Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

A highly efficient yet stable salamo-type fluorescent chemosensor for multiple responses to Cu^{2+} and S^{2-}

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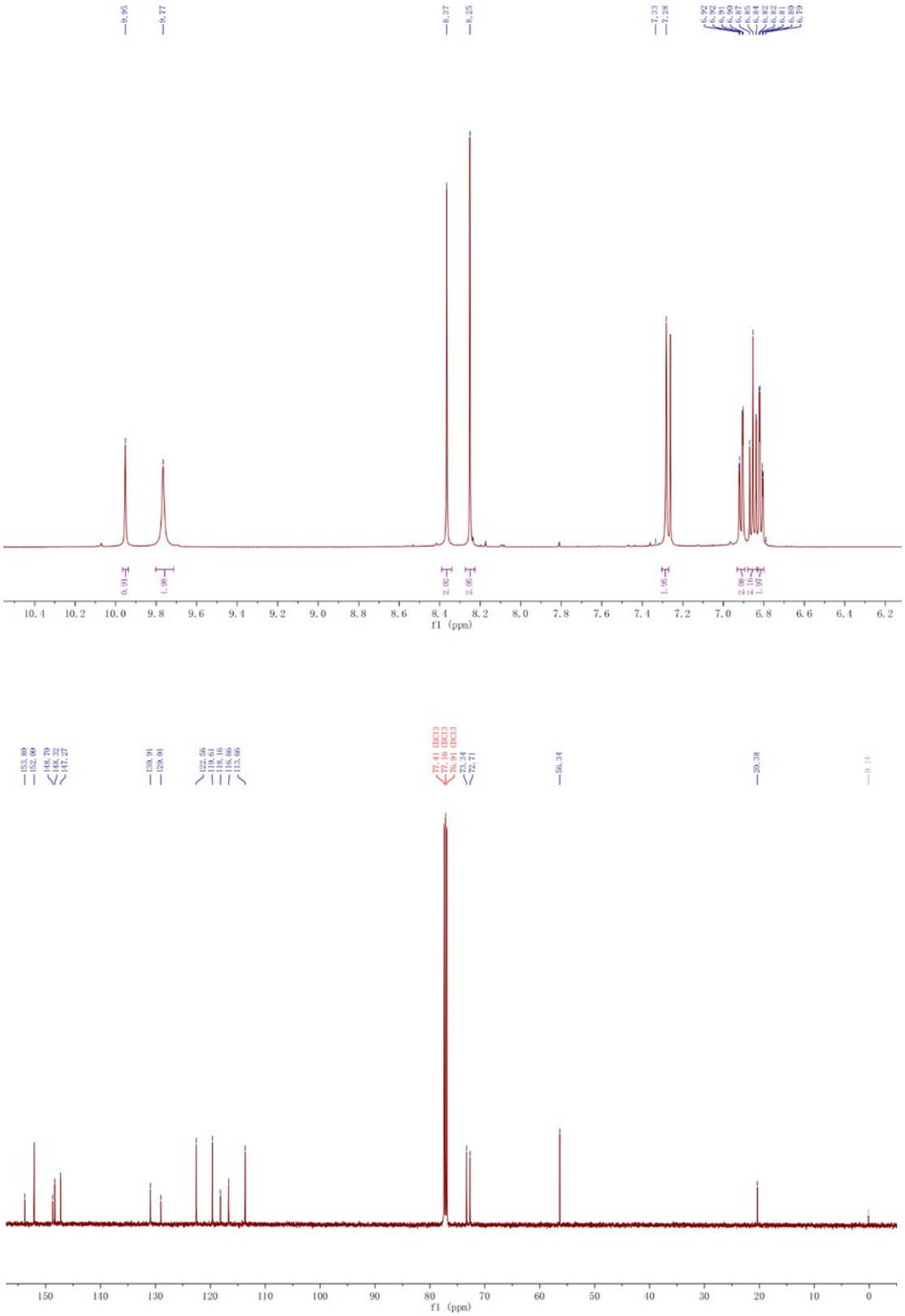

Fig. S1. ^{1}H NMR spectrum of **H_3L** in $CDCl_3$ (Up), and ^{13}C NMR spectrum of **H_3L** in $CDCl_3$ (Down).

