Electronic Supplementary Information for Dalton Transactions

Electronic Supplementary Information

A Sensitive Phosphorescent Thiol Chemosensor Based on an Iridium(III) Complex with α,β-Unsaturated Ketone Functionalized 2,2′-Bipyridyl Ligand

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Table S1. Partial Molecular Orbital Compositions (%) of **1** in DMF media under the TD-DFT Calculations.

Orbital	Energy (eV)	MO contribution (%)			
		Ir	L ligand		ppy
			2,2′-bpy	-C(O)$C_6H_4N(C_2H_5)_2$	
LUMO+6	–0.8898	4.2	22.5	19.9	53.4
LUMO+5	–0.9304	1.9	47.0	19.9	31.2
LUMO+1	–2.0512	1.1	87.7	9.1	2.1
LUMO	–2.6754	3.9	75.3	18.7	2.1
HOMO	–5.7490	0.6	1.7	97.3	0.4
HOMO−1	–5.8227	45.4	3.9	0.6	50.1
HOMO−6	–6.9232	15.6	4.9	0.3	79.2

Table S2. TD-DFT Calculated Singlet Absorption Data and the Measured Absorption Data for **1** in DMF Media.

	Transition	**CI Coef.**	***E*, nm (eV)**	**O.S.**	**Assignment**	**Measured value (nm)**
S1	HOMO−1→LUMO	0.68	513 (2.42)	0.0066	^{1}MLCT /^{1}LLCT	
S2	HOMO→LUMO	0.67	474 (2.61)	0.4502	^{1}ILCT	430,460
S6	HOMO→LUMO+1	0.68	379 (3.27)	0.1264	^{1}ILCT	
S31	HOMO→LUMO+5	0.33	287 (4.31)	0.3761	^{1}ILCT /^{1}LLCT	298, 270
	HOMO−6→LUMO+1	-0.25			^{1}MLCT/^{1}LLCT	
	HOMO→LUMO+6	-0.23			^{1}ILCT/^{1}LLCT	

Table S3. Partial Molecular Orbital Compositions(%) of **1**-Cys in DMF solution under the TD-DFT Calculations.

Orbital	Energy (eV)	MO contribution (%)			
		Ir	L ligand		ppy
			2,2′-bpy	-C(O)$C_6H_4N(C_2H_5)_2$	
LUMO+4	–1.2438	0.8	15.0	78.1	6.1
LUMO+3	–1.4692	5.7	6.7	0.8	86.8
LUMO	–2.2711	4.0	90.0	3.5	2.5
HOMO	–5.7302	0.0	0.3	99.7	0.0
HOMO−1	–5.8121	45.9	3.9	0.1	50.1
HOMO−2	–6.4437	17.4	3.6	2.4	76.6

Table S4. TD-DFT Calculated Singlet Absorption Data in DMF Media and the Measured Absorption Data for the adduct **1**-Cys in DMF media.

	Transition	CI Coef.	*E*, nm (eV)	O.S.	Assignment	Measured value (nm)
S1	HOMO−1→LUMO	0.70	462 (2.68)	0.0006	^{1}MLCT /^{1}LLCT	416
S2	HOMO→LUMO	0.71	402 (3.08)	0.0003	^{1}ILCT	
S6	HOMO−2→LUMO	0.59	361 (3.44)	0.1079	^{1}LLCT/^{1}MLCT	348
	HOMO−1→LUMO+3	0.20			^{1}MLCT /^{1}ILCT	
S18	HOMO→LUMO+4	0.60	309 (4.02)	0.7007	^{1}ILCT	312,280

Table S5 DFT Optimized Coordinates for **1-**Cys.

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	77	3.221897	-0.693707	0.033371
2	7	1.148961	-0.124759	-0.112769
3	6	5.195407	-0.984406	0.189969
4	7	3.831517	0.173164	-1.715602
5	7	2.753917	-1.729079	1.733587
6	6	3.048994	-2.532478	-0.735406
7	6	-1.515079	0.747862	-0.124880
8	6	2.682569	-3.531910	0.199530
9	6	0.827357	1.097998	0.377035
10	6	2.479657	-4.862068	-0.191467
11	1	2.197709	-5.619234	0.535220
12	6	4.145208	3.236614	1.855819
13	1	5.043450	3.725197	2.220463
14	6	3.208833	-2.932392	-2.067995
15	1	3.502085	-2.206068	-2.820802
16	6	-0.485158	1.549860	0.375120
17	1	-0.720520	2.542919	0.739964
18	6	2.640686	-5.224288	-1.519706
19	1	2.487651	-6.253872	-1.827271
20	6	1.811784	3.198925	1.374148
21	1	0.843840	3.687361	1.345524
22	6	0.174103	-0.898689	-0.600062
23	1	0.489354	-1.864543	-0.983023
24	6	1.954576	1.894409	0.903511
25	6	2.913230	3.898381	1.865099

26	6	-1.157176	-0.504655	-0.624209
27	1	-1.897508	-1.181352	-1.035778
28	6	2.663865	-1.181462	2.956863
29	1	2.854879	-0.116187	3.012804
30	6	2.539906	-3.064894	1.571131
31	6	2.132905	-3.288534	3.939590
32	1	1.892719	-3.903671	4.801281
33	6	4.225575	1.943363	1.368251
34	1	5.164520	1.399069	1.337659
35	6	2.357781	-1.920112	4.084771
36	1	2.301456	-1.431765	5.050846
37	7	3.157553	1.279091	0.903244
38	6	-2.926206	1.264239	-0.119635
39	1	-3.101210	1.843170	0.792905
40	6	5.175677	0.170332	-1.938392
41	6	5.957215	-0.455375	-0.880881
42	6	5.899076	-1.603027	1.230633
43	1	5.358940	-2.035684	2.068255
44	6	5.684690	0.733615	-3.113526
45	1	6.754247	0.724188	-3.287545
46	6	7.355701	-0.539561	-0.896112
47	1	7.929142	-0.128906	-1.722742
48	6	7.289390	-1.685305	1.214217
49	1	7.808903	-2.173648	2.034589
50	6	3.456377	1.279727	-3.802737
51	1	2.746819	1.698359	-4.507222
52	6	2.779147	5.296127	2.386903
53	1	1.795491	5.715659	2.164870
54	1	3.543243	5.951119	1.957822
55	1	2.913872	5.313772	3.474004

56	6	8.022904	-1.153718	0.152391
57	1	9.106009	-1.223237	0.143942
58	6	4.828898	1.289326	-4.048458
59	1	5.223766	1.722883	-4.962080
60	6	3.003735	0.712294	-2.625885
61	1	1.947408	0.669718	-2.387845
62	6	2.224175	-3.856351	2.680952
63	1	2.059748	-4.918955	2.546211
64	8	-5.359202	1.753815	0.999192
65	6	3.007126	-4.254996	-2.454930
66	1	3.141524	-4.536946	-3.495996
67	6	-8.985827	-1.504681	-0.293164
68	7	-10.156897	-2.169039	-0.522072
69	6	-7.772804	0.399671	0.620099
70	1	-7.765158	1.330461	1.178856
71	6	-11.419589	-1.664525	-0.001604
72	1	-12.215756	-2.084528	-0.623480
73	1	-11.460627	-0.581146	-0.159740
74	6	-7.747724	-1.989287	-0.787832
75	1	-7.704199	-2.925255	-1.330365
76	6	-5.342579	0.716202	0.342479
77	6	-6.576569	-1.283760	-0.598980
78	1	-5.661732	-1.702092	-1.009006
79	6	-8.951771	-0.286841	0.436589
80	1	-9.859123	0.120162	0.865249
81	6	-11.682128	-1.998096	1.464103
82	1	-12.624040	-1.546694	1.790984
83	1	-10.882565	-1.621863	2.108560
84	1	-11.756298	-3.078170	1.617657
85	6	-6.552856	-0.069613	0.104464

