Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

Hg^{2+} Wettability and Fluorescence Dual-Signal Responsive Switch Based on a Cysteine Complex of Piperidine-Calix[4]arene

Xiaoyan Zhang, Haiyang Zhao, Xianliang Cao, Ningmei Feng, Demei Tian and Haibing Li*

Key Laboratory of Pesticide and Chemical Biology (CCNU), Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, P. R. China. lhbing@mail.ccnu.edu.cn.

Contents

1. Synthesis and characterizations of the L

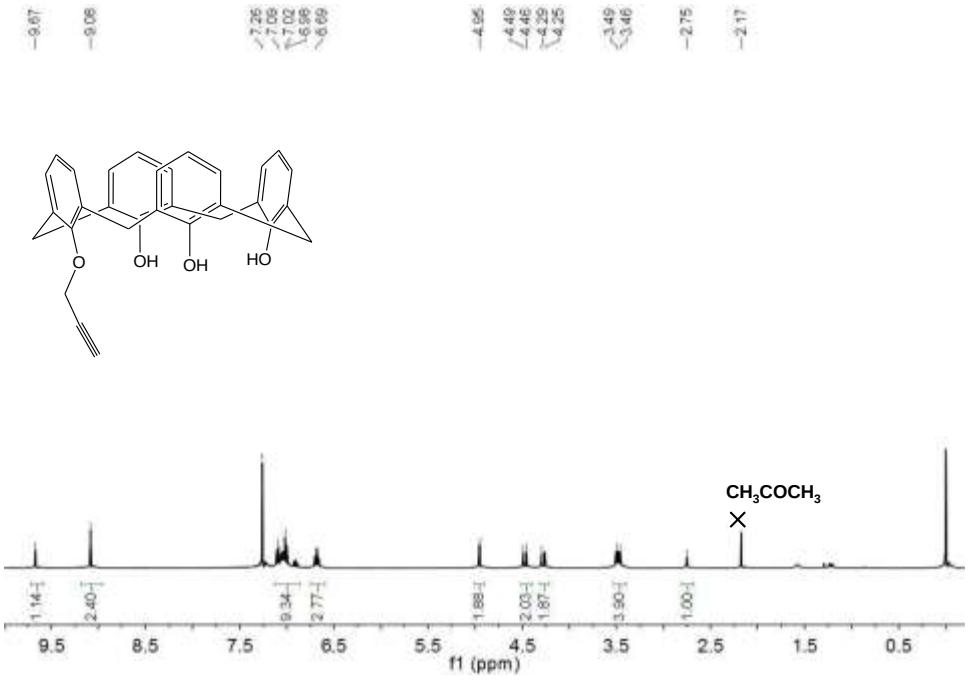


Figure S1. ^{1}H NMR spectroscopy of C4AM ($CDCl_3$, 400 MHz, 298 K).

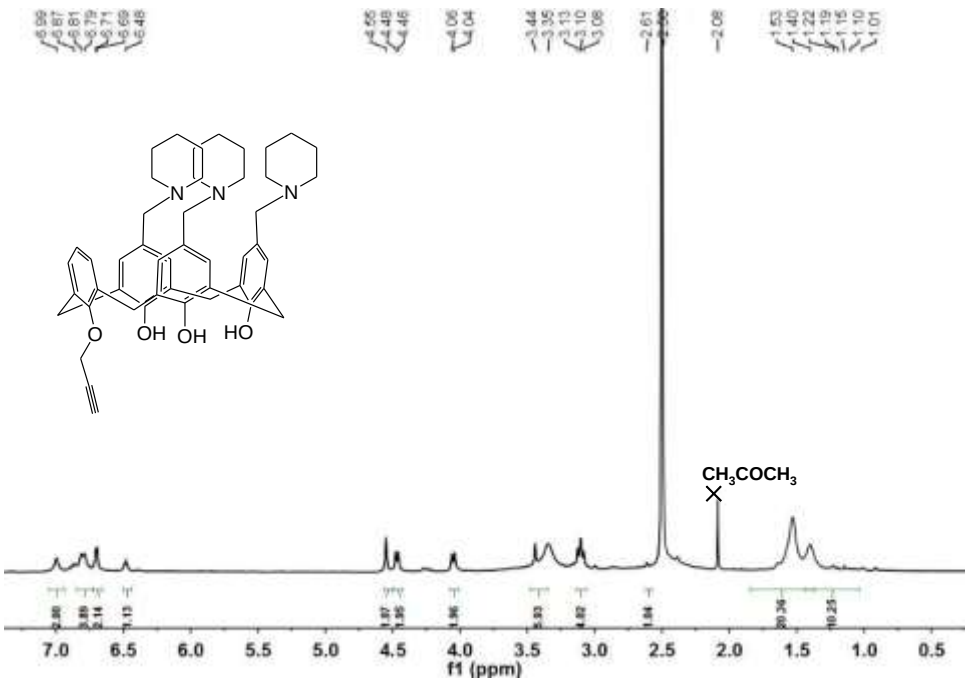


Figure S2. ^{1}H NMR of the L (DMSO, 600 MHz, 298 K).

