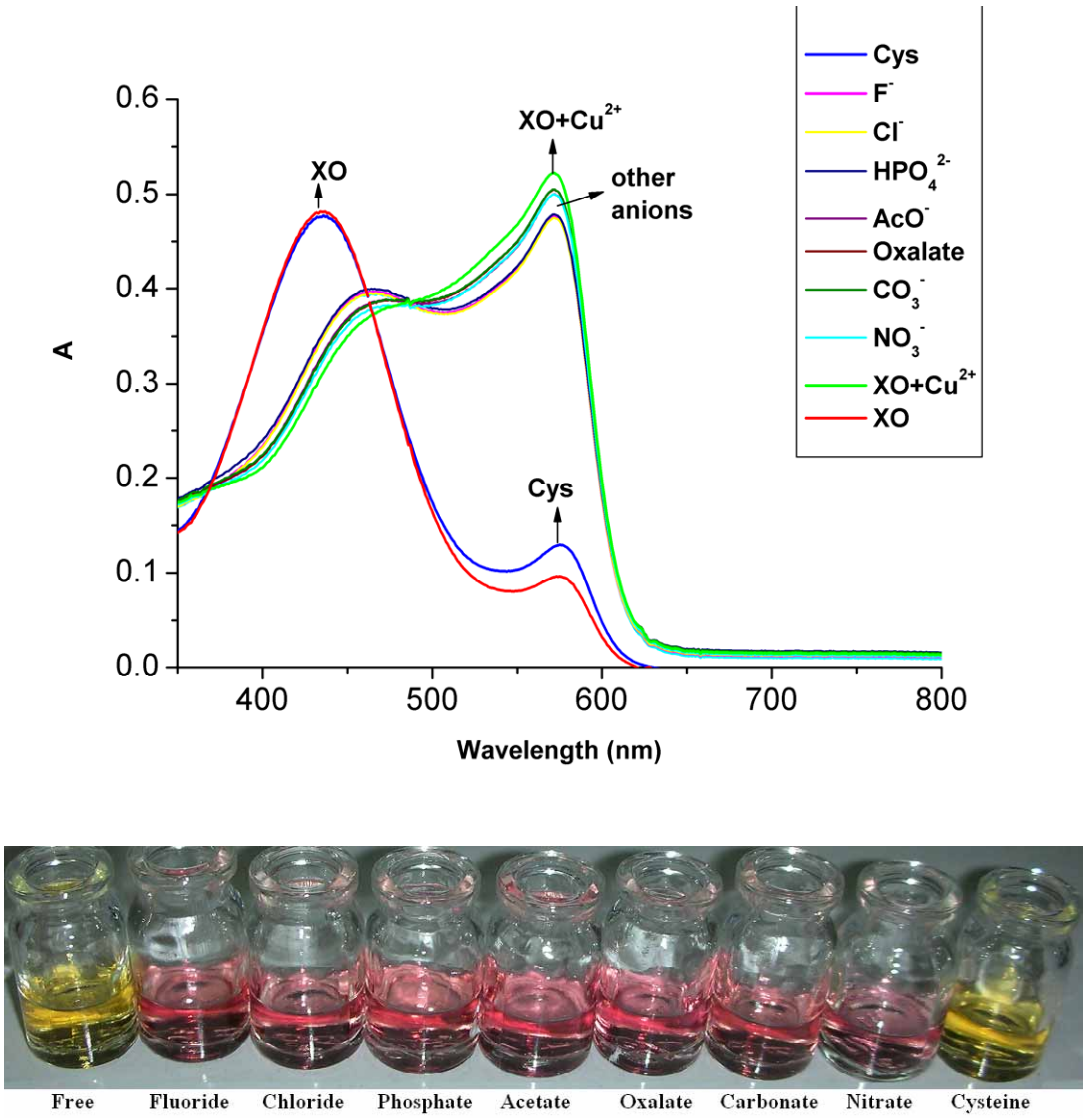
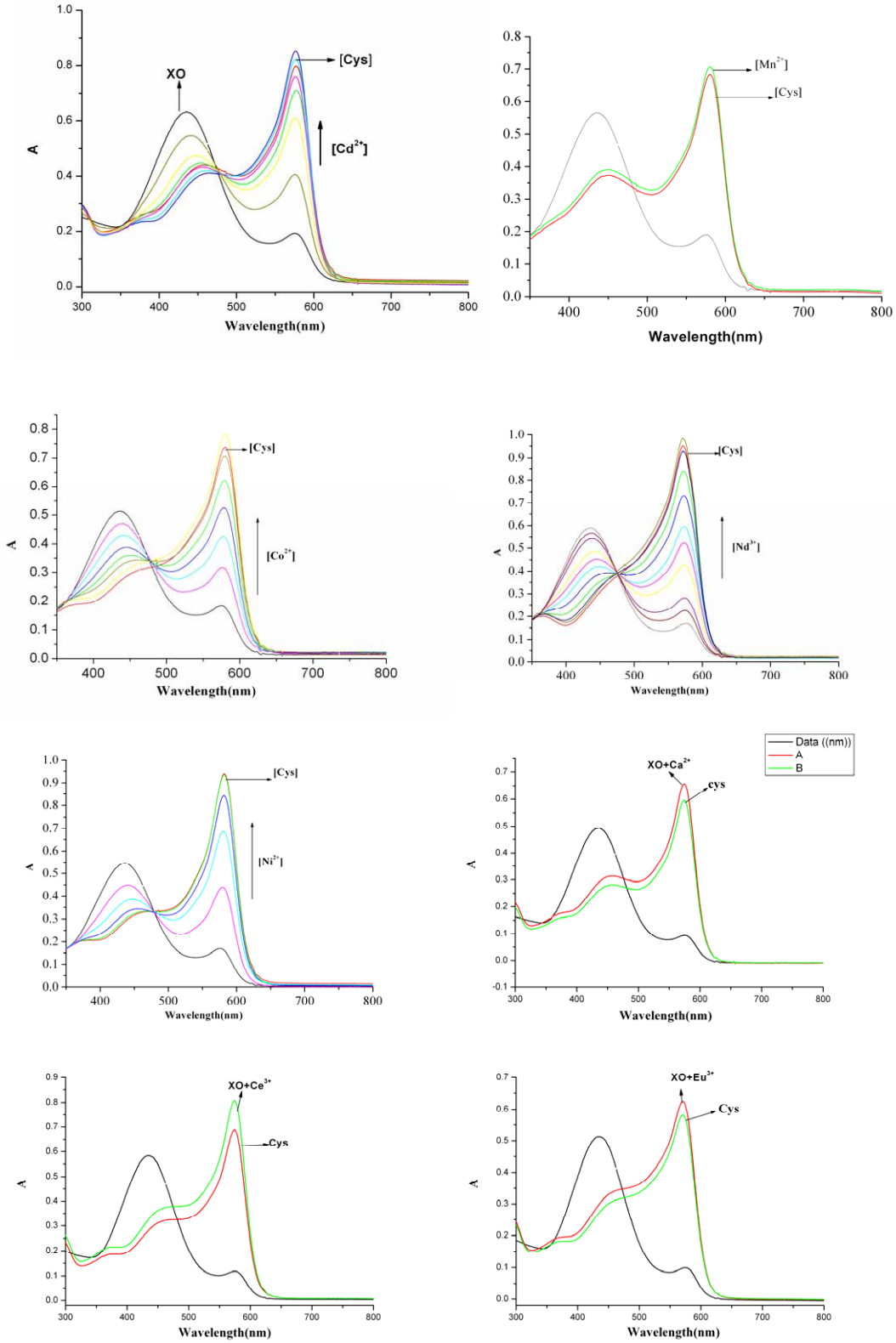