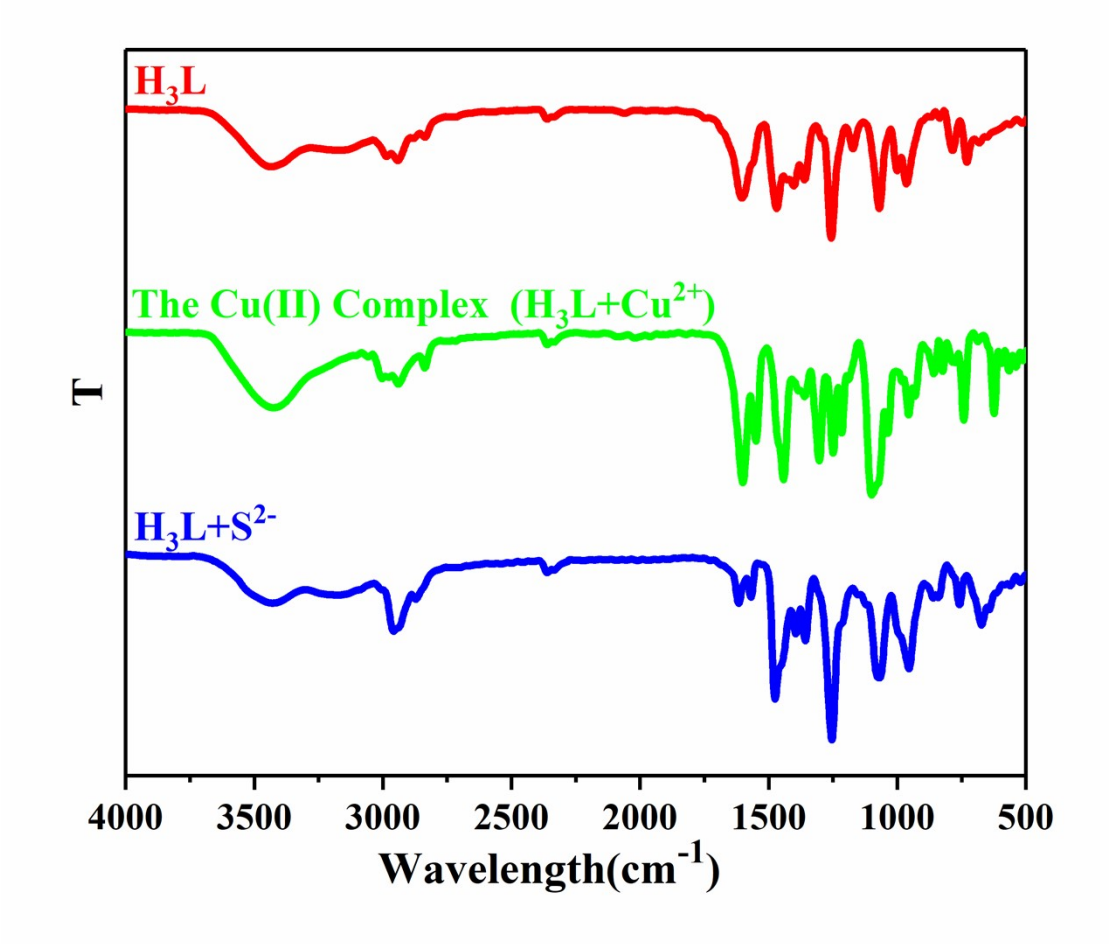

Fig. S2. Infrared spectra of chemosensor **H_3L**, the Cu(II) complex, and **H_3L**+S^{2-}.

Determination of LOD, LOQ and *K*a of detecting Cu^{2+}.