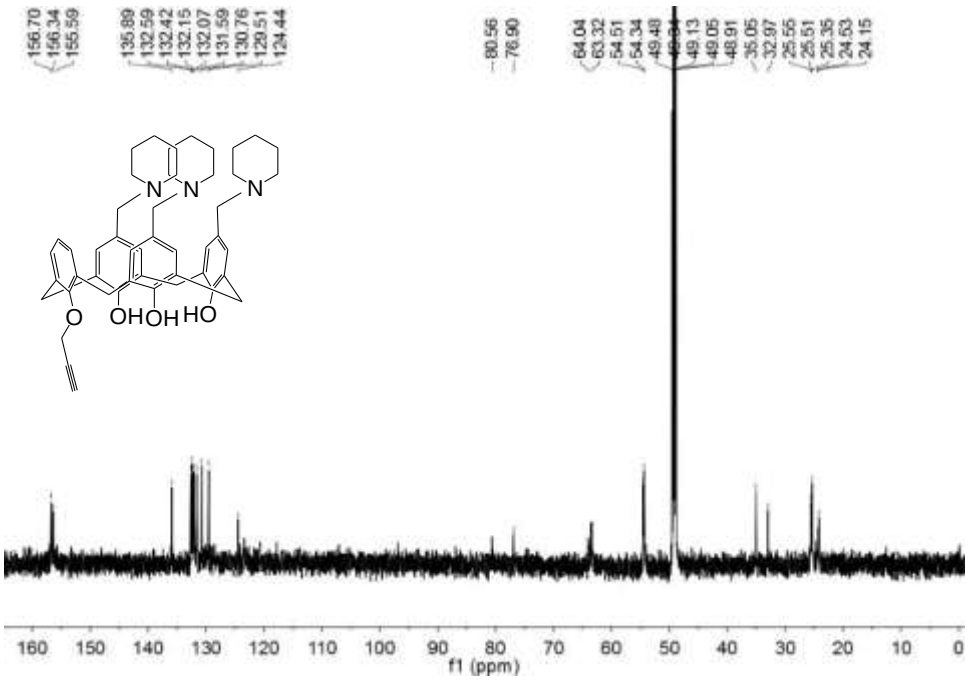


Figure S3. ^{13}C NMR of the L (DMSO, 600 MHz, 298 K).

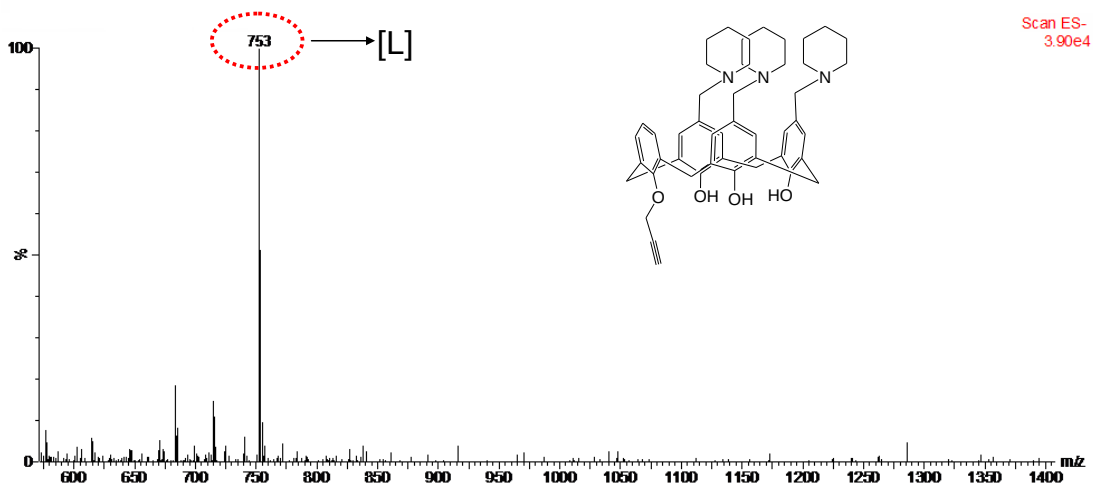
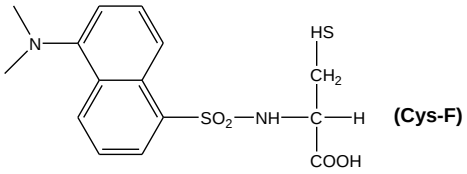


Figure S4. ESI-MS of the L (CH_3OH). The peak stood for the molecular ion (m/z) peak of the L at 753.

2. Fluorescence titration



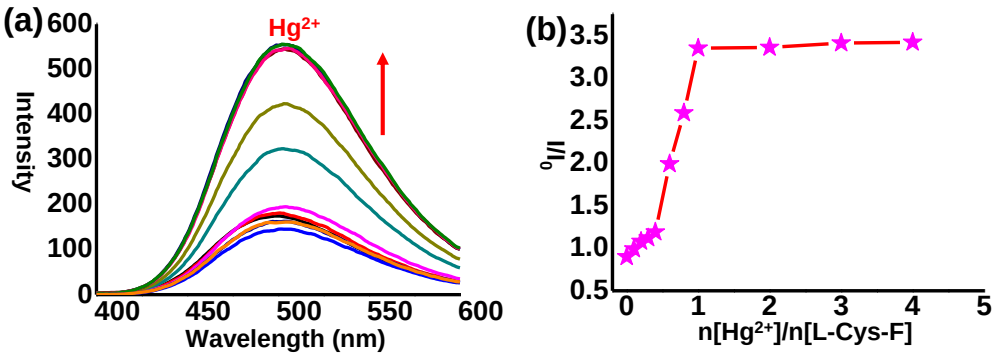


Figure S5. (a) Fluorescence spectra was obtained during the titration of L-Cys-F with Hg^{2+} in CH_3CN/H_2O (v/v, 1/1), λex = 350 nm. (b) Relative fluorescence intensity (I/I_0) as a function of $n[Hg^{2+}]/n$[L-Cys-F] mole ratio. These suggested a stoichiometric ratio of 1:1 between the [L + Cys] complex and Hg^{2+}.

