Supplementary Materials

A Copper (II) Ensemble Based Fluorescence Chemosensor and the Application in the "Naked–eye" Detection of Biothiols in Human Urine

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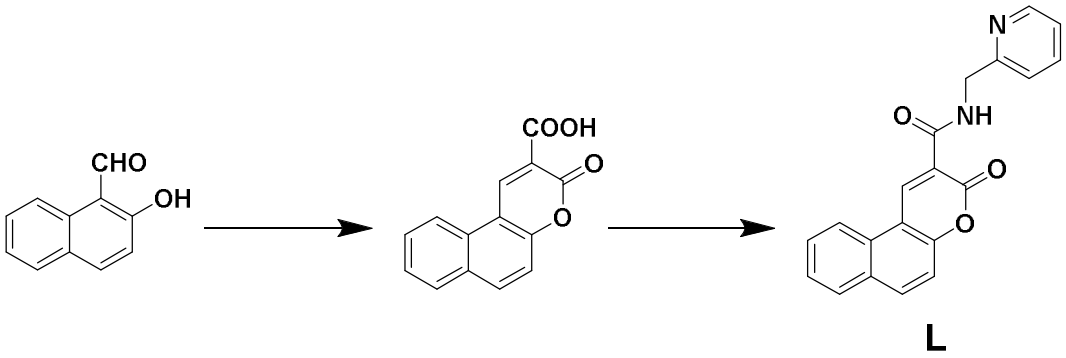

Scheme S1. Synthetic procedure of the fluorescent ligand, **L**

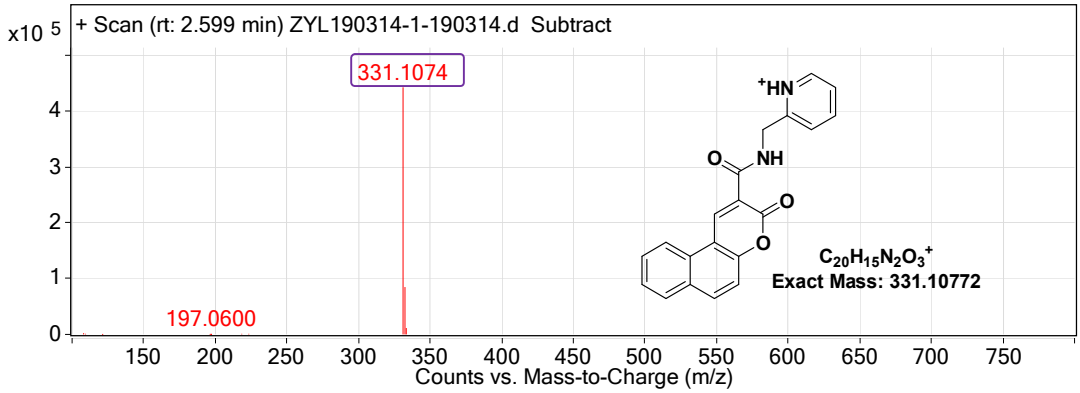

Figure S1. HRMS of fluorescent ligand, **L**.