86	6	-10.170846	-3.446668	-1.219190
87	1	-9.524638	-3.379312	-2.102188
88	1	-11.184008	-3.592350	-1.604964
89	6	-9.772992	-4.642426	-0.358679
90	1	-9.777148	-5.557919	-0.958489
91	1	-10.470880	-4.779583	0.471513
92	1	-8.771908	-4.515768	0.063209
93	1	-4.828699	3.561302	-0.210297
94	6	-3.943543	3.955592	-0.712143
95	6	-3.086427	4.750043	0.271301
96	1	-4.237567	4.597022	-1.548233
97	16	-3.056254	2.522983	-1.537416
98	6	-1.922038	5.388911	-0.463464
99	7	-3.801426	5.836224	0.917642
100	1	-2.698795	4.086441	1.051688
101	8	-0.711313	5.035360	0.017083
102	8	-2.053337	6.159814	-1.380112
103	1	-4.140868	6.484942	0.213598
104	1	-4.601770	5.475834	1.426011
105	1	-0.068760	5.512577	-0.531605
106	6	-4.011024	0.204682	-0.210438
107	1	-4.136059	-0.144177	-1.239986
108	1	-3.732814	-0.670972	0.395380

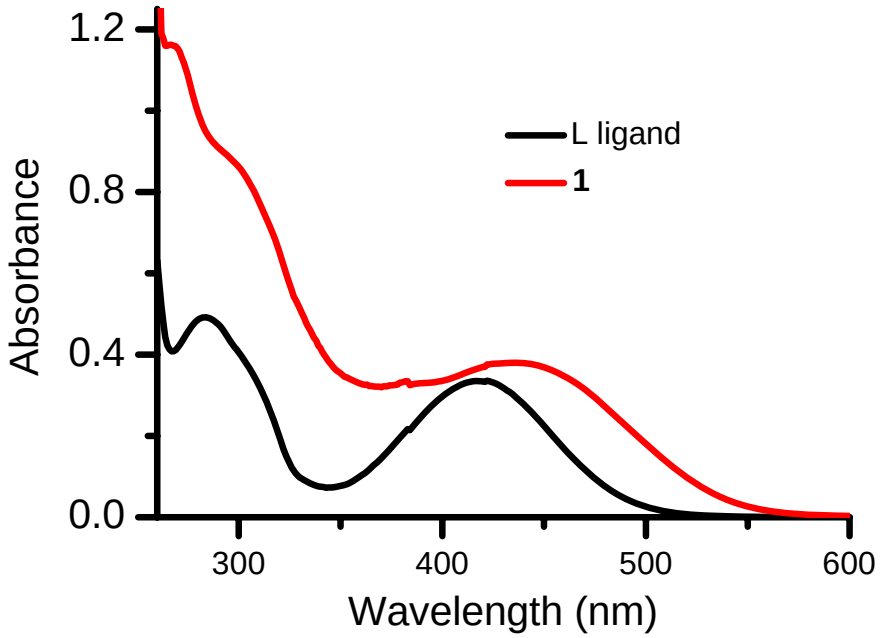

Fig. S1. UV−vis absorption spectra of complex **1** and L ligand (20 μM) in DMF−HEPES buffer solution (50 mM, pH 7.2, 4:1, v/v).

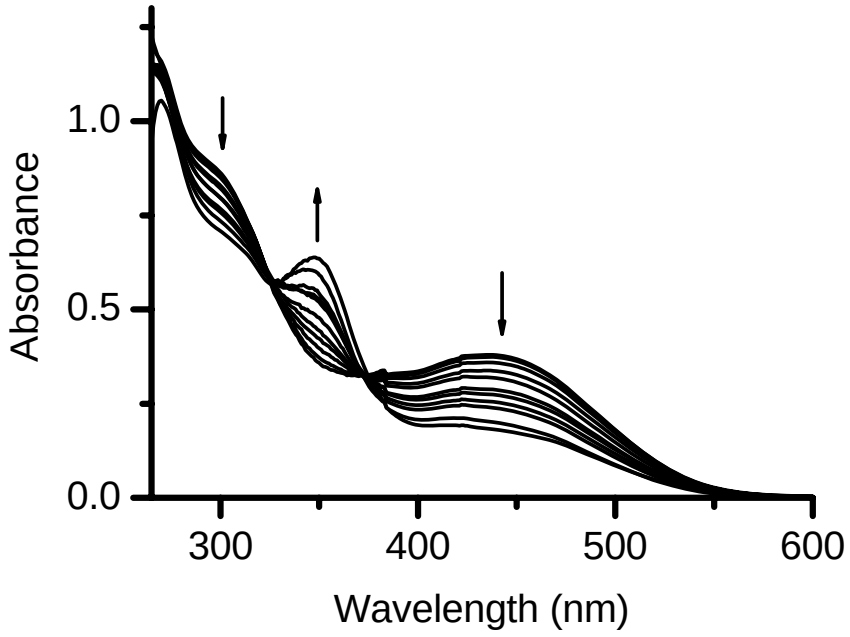

Fig. S2. Changes of UV−vis absorption spectra for complex **1** (20 μM) in DMF−HEPES buffer (50 mM, pH 7.2, 4:1, v/v) upon titration with Hcy (0–80 equiv). The equilibration time is about 300 min.

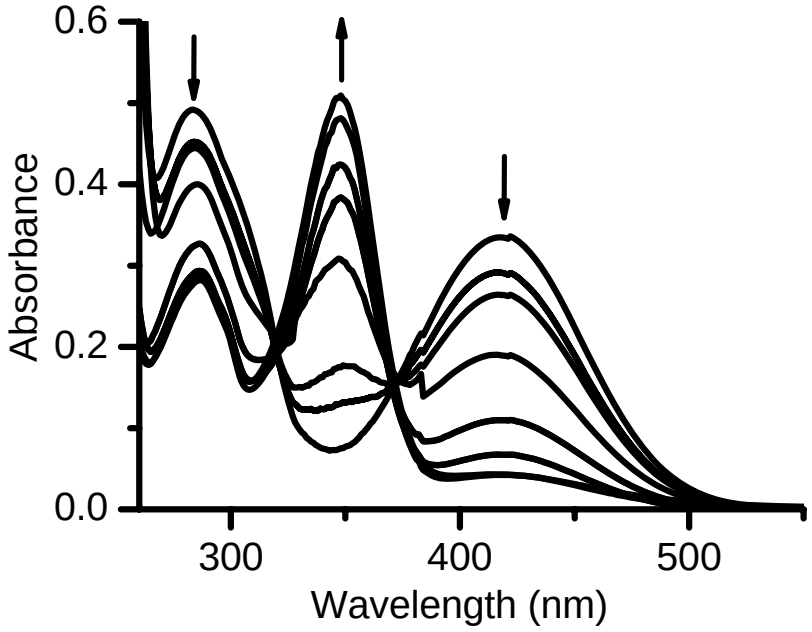

Fig. S3. Changes of UV−vis absorption spectra for the ligand L (20 μM) in DMF−HEPES buffer (50 mM, pH 7.2, 4:1, v/v) upon titration with Cys (0–60 equiv).