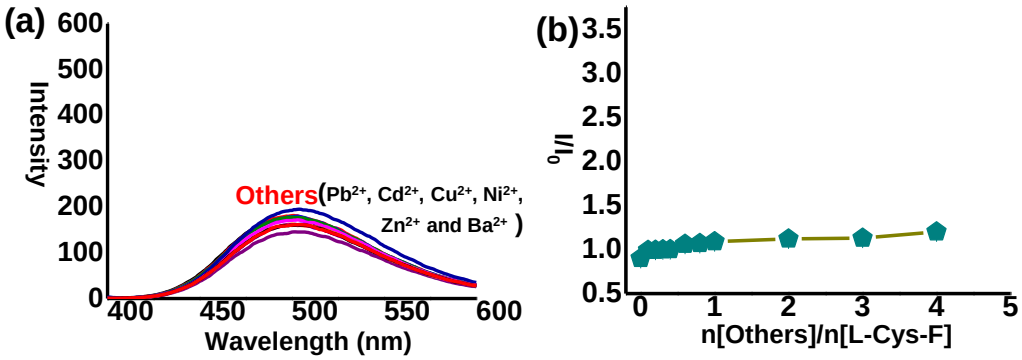


Figure S6. (a) Fluorescence spectra was obtained during the titration of L-Cys-F with others (Pb^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+} and Ba^{2+}) in CH_3CN/H_2O (v/v, 1/1), λex = 350 nm. (b) Relative fluorescence intensity (I/I_0) as a function of n[Others]/n[L-Cys-F] mole ratio. These suggested that no fluorescence changing was observed when this was titrated with the other metal ions.

3. Job plot of the L and Cys system in UV spectru

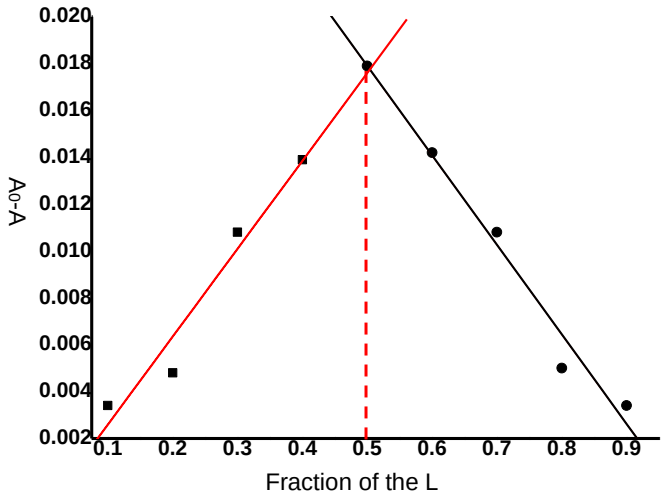


Figure S7. Continuous variation plot of the L and Cys system ([L] + [Cys] = 5.0×10^{-5} mol/ L^{-1}). Job plot indicated the conjugating ratio of the L and Cys was 1:1 by UV spectrum at 286.5 nm.

4. ^{1}H NMR control experiment of the reference compound C4AM

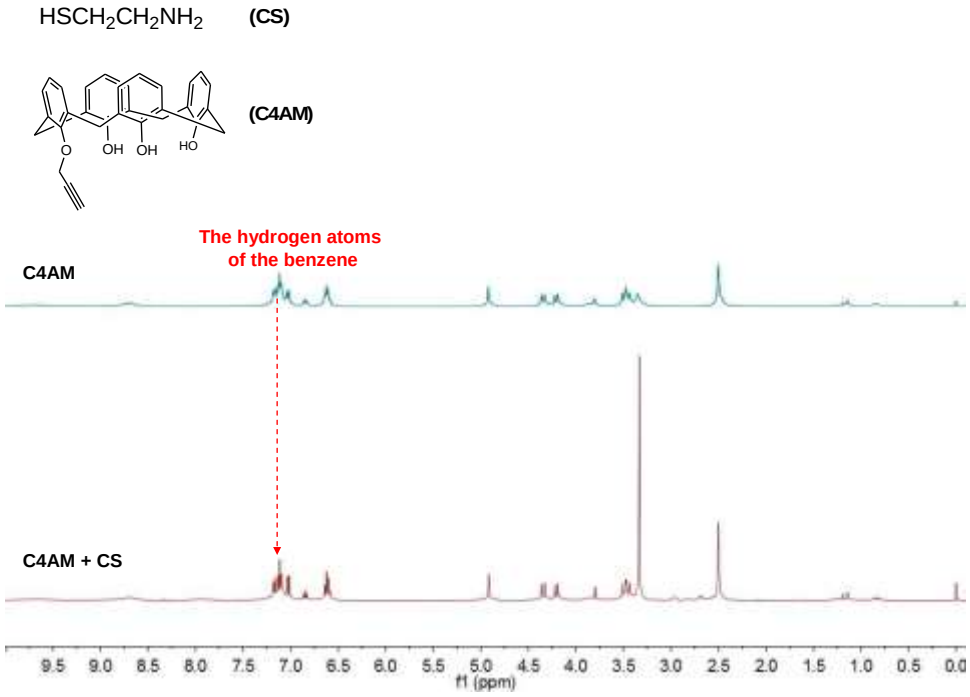


Figure S8. ^{1}H NMR spectroscopy of C4AM and [C4AM + CS] (DMSO, 400 MHz, 298 K), which indicated no interacting between C4AM and CS. The control experiment result also showed that the piperidine moiety played an important role in the efficient interacting with CS. Note: Cysteamine (CS) was used instead of Cys because of the poor solubility of the latter when taken in DMSO-d_6.