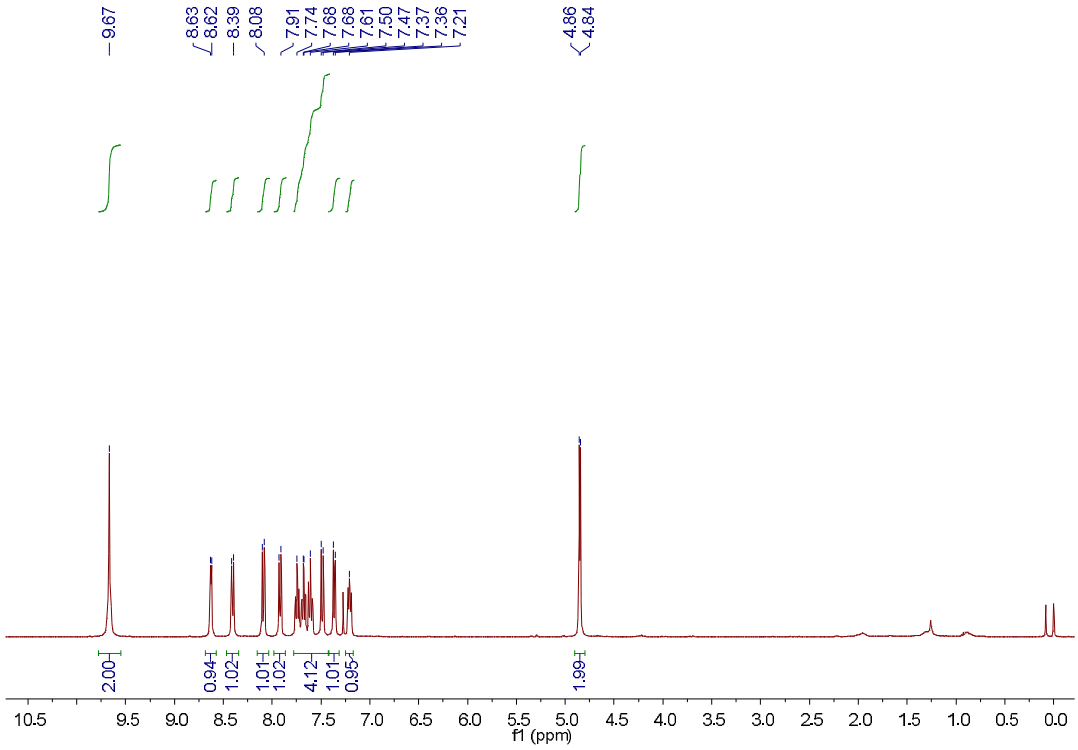

Figure S2. ^{1}H NMR of fluorescent ligand, **L** ($CDCl_3$, 600 MHz)

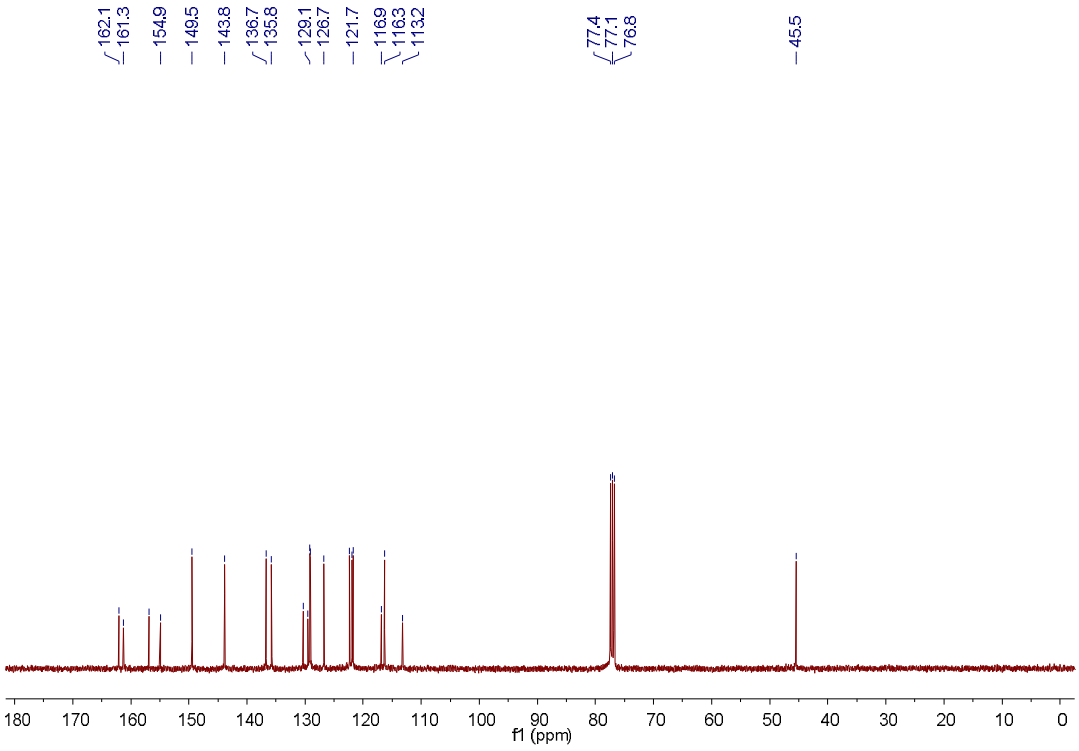

Figure S3. ^{13}C NMR of fluorescent ligand, **L** ($CDCl_3$, 150 Hz).