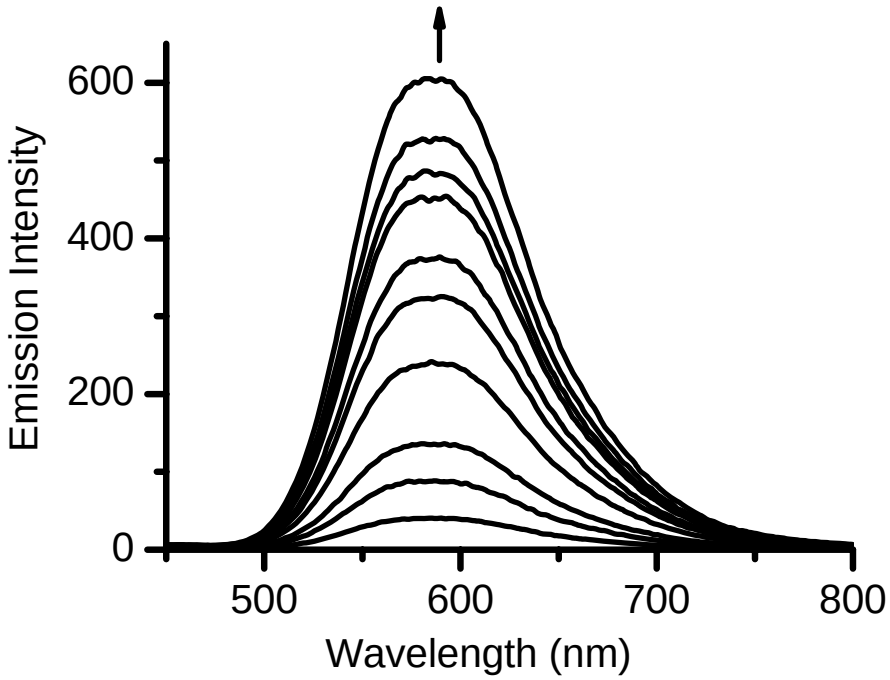

Fig. S4. Changes of emission spectra for complex **1** (20 μM) in DMF−HEPES buffer (50 mM, pH 7.2, 4:1, v/v) upon titration with Hys (0–80 equiv). The equilibration time is about 300 min.

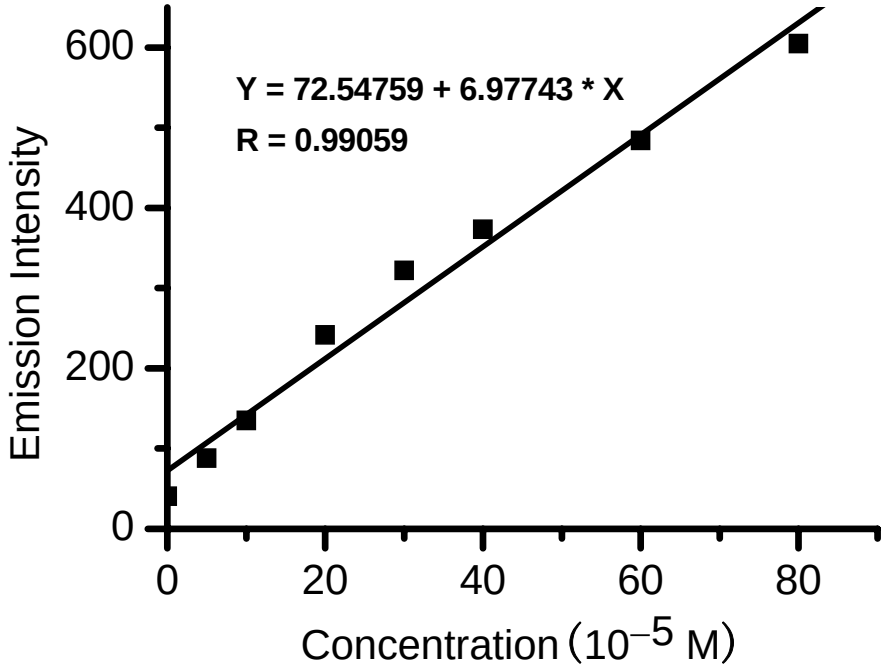

Fig. S5. Plot of Hcy concentration dependence of the emission intensity at 587 nm.

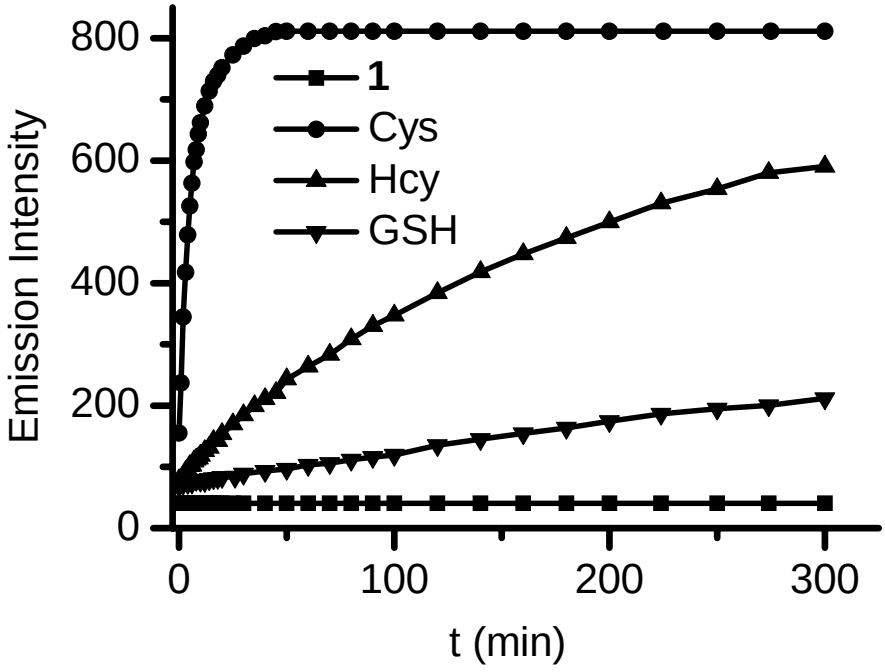

Fig. S6. Time course of the emission intensity at 587 nm for complex **1** (20 μM) upon addition of 80 equiv of Cys, Hcy, or GSH in 300 min (25^{o}C).