Studying the interaction of the L and Cys

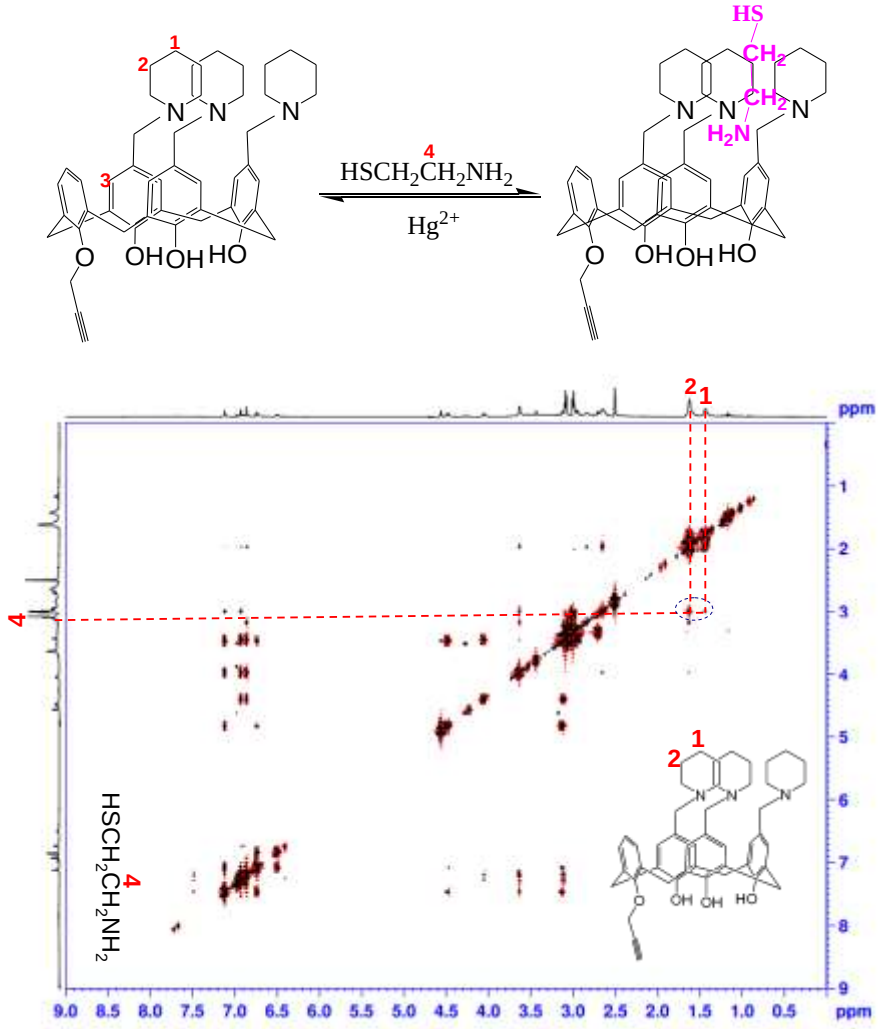


Figure S9. NOESY of the mixture of the L and Cys (DMSO, 600 MHz, 298 K), which showed the $-NH_2$ moiety of CS had an interaction with the piperidine groups of the L, instead of the $-SH$ moiety of CS. Note: Cysteamine (CS) was used instead of Cys because of the poor solubility of the latter when taken in DMSO-d_6.

5. Structural features of the [L + Cys] complex by DFT computational studies [Geometry optimization method: B3LYP/6-31G(d)]

$\Delta E_{(\text{Binding energy})} = E_{(a+b)} - [E_{(a)} + E_{(b)}]$

Table S1: The binding energy for the process that the −SH groups of Cys was placed in the upper of the L

	Energy (a.u.)
Host (a)	−2354. 9325135
Guest (b)	−718. 1698543
(a) + (b)	−3113. 4075952
$\Delta E_{(\text{Binding energy})}$	**-40.3052274**

Table S2: The binding energy for the process that the −SH groups of Cys was placed in the bottom of the L

	Energy (a.u.)
Host (a)	−2354. 9325135
Guest (b)	−718. 1698543
(a) + (b)	−3073. 1207146
$\Delta E_{(\text{Binding energy})}$	**-0.0183468**

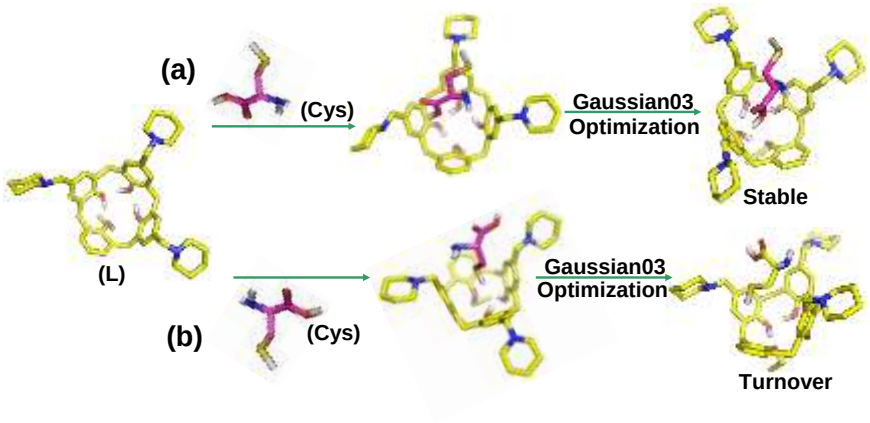


Figure S10 (a) The −SH groups of Cys was placed in the upper of the L, and the top view on the optimized structure of the [L + Cys] complex. According to the binding energy, the stable structure was that the carboxyl inserted into the low rim of the cavity and the sulfhydryl exposed outside the cavity of the calixarene. (b) The −SH groups of Cys was placed in the bottom of the L, and the top view on the optimized structure of the [L + Cys] complex. The results were the −SH groups of Cys turned over or up. The top view on the optimized structure of the [L + Cys] complex.