(1) The quantitative limit and detection limits of Cu^{2+} and **H_3L** were determined from the fluorescence titer of the sensor **H_3L** and Cu^{2+}. Use the following equations to determine the LOD and LOQ.

Fit equation: y=-121.951x+2311.418 R^2=0.96596

S=1.21951×10^8 $\delta = \sqrt{\frac{\sum (F_0 - \overline{F_0})^2}{N-1}}$ =2.677(N=15) K=3

LOD = K × δ / S=1.5398 × 10^{-7} M; (N = 15) ;

LOQ = 10 × δ / S=4.5279 × 10^{-7} M.

Where N, S, F0 and $\overline{F}$ are the number of replicates for the measurements, slope, fluorescence intensity and mean of fluorescence intensity of the blank solution of probe, respectively.

Benesi-Hildebrand equation as shown below:

log (F-Fmin)/(Fmax-F) = log *K*a + 2 log [Cu^{2+}] *K*a = 6.89× 10^9 M^{-1}

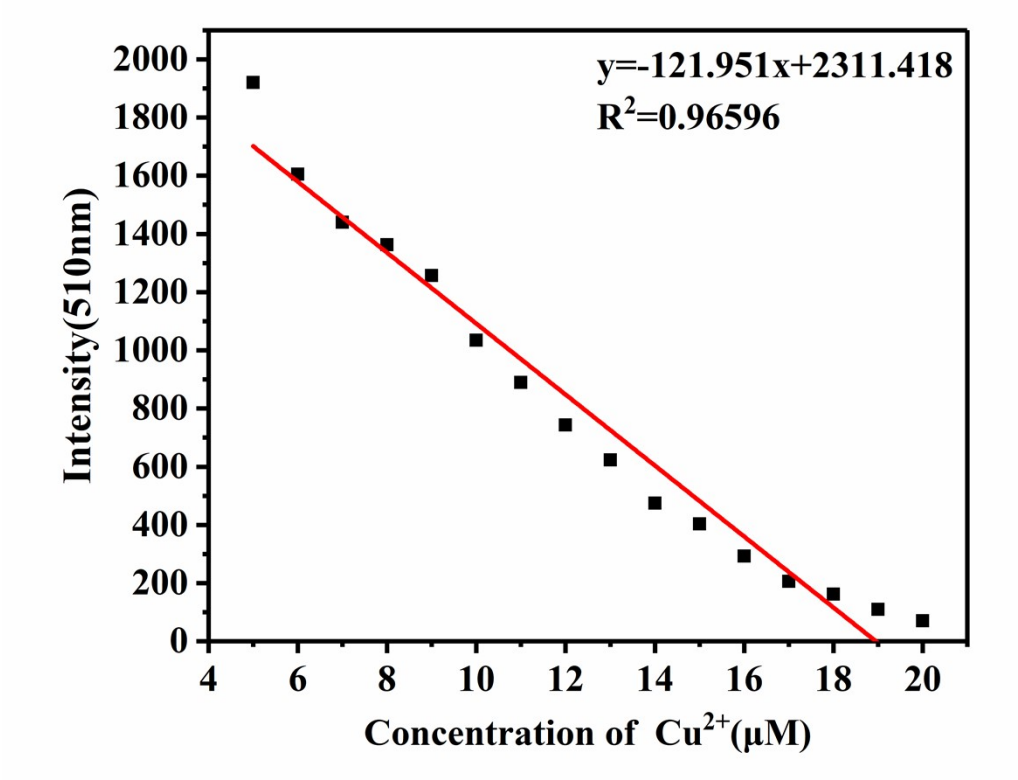

Fig. S3. Linear calibration curve of Cu^{2+}.