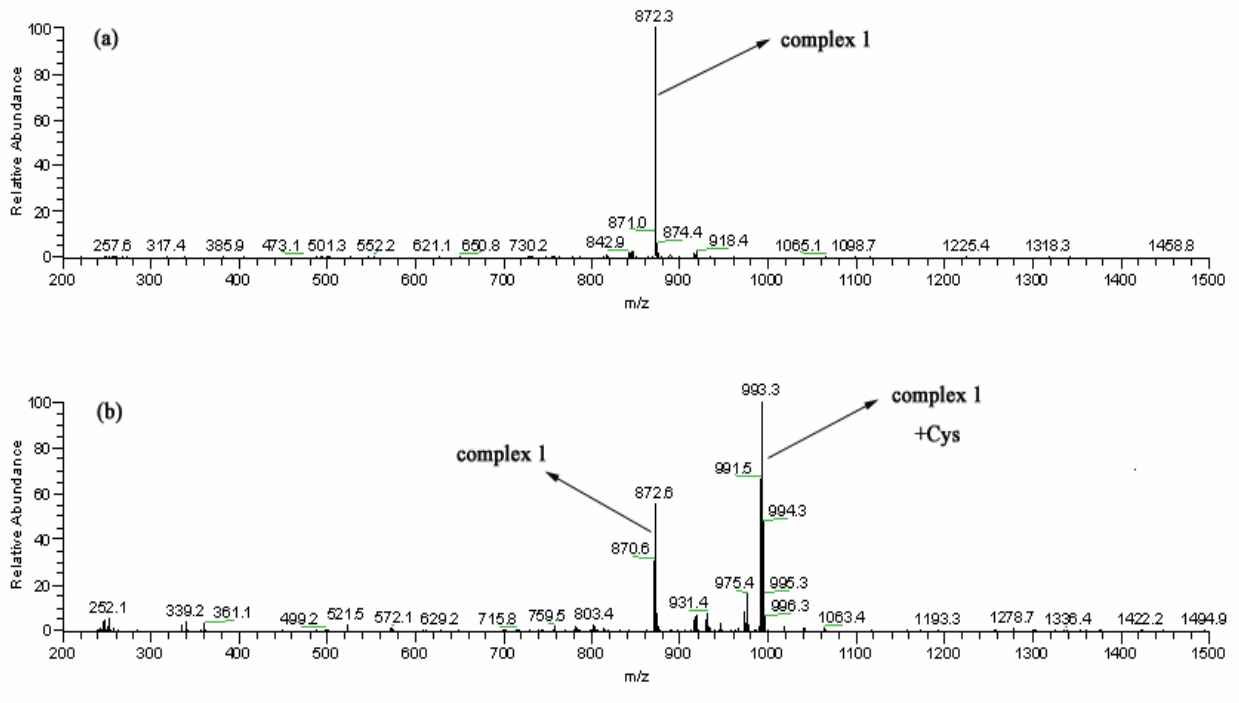

Fig. S7. Positive ion ESI spectra of **1** before (a) and after (b) addition of 80 equiv Cys.

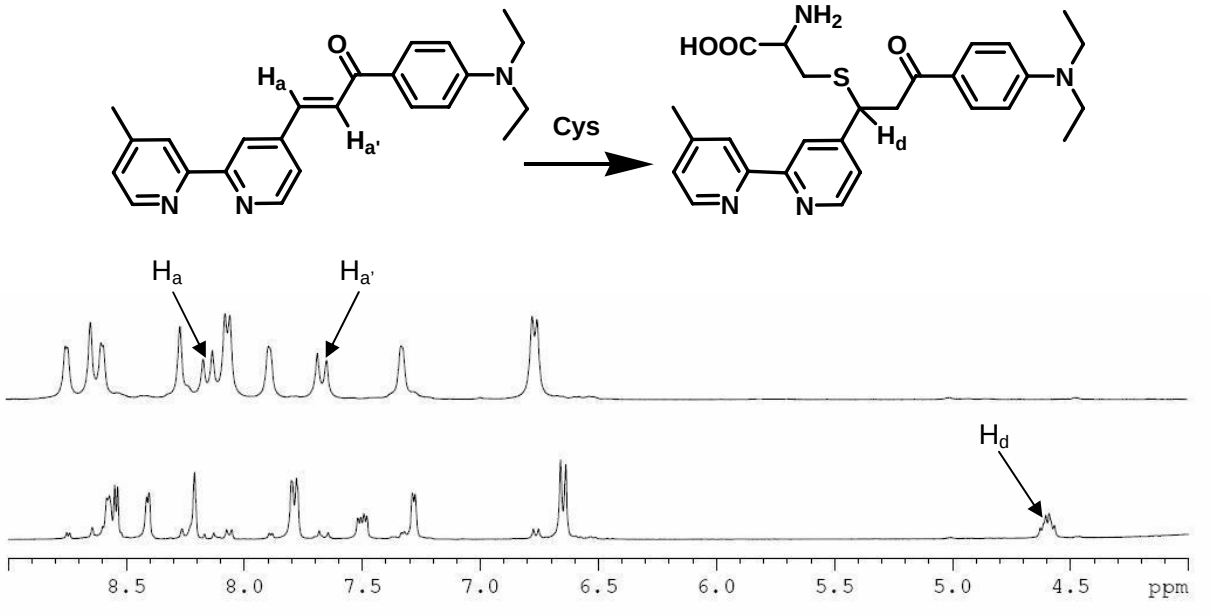

Fig. S8. ^{1}H NMR spectra of free L before (a) and after (b) addition of 5 equiv Cys in d_6-DMSO.

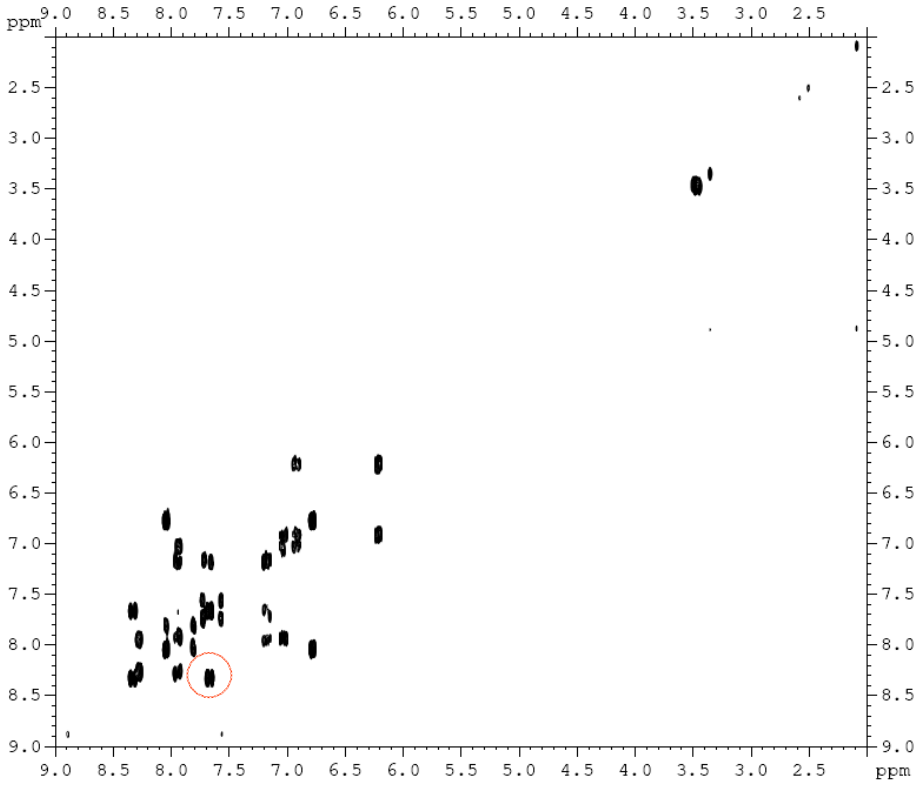

Fig. S9. The ^{1}H–^{1}H COSY spectrum of complex **1** in d_6-DMSO.