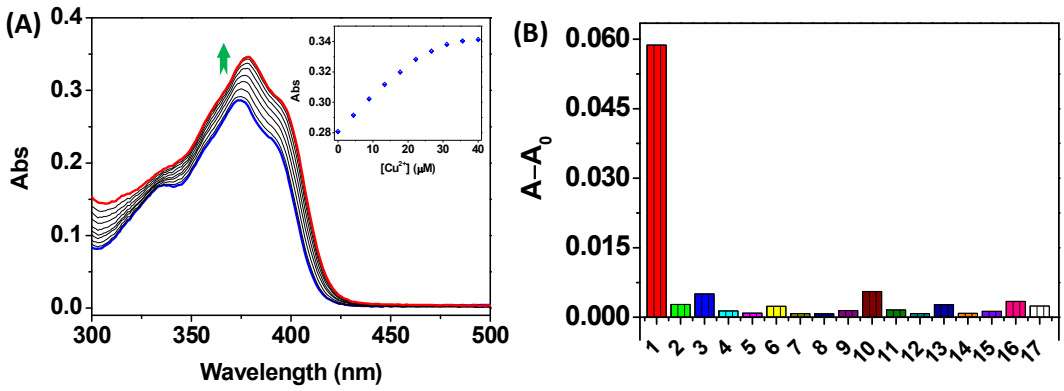

Figure S4. (A) UV-vis absorption spectra of **L** (10 μM) in the presence of different amounts of Cu^{2+} (0–60 μM) in the DMF/HEPES mixed solution (7:3, v/v, pH=7.4). Inset: normalized absorption intensities of **L** at 378 nm as a function of Cu^{2+} (0–60 μM). (B) UV-vis absorption spectra of **L** (10 μM) in the DMF/HEPES mixed solution (7:3, v/v, pH=7.4) upon addition of 60 μM various cations: 1. Cu^{2+}, 2. Pb^{2+}, 3. Ba^{2+}, 4. Ag^{2+}, 5. Al^{3+}, 6. Cd^{2+}, 7. Ca^{2+}, 8. Mg^{2+}, 9. Co^{2+}, 10. Fe^{3+}, 11. Cr^{2+}, 12. Ni^{2+}, 13. Hg^{2+}, 14. Li^{+}, 15. Na^{+}, 16. K^{+}, 17. Zn^{2+}. A_0 and A represent the absorption intensities of **L** at 378 nm in the absence and in the presence of Cu^{2+}.