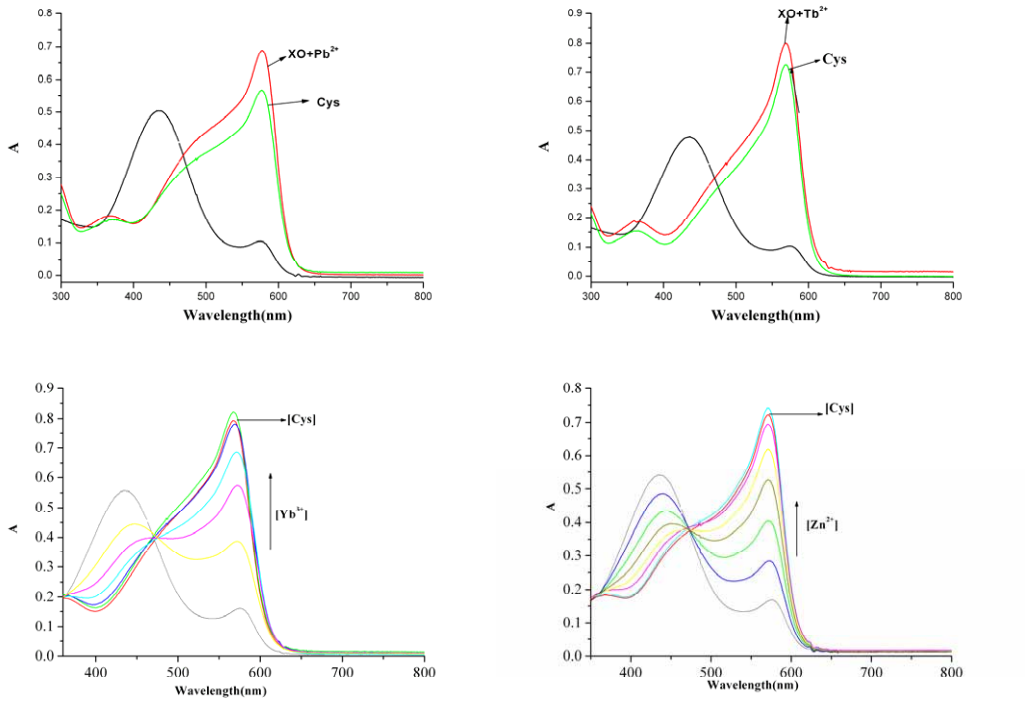