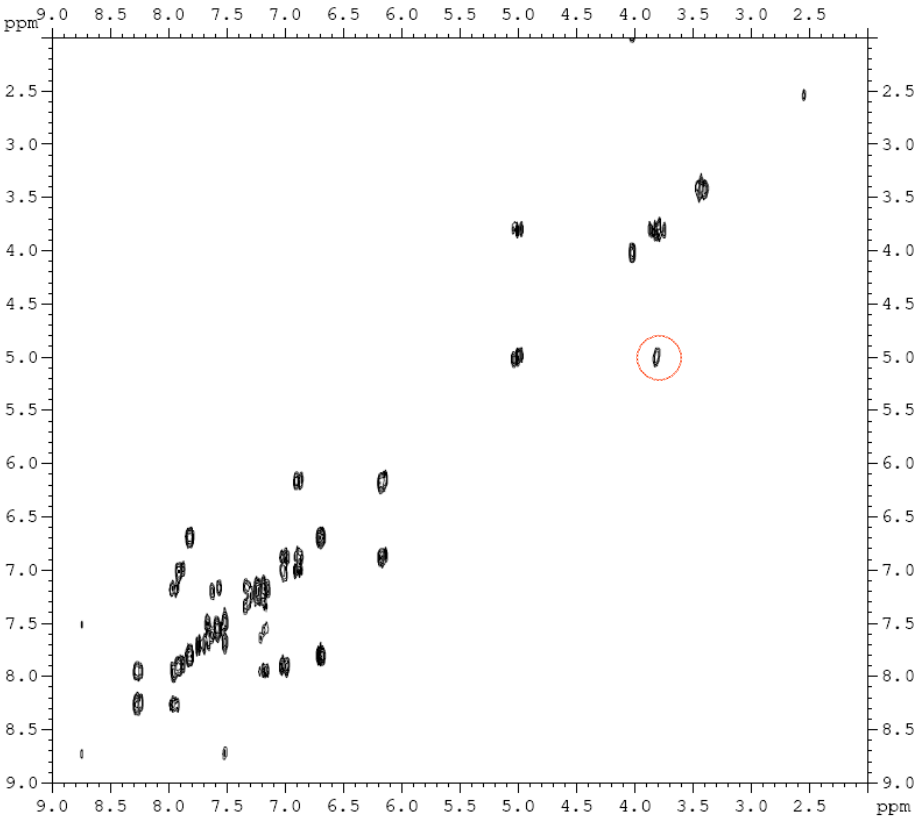

Fig. S10. The ^{1}H–^{1}H COSY spectrum of complex **2** in d_6-DMSO.

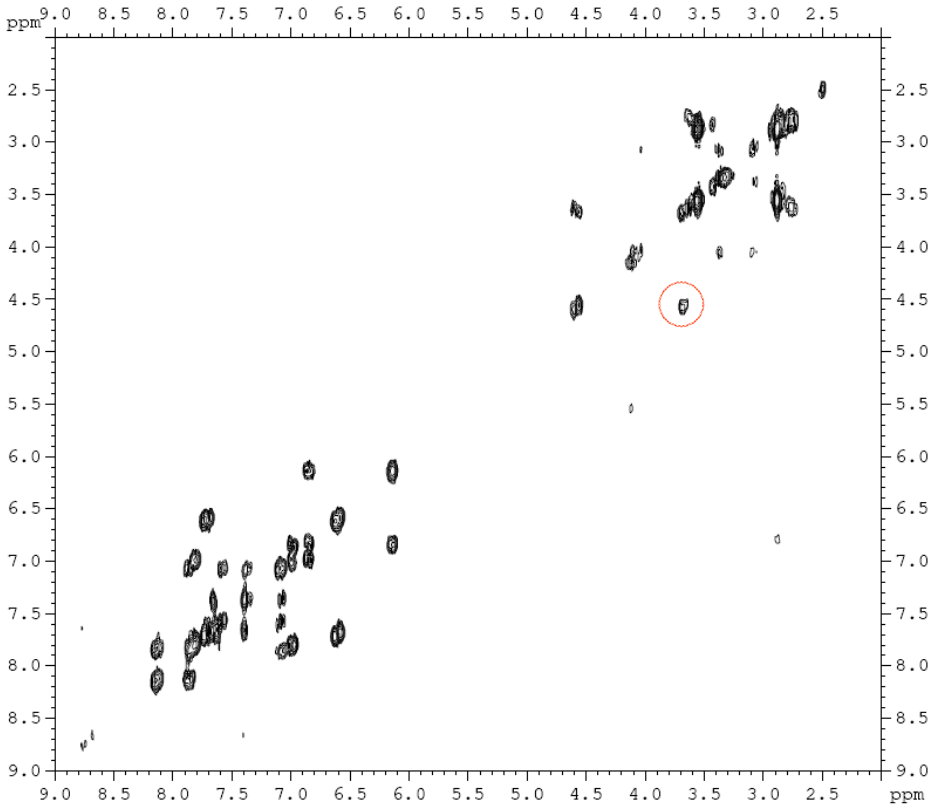

Fig. S11. The $^{1}H-^{1}H$ COSY spectrum of complex **1** and 5 equiv in d_6-DMSO−H_2O.

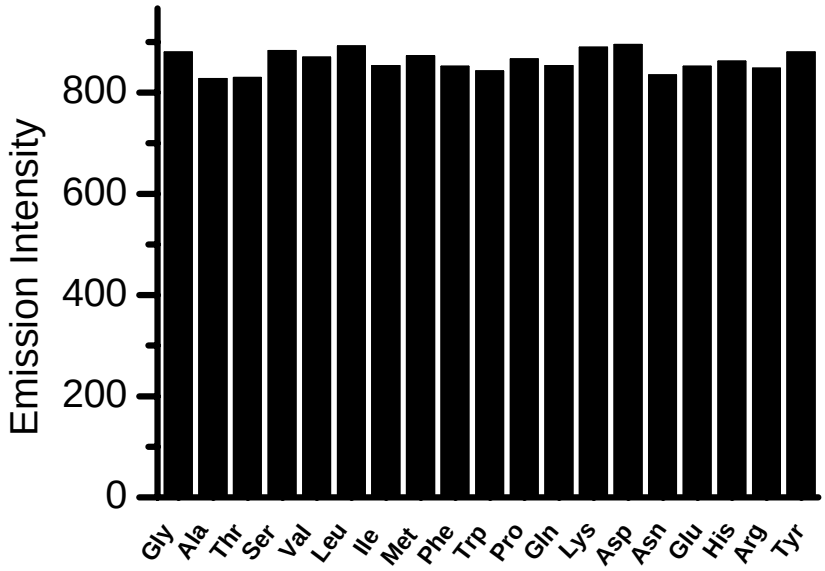

Fig. S12. Emission response of complex **1** (20 μM) in the presence of both Cys and another competing amino acid (both 80 equiv) in DMF−HEPES buffer solution (50 mM, pH 7.2, 4:1, v/v). The excitation wavelength was 358 nm.