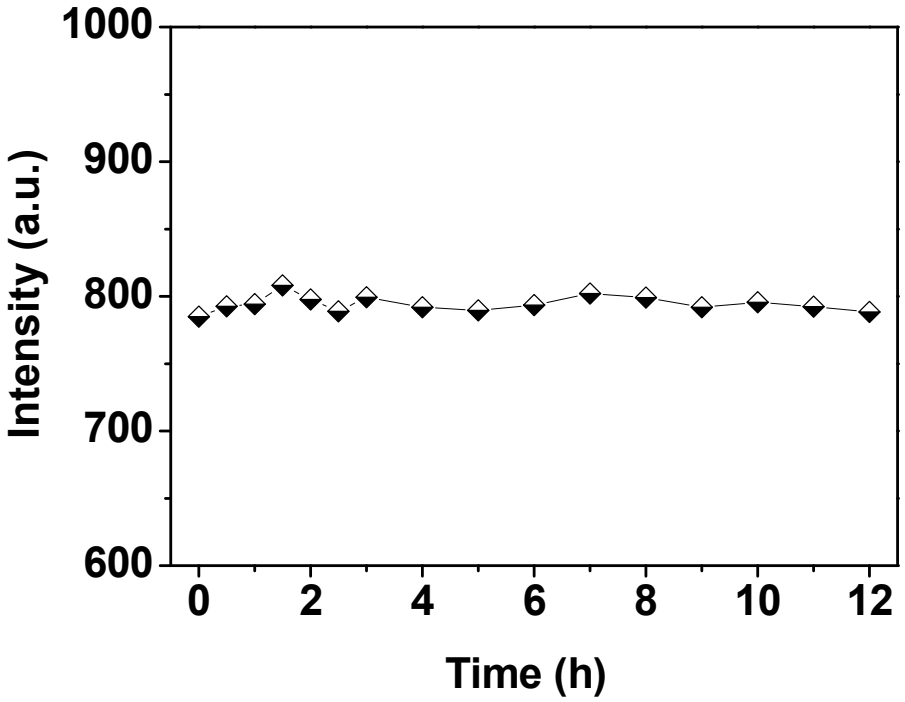

Figure S5. Fluorescence of **L** (10 μM) at different times in the DMF/HEPES mixed solution (7:3, v/v, pH=7.4). The intensities were recorded at 443 nm, and excitation was performed at 378 nm.

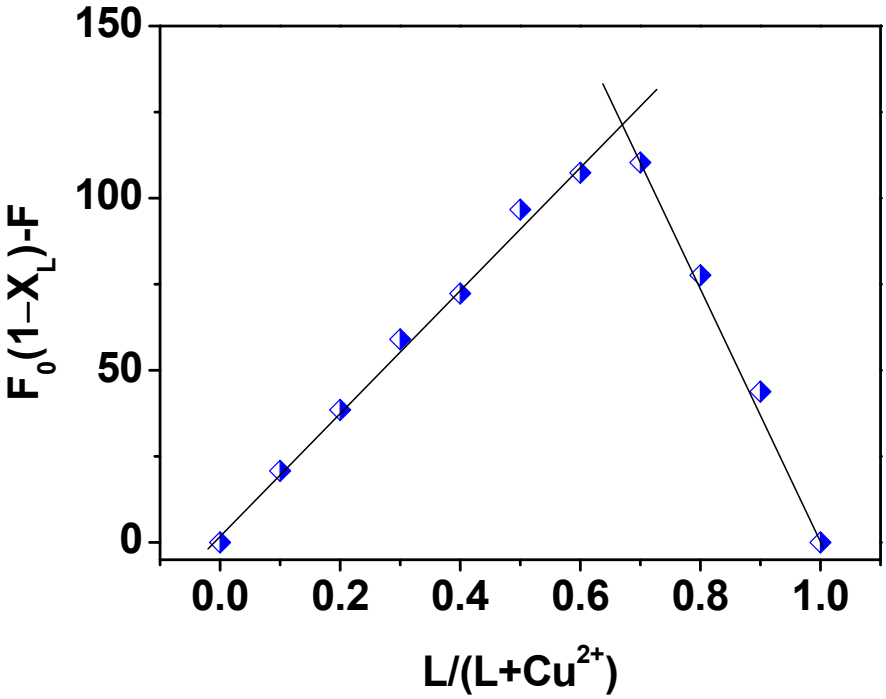

Figure S6. Job's plots according to the method for continuous variations. The total concentration of **L** (10 μM) and Cu^{2+} is 10 μM. X_L represents the proportion of **L** to the total amounts of **L** and Cu^{2+}. The intensities were recorded at 443 nm, and excitation was performed at 378 nm.