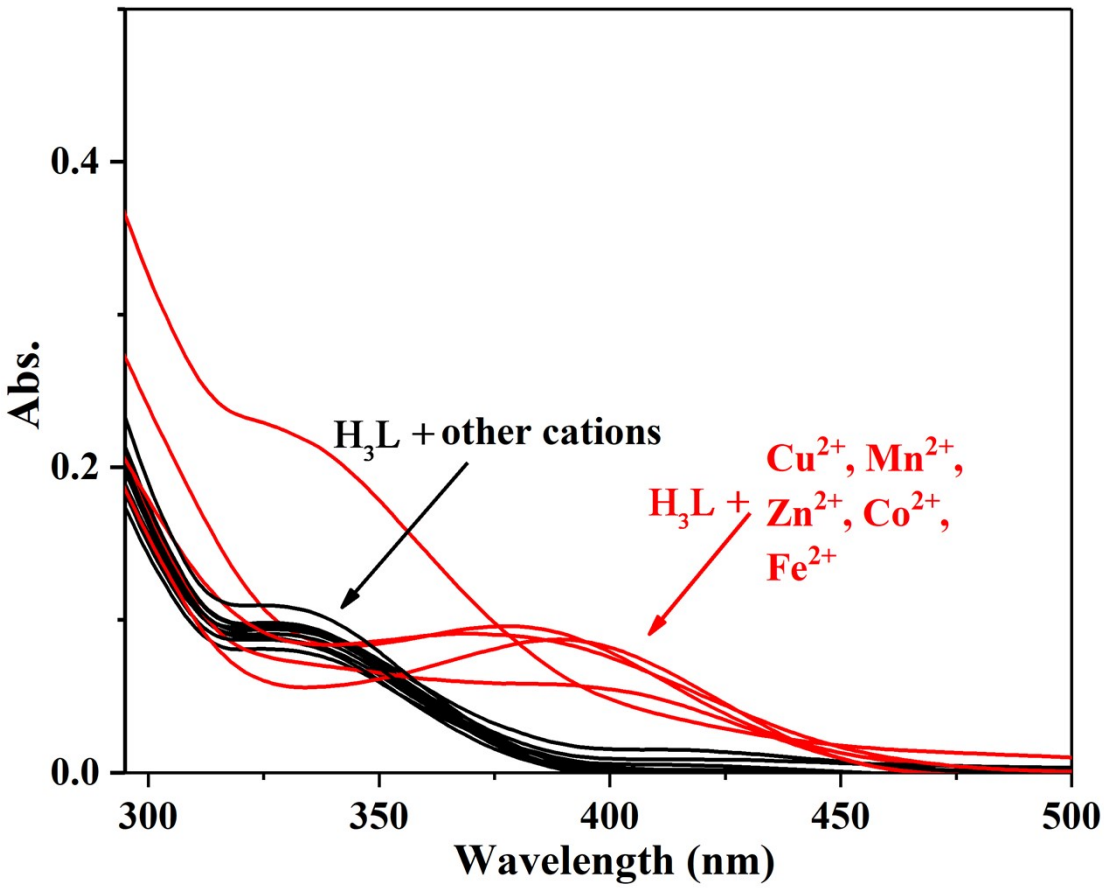

Fig. S4. Absorption spectra of **H_3L** solution in the presence of various cations (Cu^{2+}, Hg^{2+}, Cr^{3+}, Fe^{3+}, Cd^{2+}, Mn^{2+}, Ca^{2+}, Ag^{+}, Na^{+}, Li^{+}, Zn^{2+}, K^{+}, Mg^{2+}, Al^{3+}, Fe^{2+}, Co^{2+}, Pb^{2+} and Ga^{3+}).

Determination of LOD, LOQ and *K*a of detecting S^{2-}.

(1) The quantitative limit and detection limits of S^{2-} and **H_3L** were determined from the fluorescence titer of the sensor **H_3L** and S^{2-}. Use the following equations to determine the LOD and LOQ.

Fit equation: y=138.802x+1269.301 R^2=0.97487

S=1.38802×10^8 $\delta = \sqrt{\frac{\sum (F_0 - \overline{F_0})^2}{N-1}}$ =1.527(N=15) K=3

LOD = K × δ / S=1.7274 × 10^{-7} M; (N = 15) ;

LOQ = 10 × δ / S=6.4692 × 10^{-7} M.