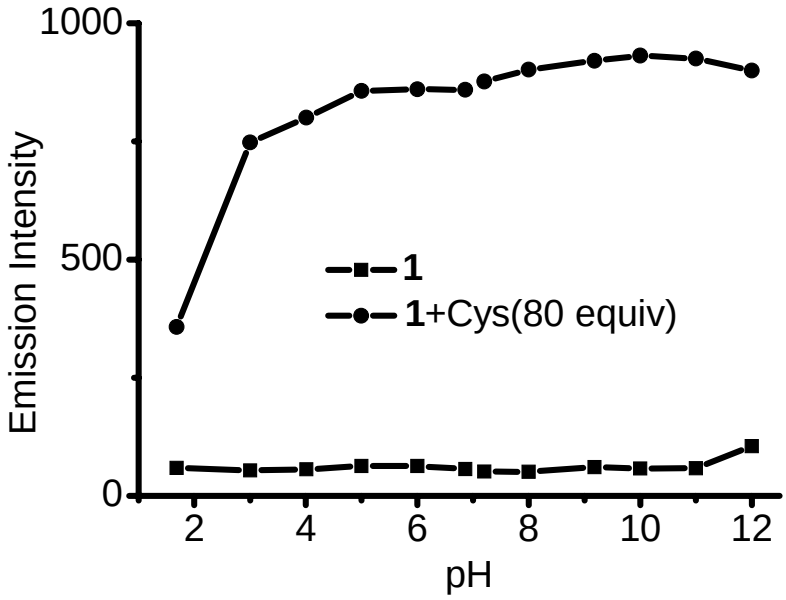

Fig. S13. The emission intensities at 587 nm for **1** (20 μM) in the absence (■) or presence (●) of Cys (80 equiv) at various pH values. The excitation wavelength is 358 nm.

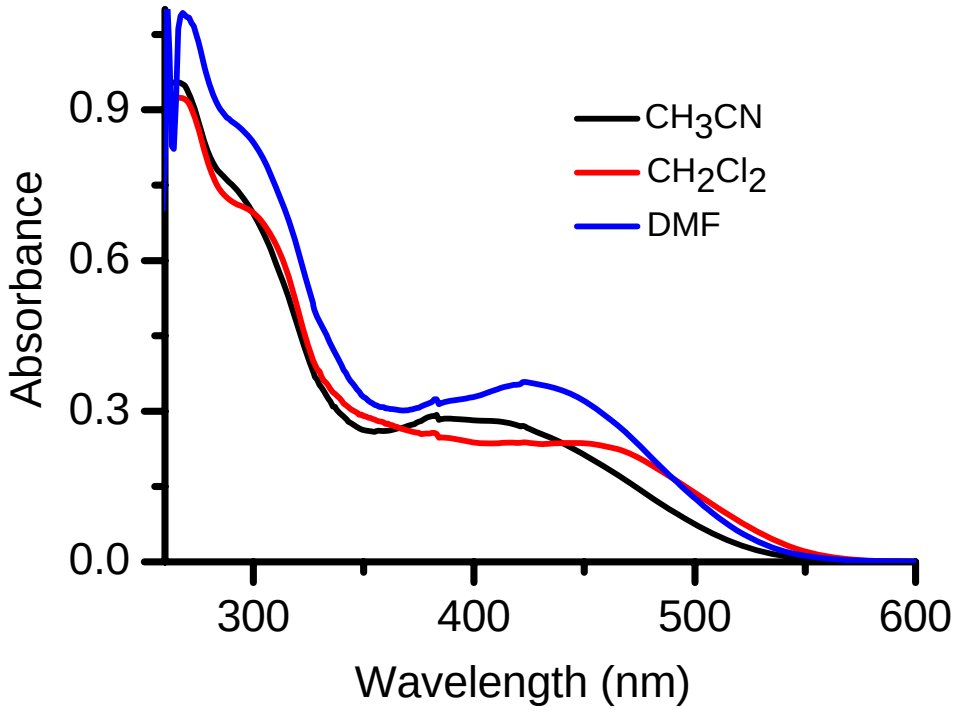

Fig. S14. UV−vis absorption spectra of complex **1** (20 μM) in CH_3CN (black), CH_2Cl_2 (red) and DMF (blue) solutions.