Table S3: Cartesian coordinates for the [L + Cys] complex

Z	Cordinations		
	x	y	z
8	0.00000000	0.00000000	0.00000000
8	3.91675790	0.00000000	0.00000000
1	2.50540443	6.74651442	0.00000000
6	4.76553350	2.82536320	-1.24677591
1	5.36918752	3.39989008	-1.95979706
6	6.77427483	1.64543955	4.75883696
6	2.49918126	0.53617957	-3.18831495
6	2.14889357	-1.93763889	2.10004279
8	2.22214166	1.58517159	-1.01309497
6	-0.56374123	2.77784309	5.00112305
1	-0.98959700	3.63705669	-0.05347431
6	6.08765628	1.18205584	3.49428596
6	5.78954091	-0.09709271	3.22192233
6	5.06508021	-0.49219182	2.00693116
6	3.40967622	-2.26701322	2.63446187
6	3.48230853	-2.79403694	3.92951798
6	2.33710114	-3.00469968	4.70675910
6	1.10139654	-2.63419149	4.16315067
6	0.99110221	-2.09395137	2.88158247
6	2.44513674	5.68489278	-0.20762419
6	3.58354529	4.98919122	-0.61124635
6	3.51799334	3.61860311	-0.89408715
6	4.68246554	-1.96250670	1.84838776
1	1.08443375	2.03395220	-2.73790397
6	-0.34022930	-1.55812872	2.37614044
6	1.22914553	5.01556166	-0.05442004
6	4.67179846	0.43377957	1.11069351
6	-0.33370696	2.75734325	2.44429648
8	2.00673331	-1.43574699	0.81480644
1	3.28500683	-3.21724872	6.63339851
6	-0.18240274	2.89661528	-0.08399466
1	-0.39410869	2.21499693	-0.90809713
6	2.28128000	2.98068853	-0.75189126
6	1.12794699	3.64351245	-0.31304854
6	-0.22175191	2.09618128	1.21816697
6	5.73229390	2.30329298	2.54358478
6	4.92219578	1.92807021	1.25142338
6	-0.44567399	2.05838213	3.65450742

1	4.55044280	-2.20486668	0.79016259
6	-0.18394204	0.68888768	1.19515981
6	-0.47123047	0.65685394	3.60336456
6	-0.34061635	-0.03037387	2.39414769
1	0.72621719	-0.70481048	0.19489926
1	3.31578236	0.72936110	-0.43047561
1	-0.54738160	-1.90474744	1.36005295
1	-1.13931374	-1.92292703	3.02948875
1	5.49501110	-2.58737313	2.23459017
1	4.49764451	1.88527413	-1.72935819
1	0.76445196	0.45904507	-1.94183404
6	3.29261686	0.00192096	-3.92208002
1	1.51498070	-3.33572700	6.65639694
1	0.12410787	3.63209011	5.02291931
1	3.98683066	-0.46595047	-4.57569038
1	-0.25663213	2.07639335	5.78682440
6	2.41787449	-3.62529933	6.10166229
6	1.53853740	1.14731327	-2.28415077
1	6.08089604	2.33509227	5.26405955
1	6.97740126	0.78609154	5.42743807
1	6.08180473	-0.88878849	3.90700442
1	4.45859782	-3.03753824	4.33654100
1	0.20472830	-2.73392775	4.76609381
1	4.53132137	5.50626597	-0.71265844
1	0.34954230	5.55801863	0.27357463
1	-0.30615795	3.84192107	2.45724262
1	2.86860243	-0.97228801	0.43326697
1	5.16648820	3.04581624	3.12214398
1	-0.54908804	0.09516683	4.52865375
6	9.56846516	4.23008177	5.03705404
6	8.42105707	3.32599309	5.52793385
7	8.00430185	2.41169361	4.43593059
6	9.11667309	1.53069134	4.00534228
6	10.28804475	2.37839008	3.47609582
6	10.76093547	3.37313514	4.55846787
1	9.87651556	4.90404631	5.84546111
1	9.19516346	4.83403187	4.20197360
1	8.76023978	2.76550018	6.42213472
1	7.55170405	3.92863216	5.80970596
1	9.47180330	0.89875114	4.84484992
1	8.73611184	0.86895425	3.22069822
1	11.11018649	1.72025353	3.16935548
1	9.94117630	2.93532274	2.59767405