Where N, S, F0 and $\overline{F}$ are the number of replicates for the measurements, slope, fluorescence intensity and mean of fluorescence intensity of the blank solution of probe, respectively.

Benesi-Hildebrand equation as shown below:

log (F-Fmin)/(Fmax-F) = log *K*a + 2 log [S^{2-}] *K*a = 1.59× 10^9 M^{-1}

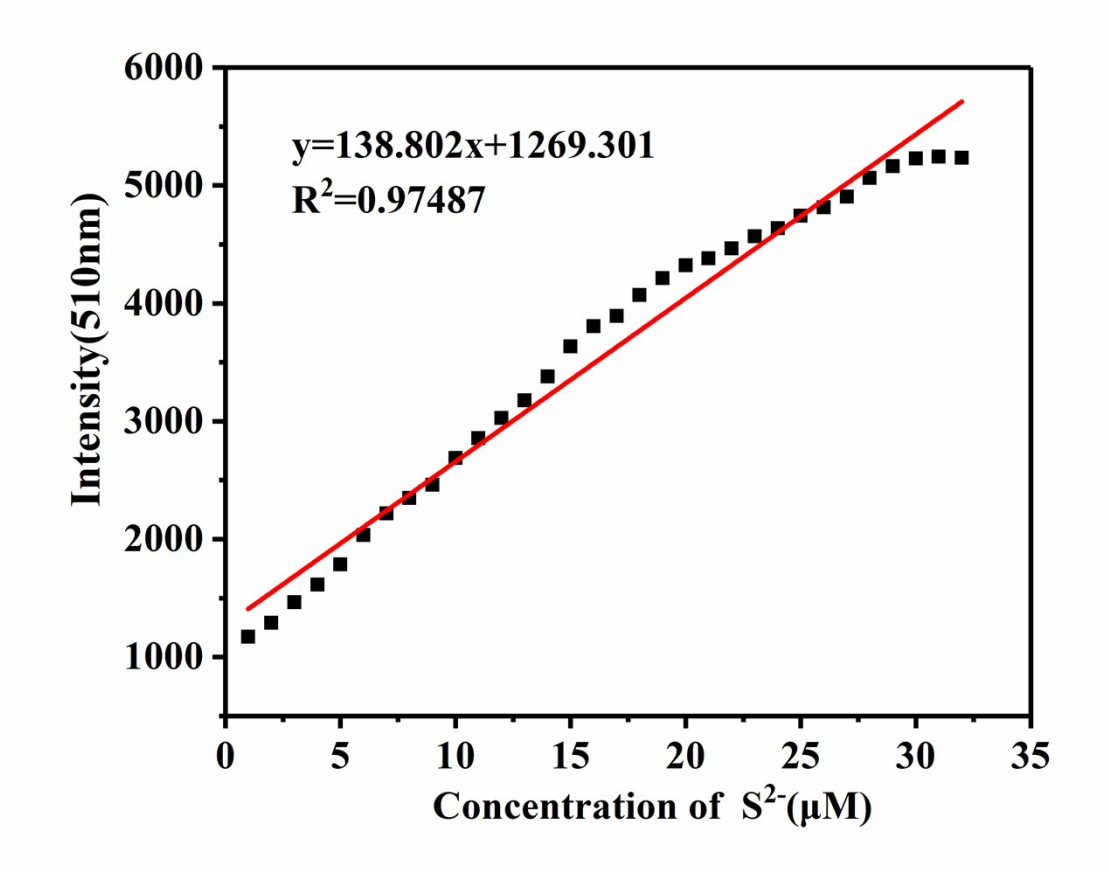

Fig. S5. Linear calibration curve of S^{2-}.

