Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

Copper(II)-Benzimidazole Complexes as an Efficient Fluorescent Probe for L-Cysteine in Water

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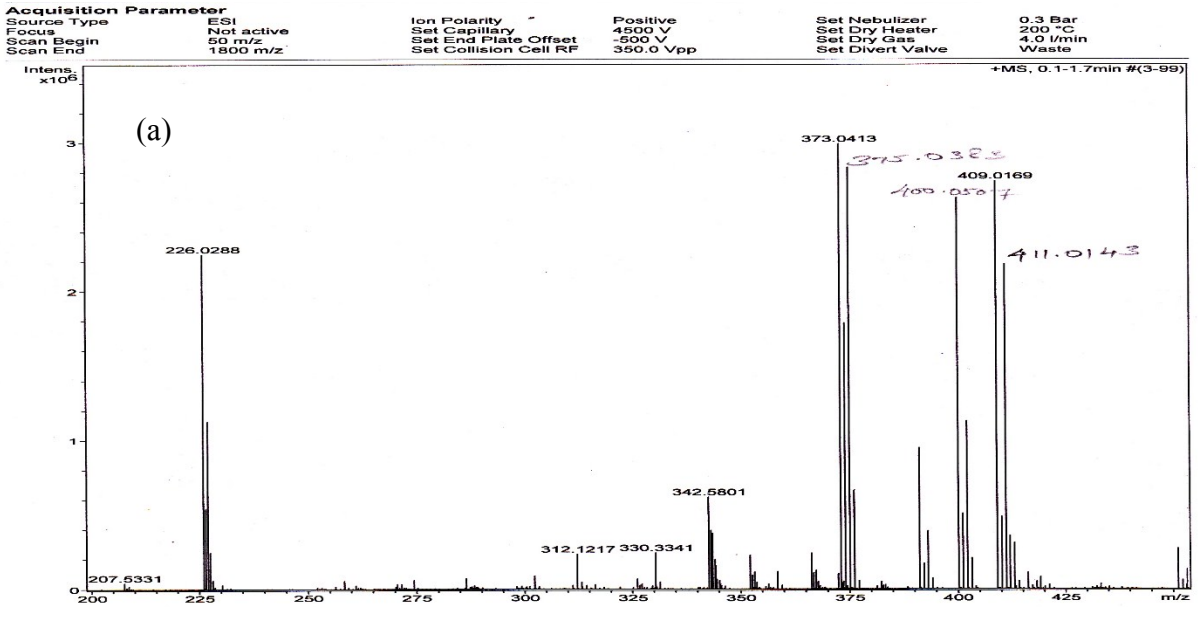
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Set End Plate Offset -500 V
Set Collision Cell RF 350.0 Vpp
Set Nebulizer 0.3 Bar
Set Dry Heater 200 °C
Set Dry Gas 4.0 l/min
Set Divert Valve Waste
+MS, 0.1-1.7min #(3-99)
Intens. x10^6
(a)
373.0413
409.0169
226.0288
411.0143
342.5801
312.1217
330.3341
207.5331
m/z