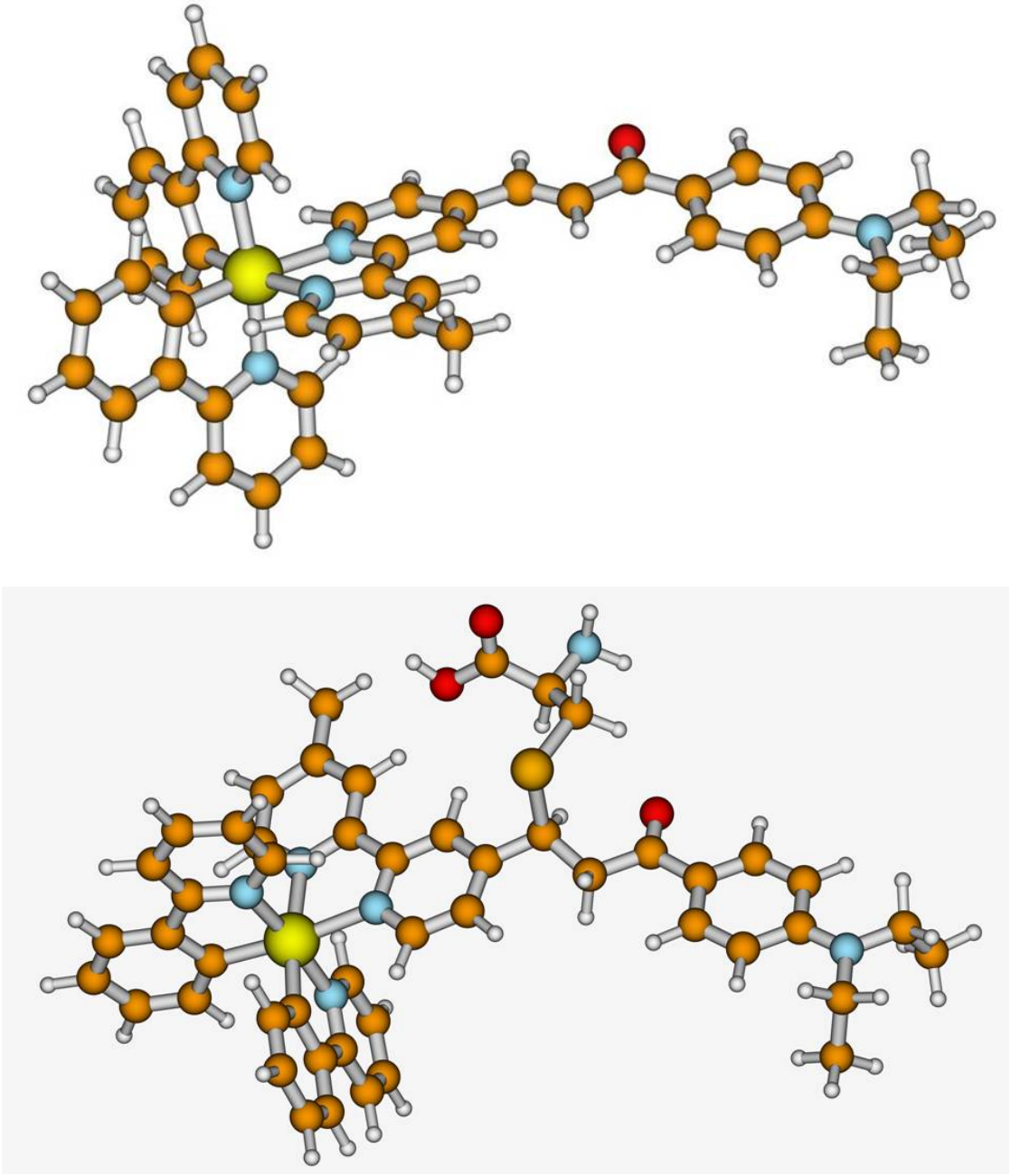

Fig. S15. Optimized structures of **1** (top) and **1**-Cys (bottom) in the ground state by DFT method.

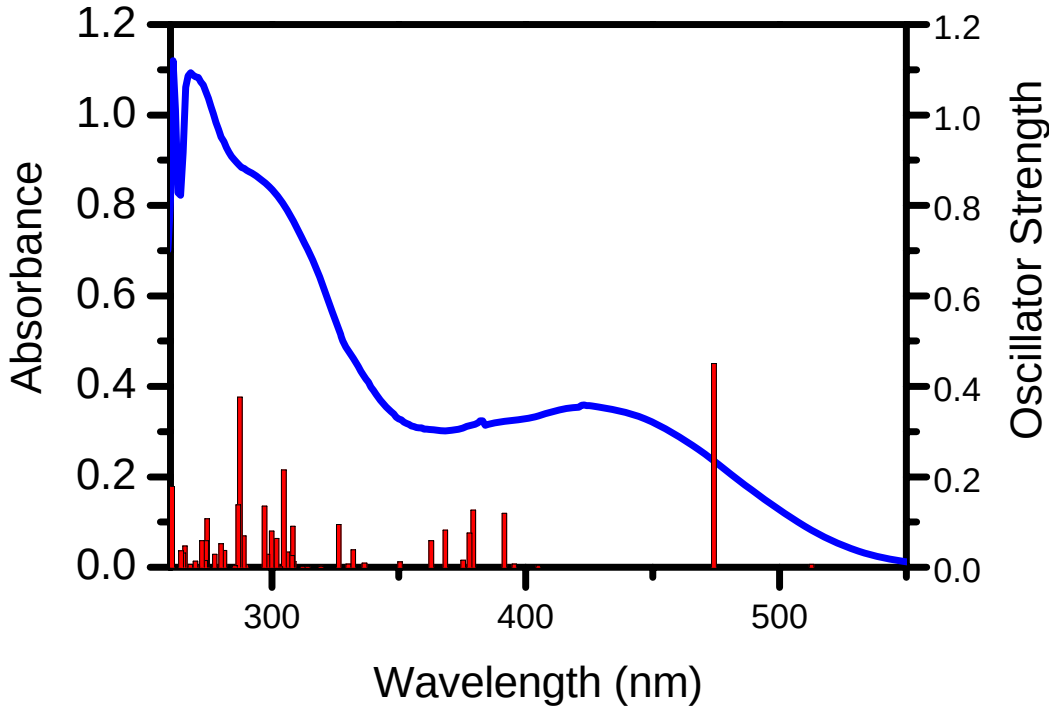

Fig. S16. Calculated (red bars) absorption and experimentally measured (blue line) UV−vis spectrum (20 μM) of **1** in DMF solution at ambient temperature.

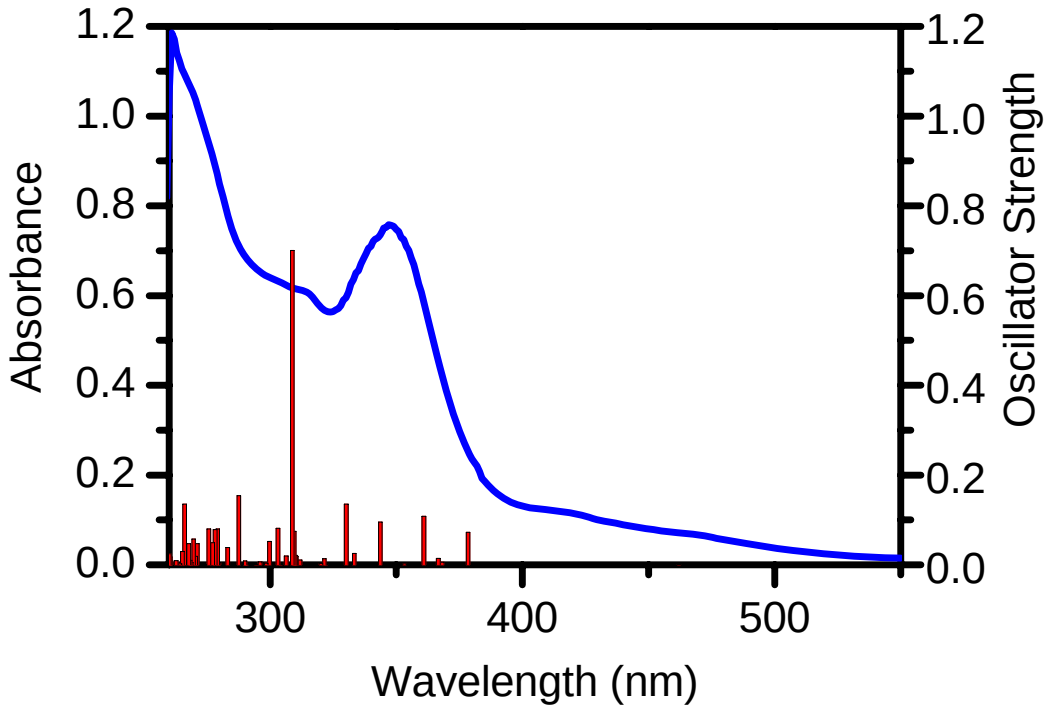

Fig. S17. Calculated (red bars) absorptions in DMF media and experimentally measured (blue line) UV−vis spectrum (20 μM) of the adduct **1**-Cys in DMF−HEPES buffer solution (50 mM, pH 7.2, 4:1, v/v).