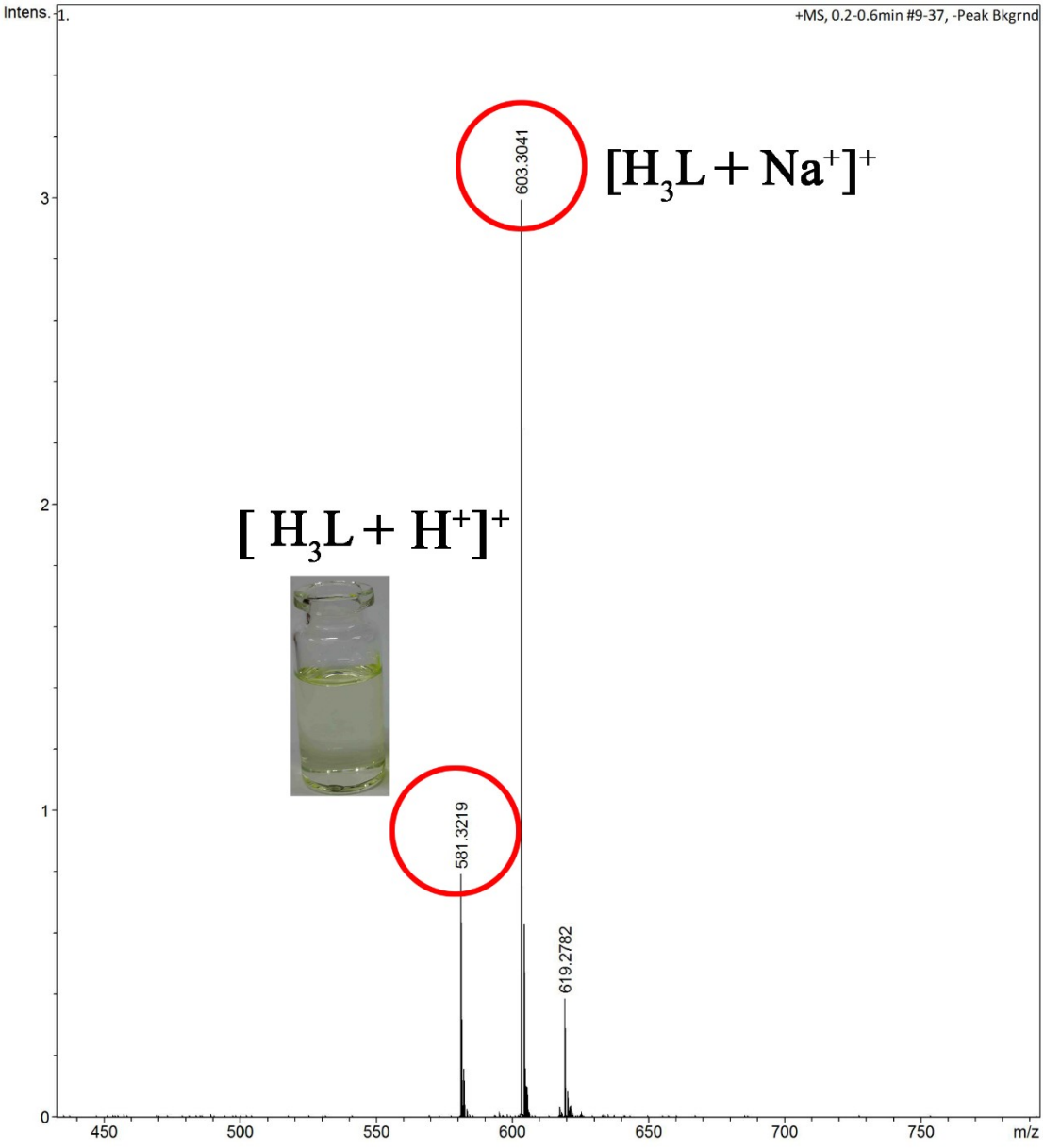

Fig. S6. Mass spectrum of chemosensor **H_3L**.