1	11.16654943	2.81124945	5.41152774
1	11.56130586	4.01311137	4.16809996
6	-3.66874979	4.99831944	5.16252645
6	-2.41311243	4.37794312	4.51766346
7	-1.91742526	3.26675057	5.36219353
6	-2.92285936	2.18706245	5.50732683
6	-4.19266215	2.74765225	6.17730196
6	-4.75911278	3.92164735	5.35003814
1	-4.03789728	5.81708951	4.53275402
1	-3.38827222	5.40706234	6.13995104
1	-2.66270048	4.04328147	3.49306278
1	-1.61669690	5.12835500	4.44758842
1	-3.19209715	1.73750807	4.53382567
1	-2.48335602	1.40077661	6.13213026
1	-4.93826177	1.94915726	6.27592413
1	-3.92657438	3.10431588	7.17899615
1	-5.07393074	3.55029977	4.36457545
1	-5.63980872	4.34949182	5.84384636
6	1.35443029	-7.28507505	5.95965364
6	1.31795261	-5.78949171	5.58942603
7	2.50214704	-5.10427282	6.16341065
6	3.77261060	-5.66246742	5.64214526
6	3.87538923	-7.15340024	6.01899268
6	2.66450998	-7.92974500	5.45706919
1	0.48363857	-7.79086982	5.52535521
1	1.30172962	-7.37334777	7.05100998
1	1.27191673	-5.68341286	4.49082088
1	0.42055549	-5.32090733	6.01101968
1	3.85227333	-5.55997724	4.54453886
1	4.59828354	-5.10229621	6.09784482
1	4.81381141	-7.56587062	5.62902872
1	3.88470870	-7.23445268	7.11204988
1	2.68889052	-7.89133659	4.35899154
1	2.71241354	-8.98331959	5.75665865
1	3.66178566	2.17807084	7.43667748
6	3.01559293	2.21489382	6.55876233
1	1.98464780	2.39660612	6.87465956
6	3.08699931	0.80104207	5.85865004
1	4.10555652	0.42421958	5.87013602
6	2.14458240	-0.13683031	6.55910570
8	0.93368978	-0.23854318	6.36805381
8	2.81401521	-0.81671483	7.54725491
1	2.16123141	-1.35539972	8.07479960

7	2.66292141	0.97065850	4.41633302
1	1.64041015	0.84056737	4.28966332
1	3.18720773	0.34831479	3.78117614
16	3.54765265	3.57465528	5.35538235
1	2.93096936	2.04929470	4.24470264
1	6.03379235	3.52614247	0.34702116
6	5.64124808	2.55755782	0.01387757
1	6.49887410	1.93108157	-0.25875885
1	6.68145182	2.78088759	2.27218549
1	3.93657824	2.41131566	1.32076922

6. The click reaction and interface characterizations

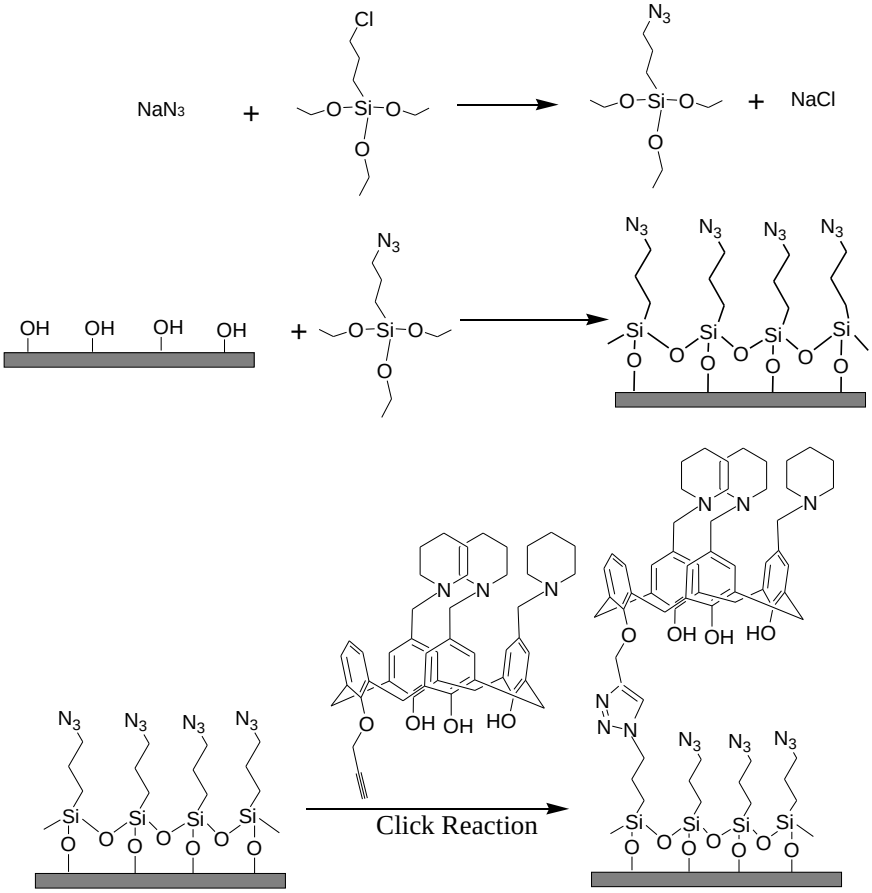


Figure S11. The process of the functional L-SAMs formed, which indicated the L was successfully modified on a silicon surface by the click reaction.

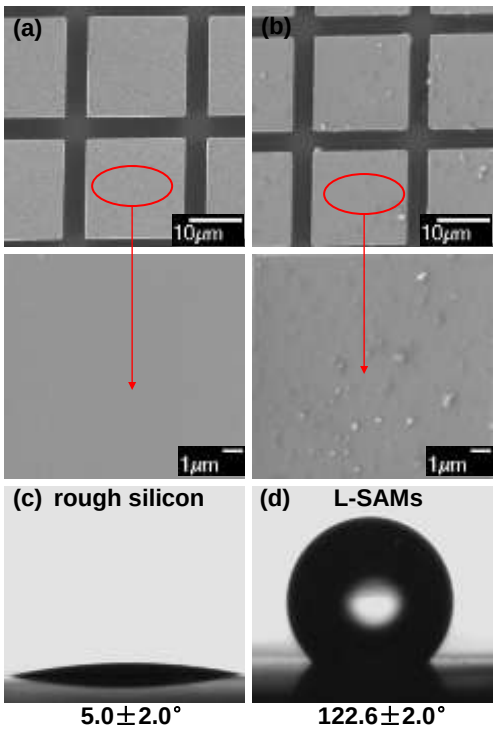


Figure S12. SEM images of the rough silicon surface before **(a)** and after the L modified **(b)**. Water-drop profiles on bare silicon wafer **(c)** and L-SAMs **(d)**, which indicated that the L was successfully modified on a silicon surface.