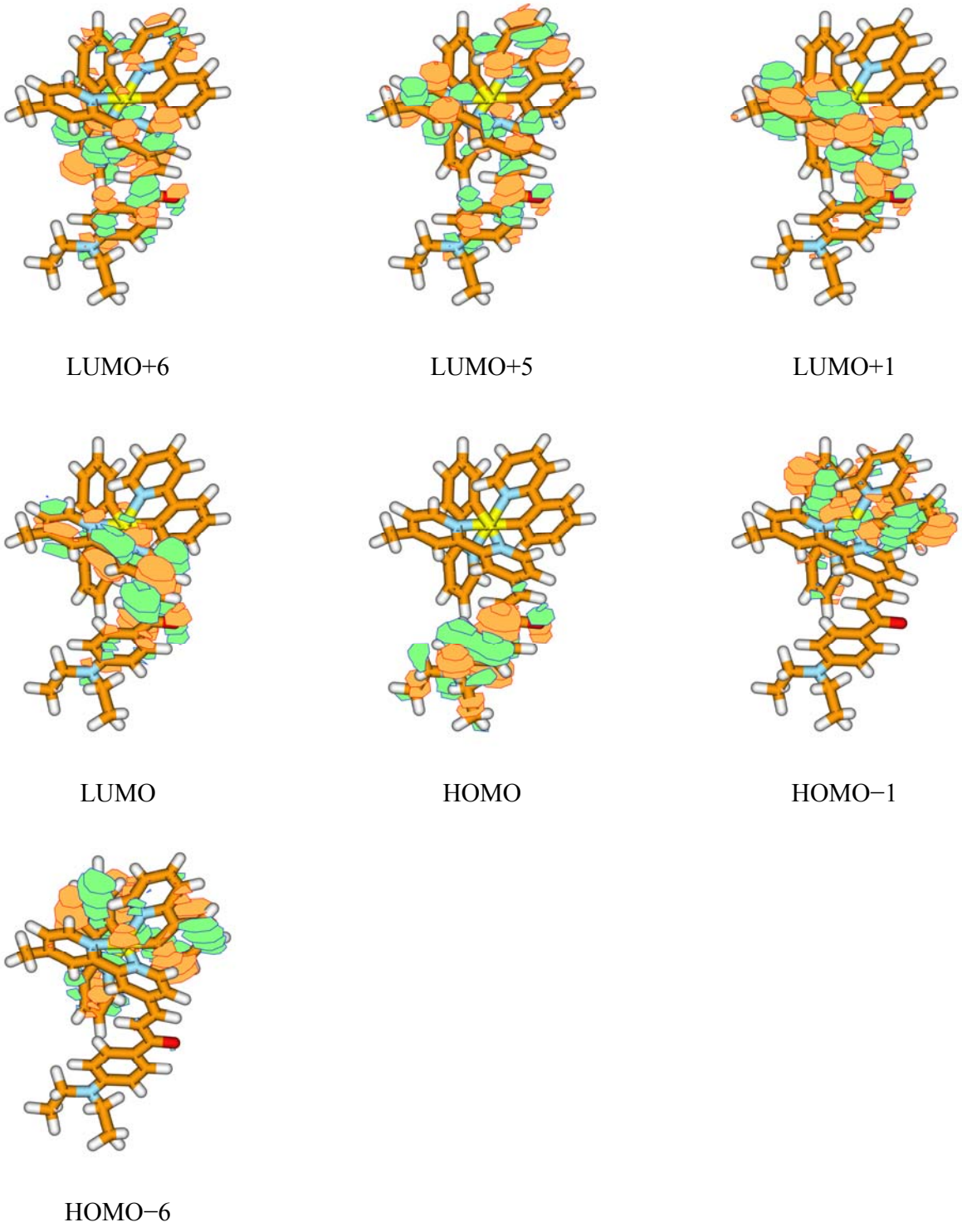

Fig. S18. Electron-density diagrams of the frontier molecular orbitals involved in absorption of **1** in DMF media.

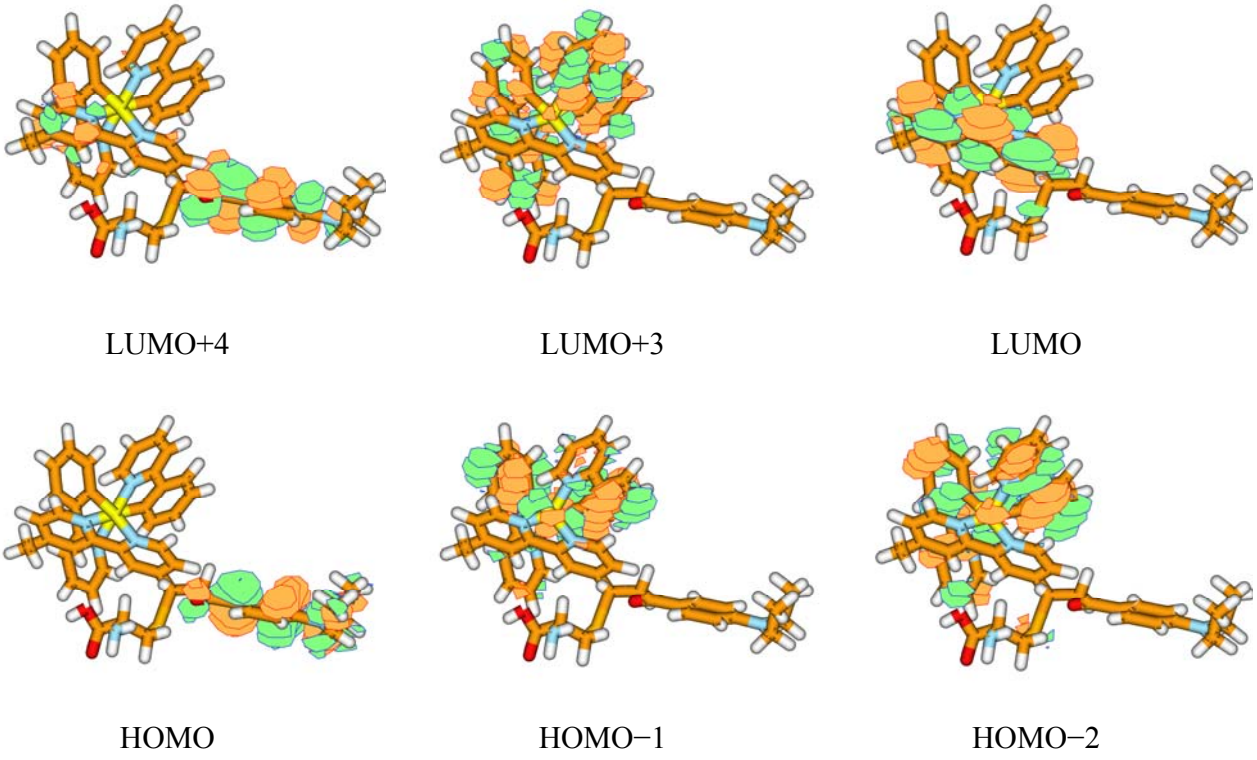

Fig. S19. Electron-density diagrams of the frontier molecular orbitals involved in absorption of **1**-Cys in DMF media.