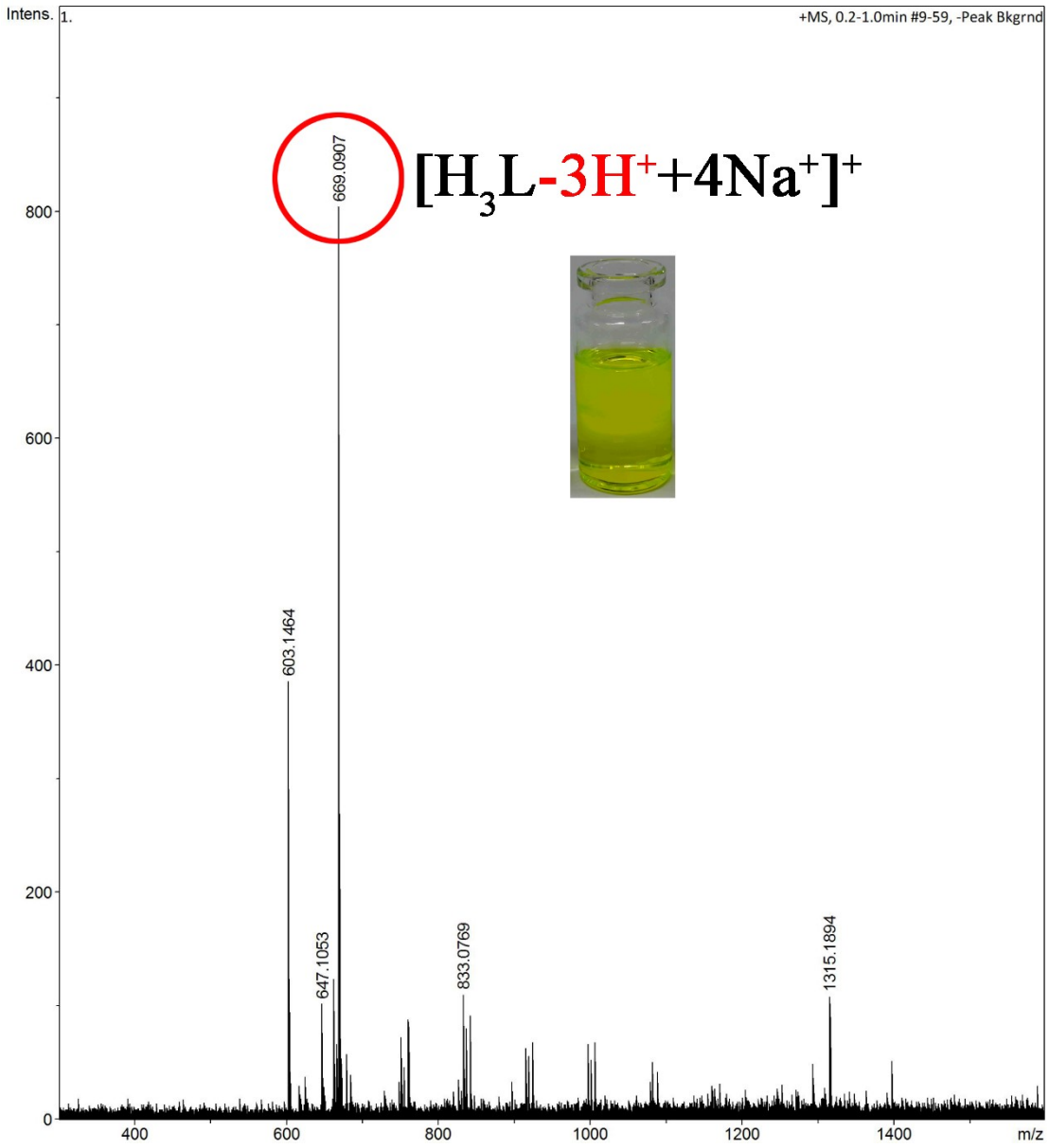

Fig. S7. Chemosensor **H_3L** recognizes S^{2-}, the color of the solution deepens obviously under natural light.

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Table S1: Structure refinement and crystal data for the Cu(II) complex.