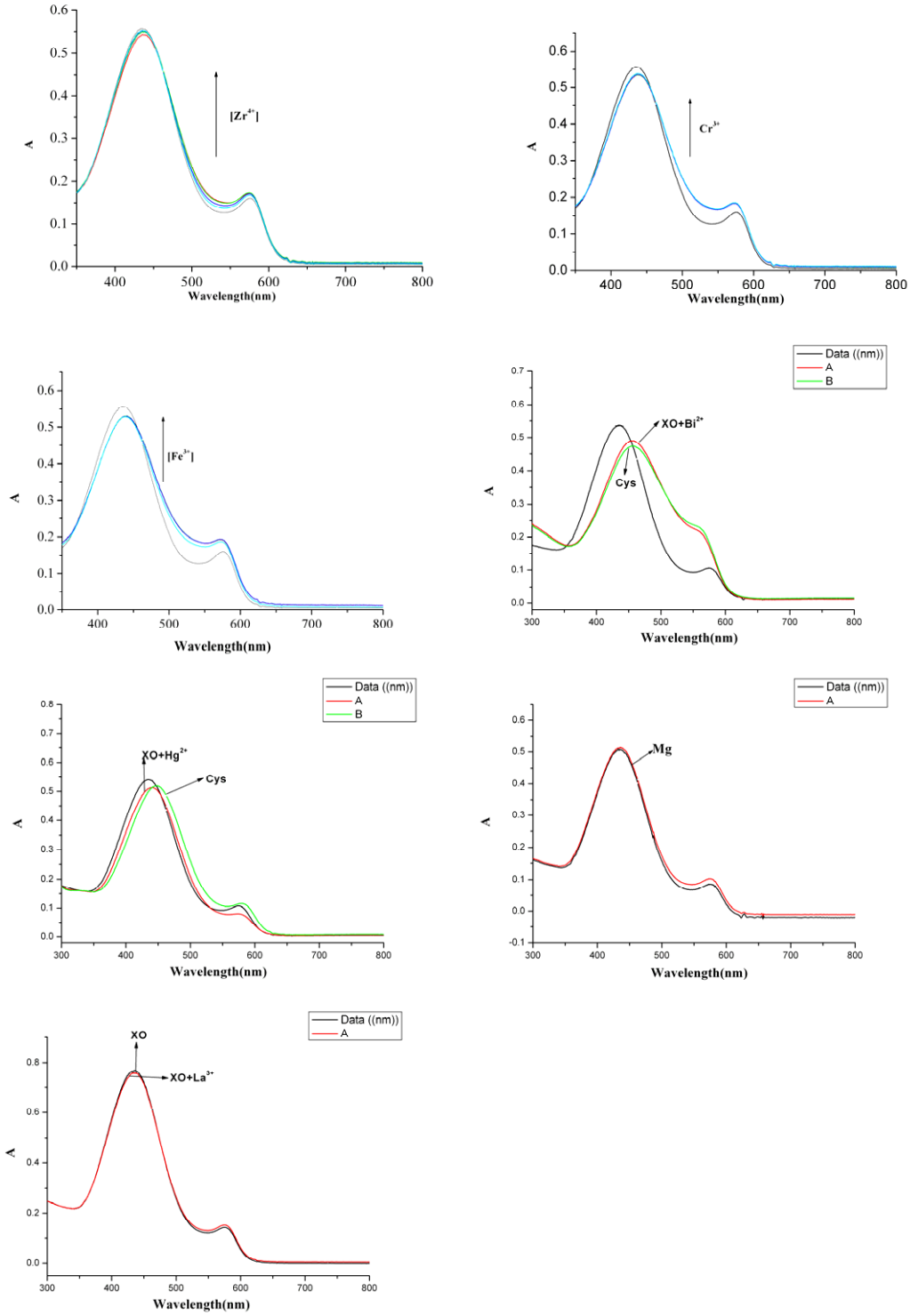
Figure S8 Cd^{2+}, $Zn^{2+,}$ Ca^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}, Pb^{2+}, Yb^{3+}, Tb^{3+}, Eu^{3+}, Ce^{3+}, Nd^{3+} ions (metal ions Part I).