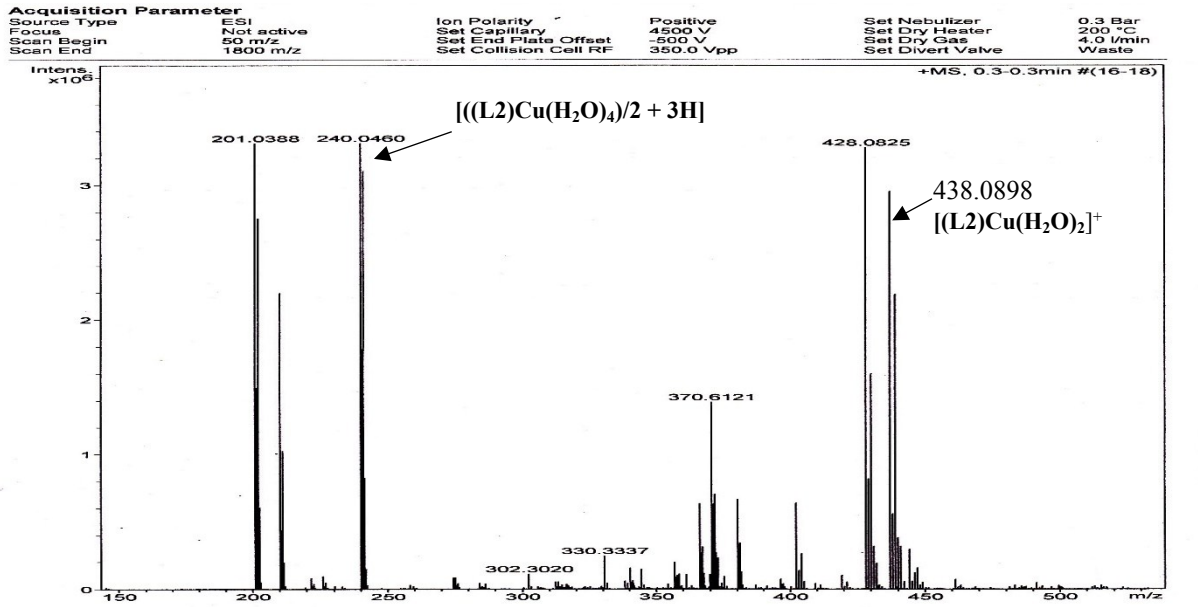

Acquisition Parameter
Source Type ESI
Focus Not active
Scan Begin 50 m/z
Scan End 1800 m/z
Ion Polarity Positive
Set Capillary 4500 V
Set End Plate Offset -500 V
Set Collision Cell RF 350.0 Vpp
Set Nebulizer 0.3 Bar
Set Dry Heater 200 °C
Set Dry Gas 4.0 l/min
Set Divert Valve Waste
+MS, 0.3-0.3min #(16-18)
Intens. x10^6
[((L2)Cu(H2O)4)/2 + 3H]
201.0388
240.0460
428.0825
438.0898
[(L2)Cu(H2O)2]+
370.6121
330.3337
302.3020
m/z

Figure S1. HR-ESI mass spectra of **1** (a) and **2** (b).