Compound code	$[Cu_2(L)]ClO_4 \cdot 2CH_3OH$
CCDC number	2077985
Empirical formula	$C_{31}H_{37}ClCu_2N_4O_{15}$
Molecular weight	868.17
Temperature(K)	173
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P21/c
a(Å)	11.3598(4)
b(Å)	28.8890(8)
c(Å)	10.9160(3)
α°	90
β°	100.7080(10)
γ°	90
Volume(Å^3)	3519.96(19)
Z	4
Dx (gcm $^{-3}$)	1.638
μ(mm-1)	1.362
F(000)	1784
Crystal size(mm^3)	0.19 × 0.17 × 0.16
θ range (˚)	2.306-26.748
Index ranges	$-13 \le h \le 14$, $-36 \le k \le 36$, $-13 \le l \le 13$
R_{int}	0.0717
Data completeness	99.70%
Reflns/restraints/parameters	7471/235/532
Final R indexes [$I>=^2\sigma(I)$][a]	$R_1 = 0.0694$, $wR_2 = 0.1610$
Final R indexes (all data)[b]	$R_1 = 0.0960$, $wR_2 = 0.1774$
Goodness-of-fit on F^2	1.069
$\Delta r_{max,min}$ (eÅ^{-3})	0.88 and -1.11

Table S2: Selected bond lengths (Å) and angles (º) of $[Cu_2(L)]ClO_4 \cdot 2CH_3OH$.

Bond	Bond length (Å)	Bond	Bond length (Å)
Cu1-O2	1.905(4)	Cu2-O8	1.897(4)
Cu1-O5	1.960(4)	Cu2-O5	1.948(3)
Cu1-N1	1.962(4)	Cu2-N3	1.964(4)
Cu1-N2	1.964(4)	Cu2-N4	1.962(4)

Bond	Bond length (Å)	Bond	Bond length (Å)
O2-Cu1-O5	84.38(15)	O8-Cu2-O5	82.64(15)
O2-Cu1-N1	89.78(17)	O8-Cu2-N3	166.55(16)
O2-Cu1-N2	164.72(17)	O8-Cu2-N4	90.91(17)
O5-Cu1-N1	172.75(17)	O5-Cu2-N3	85.40(16)
O5-Cu1-N2	85.75(16)	O5-Cu2-N4	173.55(17)
N1-Cu1-N2	100.83(18)	N4-Cu2-N3	101.00(17)
C1-O2-Cu1	124.2(3)	C24-O8-Cu2	127.7(3)
Cu2-O5-Cu1	103.06(16)	C13-O5-Cu2	129.2(3)
C13-O5-Cu1	127.7(3)	O6-N3-Cu2	119.0(3)
O3-N1-Cu1	124.8(3)	C19-N3-Cu2	129.3(3)
C8-N1-Cu1	123.5(4)	O7-N4-Cu2	123.7(3)
O4-N2-Cu1	119.2(3)	C22-N4-Cu2	125.8(4)
C11-N2-Cu1	128.9(4)		

Table S3: Putative hydrogen bond interactions (Å) for the Cu(II) complex.

D–X···A	d(D–X)	d(X···A)	d(D···A)	∠D–X···A
O10 --H10···O13	0·84	2·43	2·921(18)	118
O11--H11A···O15	0·84	2·5	3·30(2)	160
C8--H8···O10	0·95	2·5	3·436(10)	169
C9--H9A···O8	0·99	2·44	3·392(7)	162
C9--H9B···O4	0·99	2·29	3·213(6)	155
C10--H10A···O6	0·99	2·54	3·342(7)	138
C15--H15···O12	0·95	2·6	3·528(15)	165
C20--H20A···O4	0·99	2·59	3·323(7)	130
C21--H21A···O2	0·99	2·44	3·417(7)	169
C21--H21B···O6	0·99	2·35	3·259(6)	152
C22--H22···O11	0·95	2·49	3·403(15)	162
C29--H29A···O15	0·98	2·57	3·538(17)	172