UV/Vis spectrophotometry showed that other metal ions could not play the same sensor-role for the assay. These metal ions can lead XO indicator color change from yellow to purple-red and give rise to UV-vis spectra variation, however, their XO ensembles were incapable of detecting Cys based on the above facts that the systems had almost not any response to adding Cys in UV-vis spectra.

Figure S9 With Fe^{3+}, Cr^{3+}, Zr^{4+}, Bi^{2+}, Hg^{2+}, Mg^{2+}, La^{3+} cations (metal ions Part II).



UV/Vis spectrophotometry showed that other metal ions could not play the same sensor-role for the assay. They could not bring the UV-vis spectrum change of XO molecule.

Figure S10 The binding constants

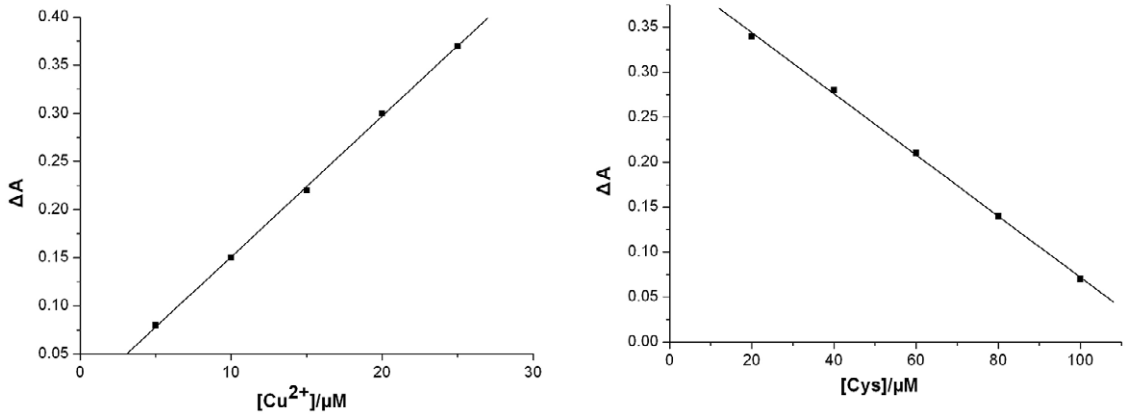
We calculated binding constants of them by spectrophotometric titration on UV-Vis as followings:

A curve of absorbance with increasing Cu^{2+} and ΔA has been developed (left). A curve on [Cys] to ΔA is also presented(right). From the curves, the related binding constants in the coordination equation have been calculated:

$XO + Cu^{2+} = CuXO$ $\qquad K_{Cu\text{-}XO}^{298K} = 2.41 \times 10^{8}$ (1)

$4Cys + CuXO = Cu(Cys)_4 + XO$ $\qquad K_{Cu\text{-}XO}^{298K} = 1.07 \times 10^{15}$ (2)

From the data, one could find that Cys binded with Cu^{2+} much more tight than with XO, quantitatively, over 7 orders.



Left: In a XO (25μM) solution, the value of Δ*A* at 572nm changes with the addition of Cu^{2+}; right: in the solution of CuXO (25μM), the value of Δ*A* at 572nm changes with the addition of [Cys].

Figure S11 Xylenol orange changes its color from yellow to red due to the solution pH change with a conversion point at pH≈6.3 (yellow when pH<6.3 and red while pH>6.3)

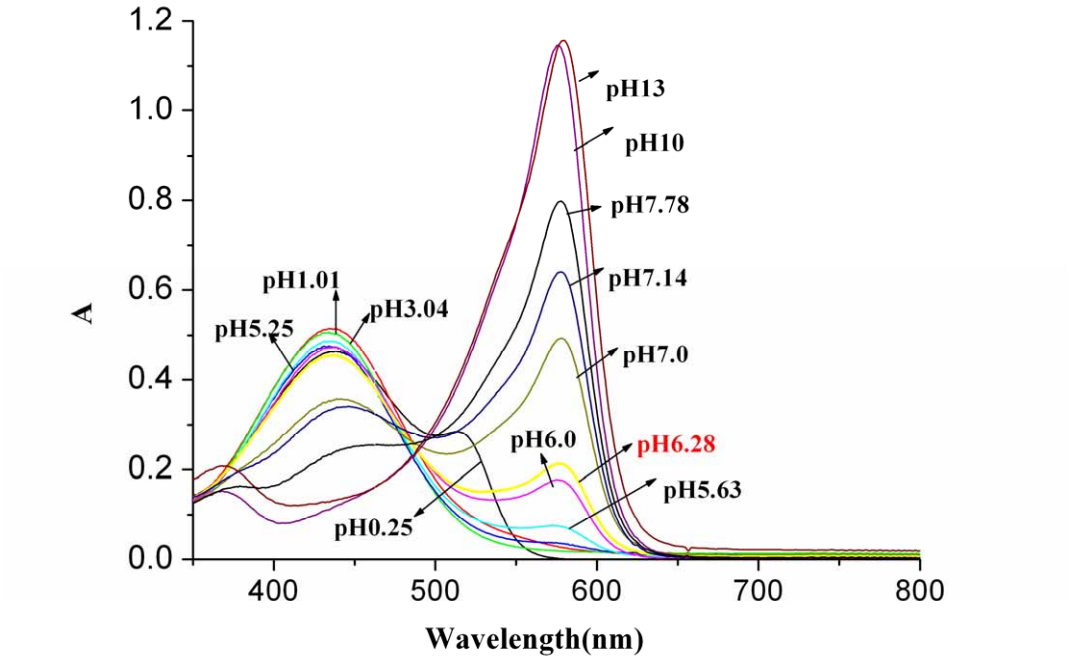
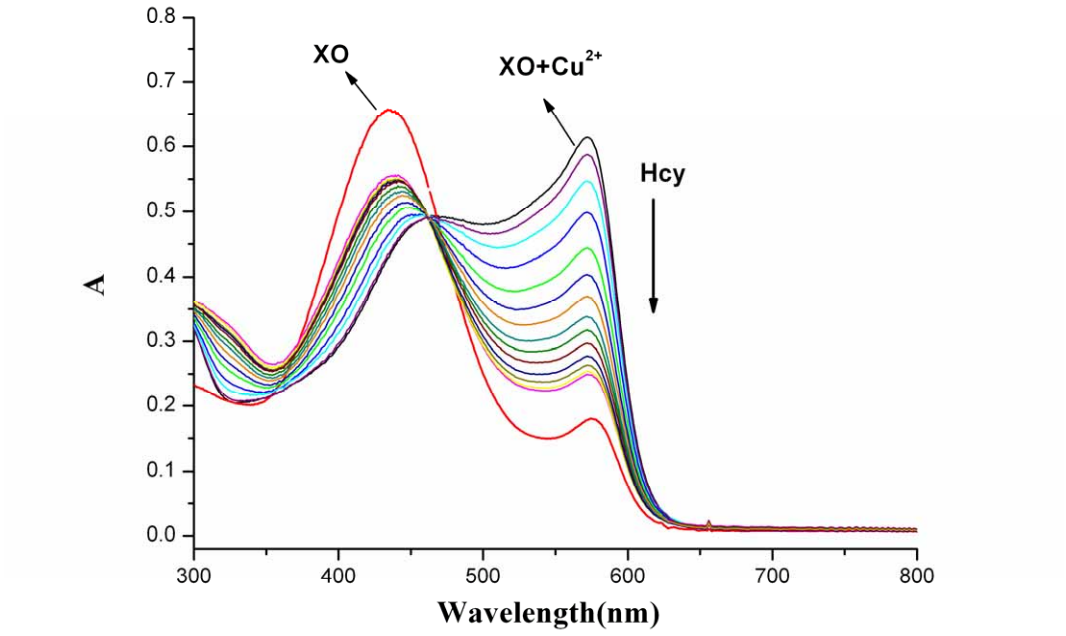
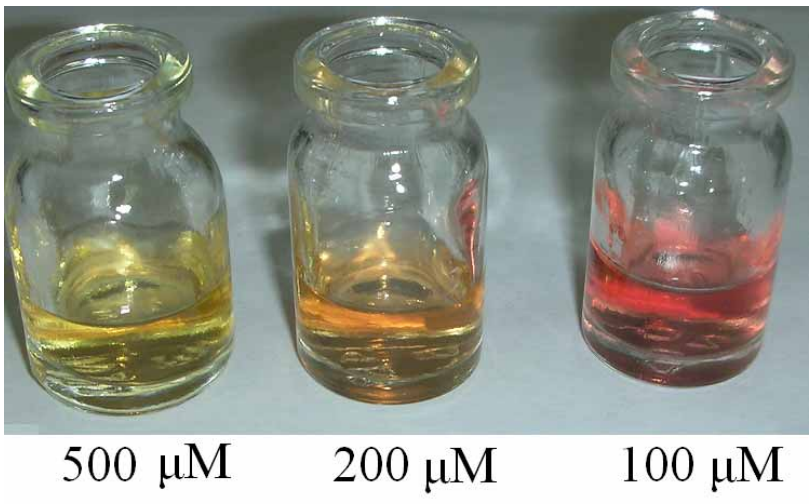


Figure S12 A detection of Cu^{2+}-XO for Homocysteine (Hcy) by UV-vis spectra and naked-eye.



The UV-vis spectral changes of Cu^{2+}-XO (25 μM) upon addition of Hcy [final concentration: 0, 40, 80, 120, 160, 200, 240, 280, 320, 360, 400, 440, 480, 500 μM]



The Hcy detection color changes picture of different concentrations based on Cu^{2+}-XO (25 μM) system

Figure S13 The color picture of aminothiols from plasma.