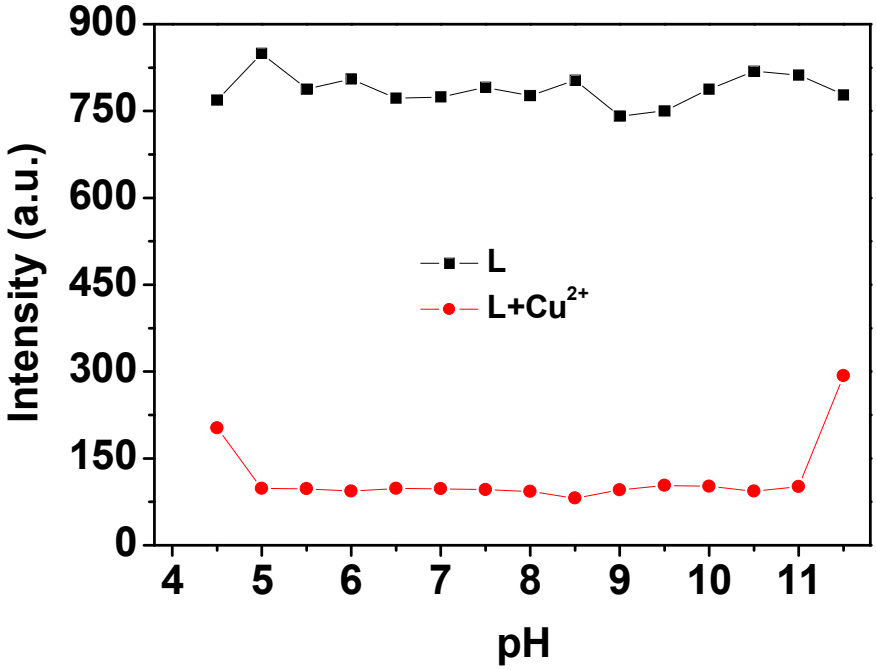

Figure S7. Effect of pH on the fluorescence intensities of **L** (10 μM) in the absence and presence of Cu^{2+} (60 μM) in the DMF/H_2O mixed solution. The intensities were recorded at 443 nm, and excitation was performed at 378 nm.

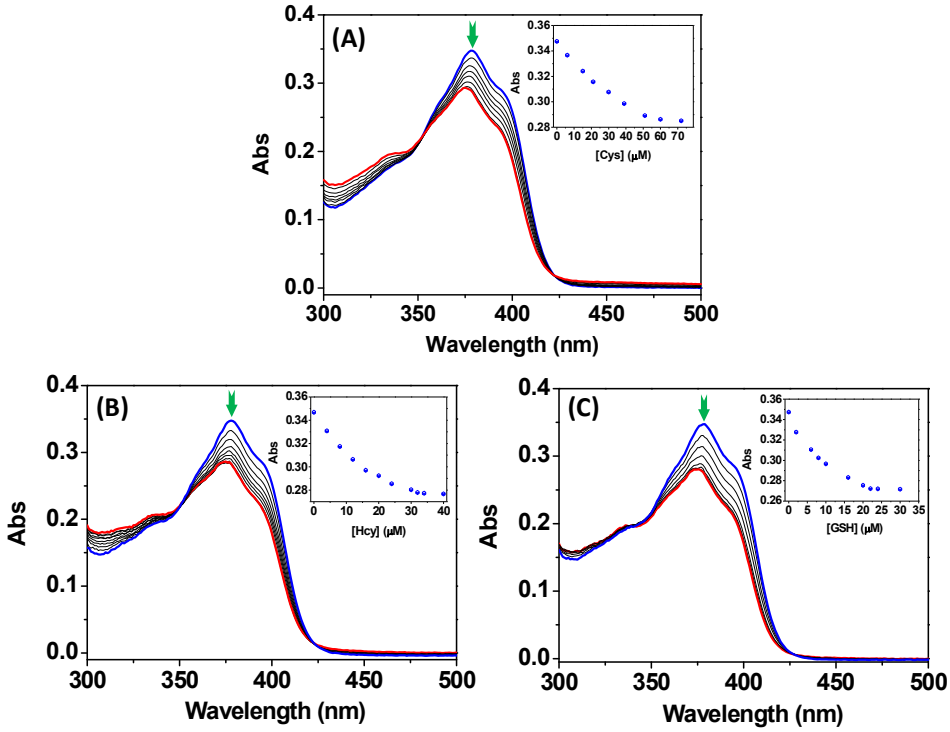

Figure S8. Absorption spectra of **L**-Cu^{2+} (10 μM) in the presence of different amounts of Cys (0–70 μM), Hcy (0–40 μM), GSH (0–30 μM) in the DMF/HEPES mixed solution (7:3, v/v, pH=7.4).