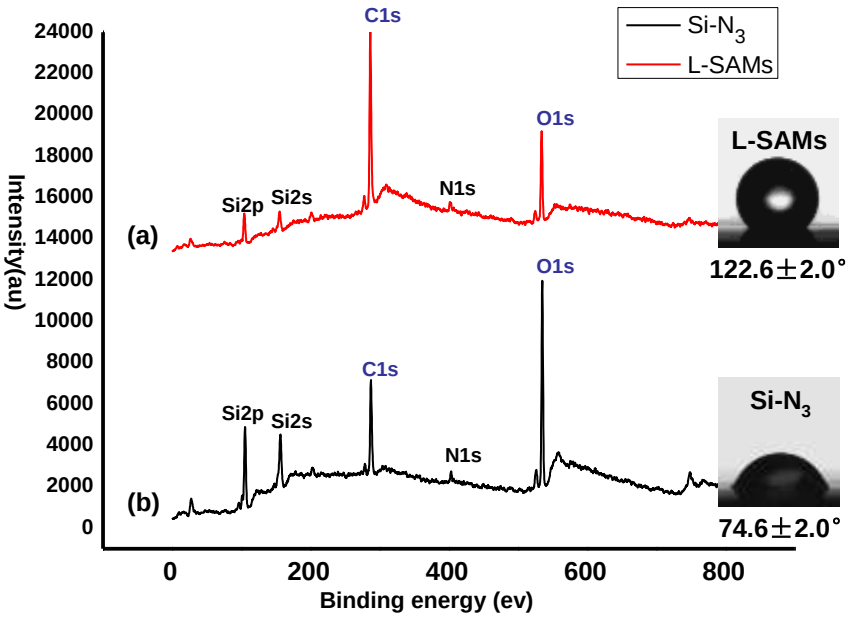


Figure S13. (a) X-ray photoelectron spectra and CA of Si-N_3 modified silicon substrate (black line). **(b)** X-ray photoelectron spectra and CA of L-SAMs modified silicon substrate (red line). These showed the concentration of carbon had a significant increase and the concentration of oxygen had an obvious decrease in the XPS-derived atomic concentration analysis for the SAMs after the click reaction. We concluded that the L-SAMs were constructed perfectly.

7. Wettable selective recognition of Hg^{2+} and some control experiments

The wettability property was performed with a water droplet (1.000 μ L) and side-view photographs were obtained after 10 second of adding the water droplet. The successfully modified rough silicon surface of the L was firstly performed by CA as control experiments. The surface modified L-SAMs was immersed into Cys solution, then solutions containing Hg^{2+} (0.1 mL, 1.0 m M) for 10 min, and then were flushed by little water, dried by nitrogen and then measured.

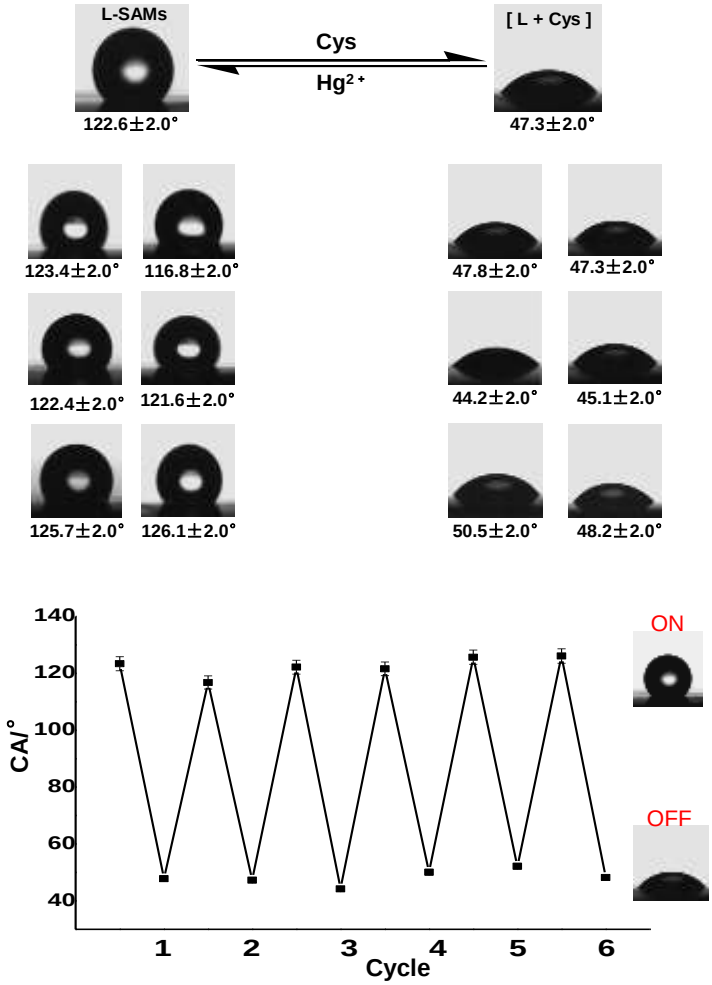


Figure S14. Cycling experiment of the wettability switching between Cys and Hg^{2+} on the L-modified silicon surface, which indicated a significant change of CAs between hydrophobicity and hydrophilicity.