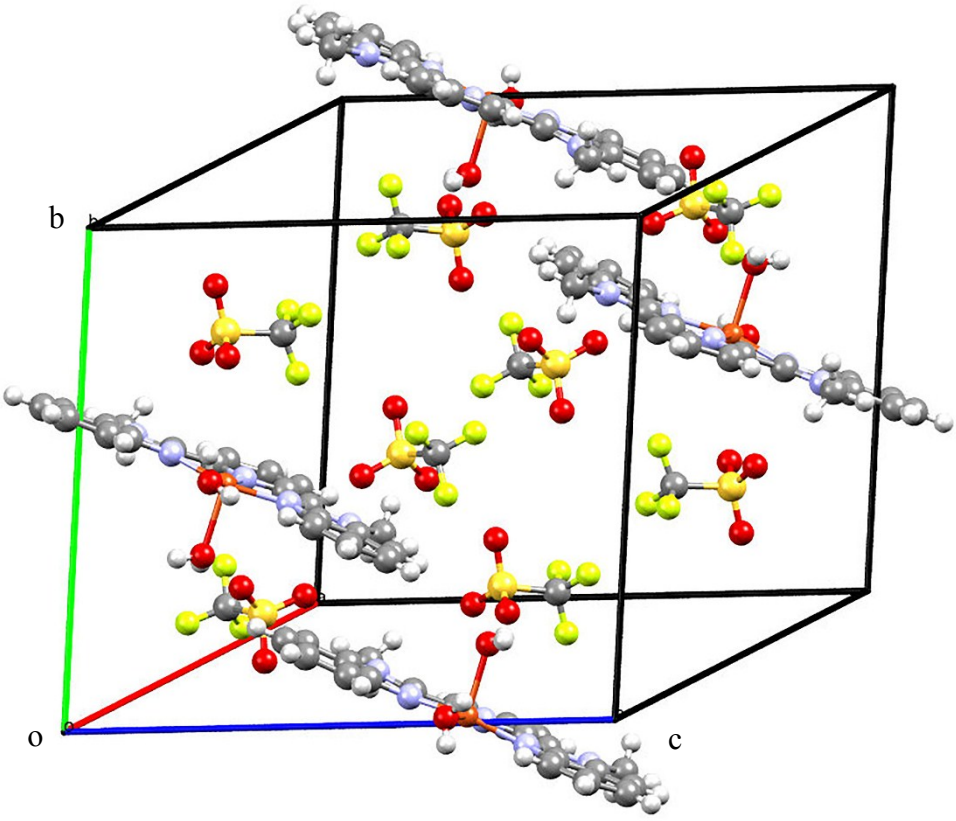


Figure S2. Unit

cell packing diagram of **2** in the triclinic space group P-1 with **Z** = 4.