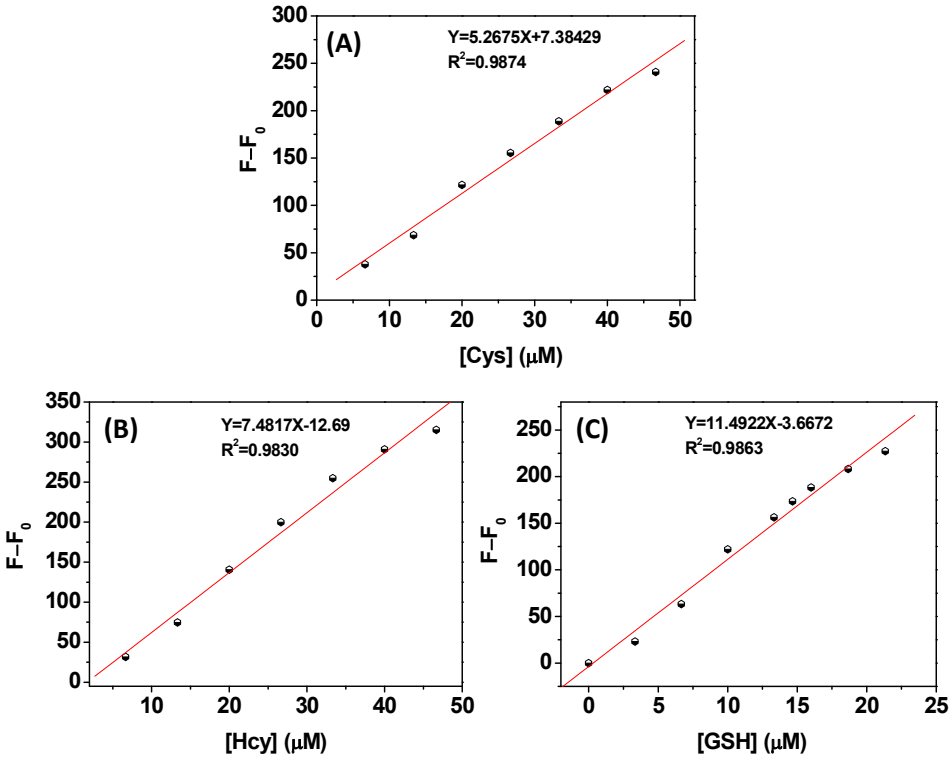

Figure S9. The linear relationship between fluorescence intensity of **L**-Cu^{2+}(1 μM) at 443 nm versus the concentration of (A) Cys, (B) Hcy and (C) GSH in the DMF/HEPES mixed solution (7:3, v/v, pH=7.4). Excitation was performed at 378 nm. Intensities were recorded at 443 nm.

Table S1. Comparison of this work with reported fluorescent chemosensors for biothiols detection.

Probes	Selectivity	Detection limit	Response time	Detection of Biothiols by "Naked–eye"	Detection of biothiols in Human Urine	Test papers	Ref.
RhAN	GSH	0.1 μM	< 5 s	Yes	No	No	S1
probe	biothiols	GSH 3.7 μM	~ 120 min	No	No	No	S2
Compoud 1	biothiols	GSH 10.3 nM	< 5 s	Yes	No	No	S3
Probe1	Cys	1.4 nM	~ 30 min	No	No	No	S4
SATZ	Cys/Hcy	2.843 μM (Cys)	12 min	Yes	No	No	S5
CI	Cys	0.014 μM	25 min	Yes	No	No	S6
	Hcy	0.081 μM	55 min				
	GSH	0.097 μM	50 min				
BT-AC	Cys	36.2 nM	--	No	No	test strip	S7
CPR	Cys	12 nM	40 min	No	No	No	S8
	Hcy	13 nM	100 min				
	GSH	30 nM	38 min				

NIRHA	Cys	77.6 μM	15 min	Yes	No	No	S9
SHCy-C	Cys	21.2 nM	5 min	No	No	No	S10
HN-NBD	Cys Hcy GSH	31 μM 66 μM 58 μM	5 min	No	No	No	S11
CPA	Cys Hcy	49 nM 51 nM	~3 min	No	No	No	S12
Nap-Cys	Cys	1.8 μM	5 min	No	No	No	S13
PYR	Cys Hcy	22 nM 23nM	5min 10min	Yes	No	No	S14
Lyso-RC	Cys Hcy GSH H_2S	27 nM 33 nM 16 nM	--	No	No	No	S15
probe 1	Cys Hcy GSH	Cys 0.11 μM	20 min	No	No	No	S16
EuTc-H_2O_2	Cys Hcy GSH	100 nM 200 nM 400 nM	--	No	Yes	No	S17

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