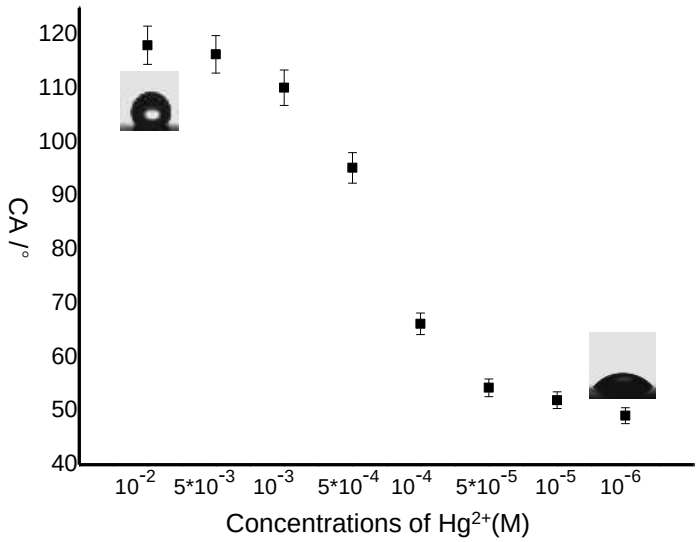


Figure S15. The contact angle of the [L + Cys] complex with various concentrations of Hg^{2+} (1.0×10^{-2} ~ 1.0×10^{-6} M), which clearly showed that the detection limit for Hg^{2+} was 1.0×10^{-6} mol/L.

CA control experiments of different thiols

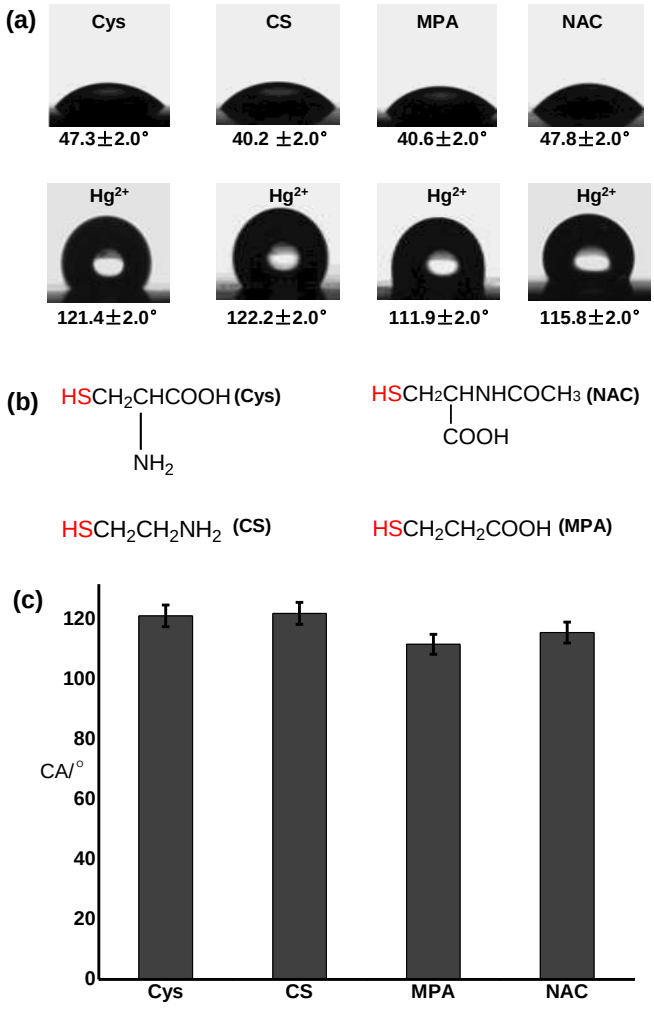


Figure S16. (a) CA control experiments showed CA changes of Hg^{2+} with different thiols. **(b)** The structure of different thiols. **(c)** The histogram showed CA changes of Hg^{2+} with different thiols. These results suggested that the [L + Cys] complex was selective for only Hg^{2+} owing to their unique $Hg^{2+}\cdots SH$ interaction.

CA control experiment of the reference compound C4AM

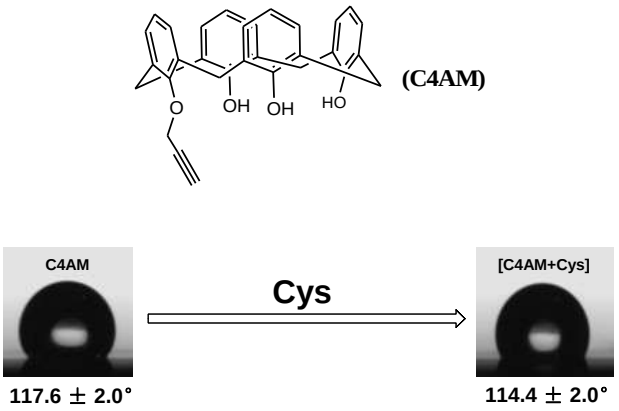


Figure S17. CA of C4AM and [C4AM + Cys] modified silicon surface, which showed scarcely change upon addition of Cys compared with C4AM. Thus, the control experiment result indicated that the piperidine moiety played an important role in the efficient interacting with Cys.