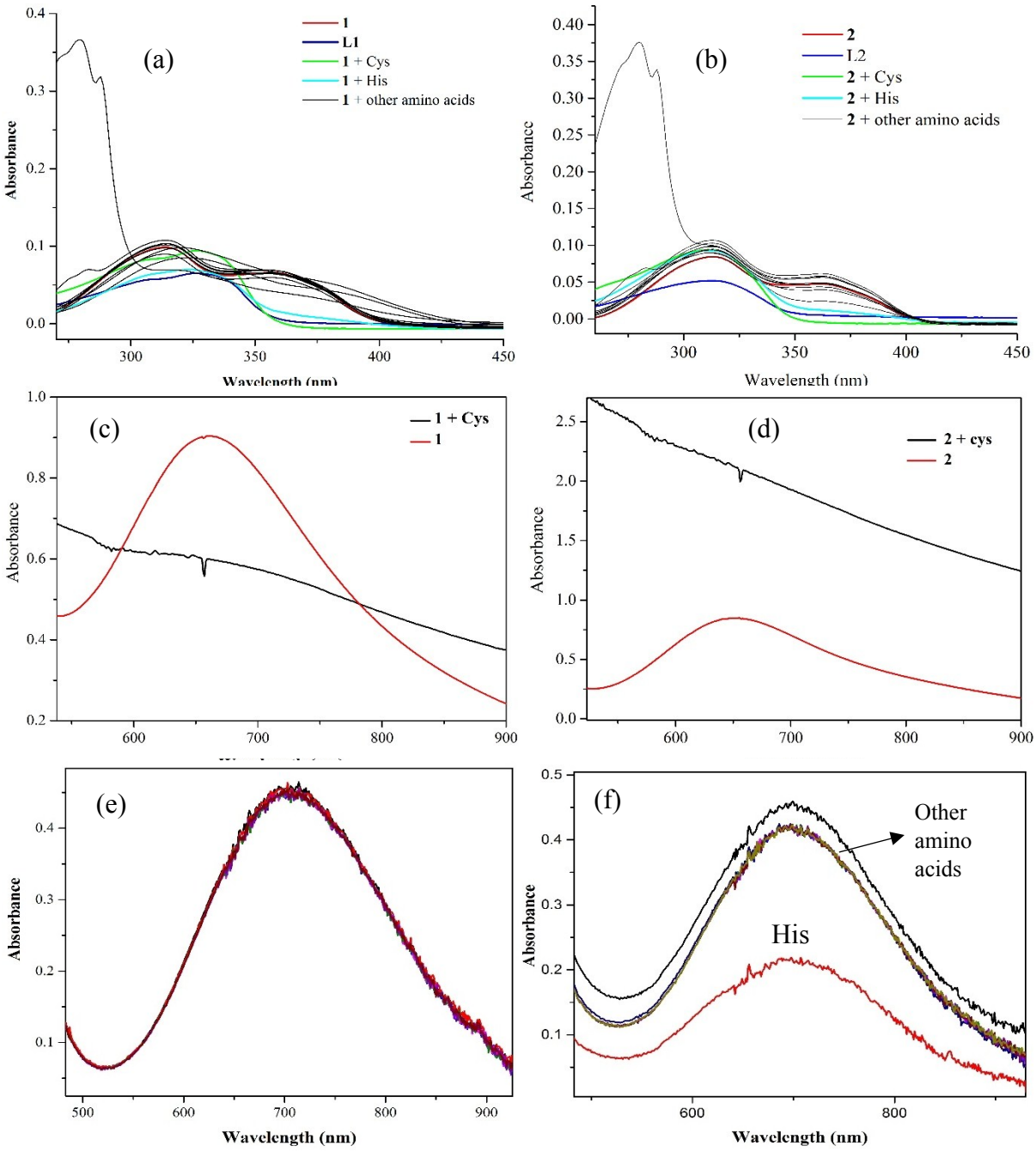
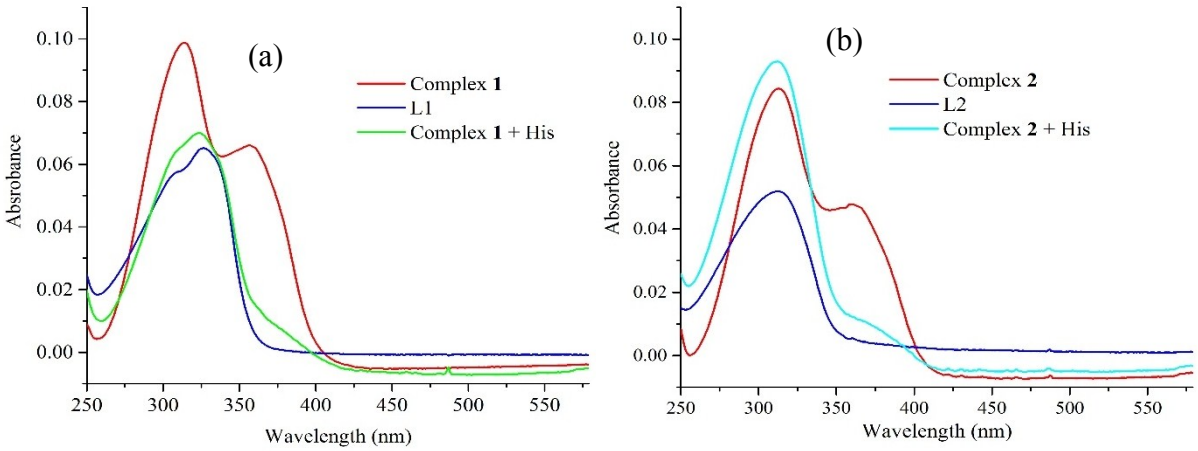


Figure S3. UV-Visible spectra of **1** (5×10^{-6} M) (a) and **2** (5×10^{-6} M) (b) with various amino acids (20 equivalents). The changes in d-d band of **1** (c) and **2** (d) with Cys; **1** (e) and **2** (f) with other natural amino acids (Red line: L-Histidine; Other lines: other amino acids) in HEPES buffer (pH 7.34) at 25°C.


(a)
Complex 1
L1
Complex 1 + His
Absrobance
Wavelength (nm)
0.10
0.08
0.06
0.04
0.02
0.00
250
300
350
400
450
500
550
(b)
Complex 2
L2
Complex 2 + His
Absorbance
Wavelength (nm)

buffer (pH 7.34) at 25°C (5×10^{-6} M).

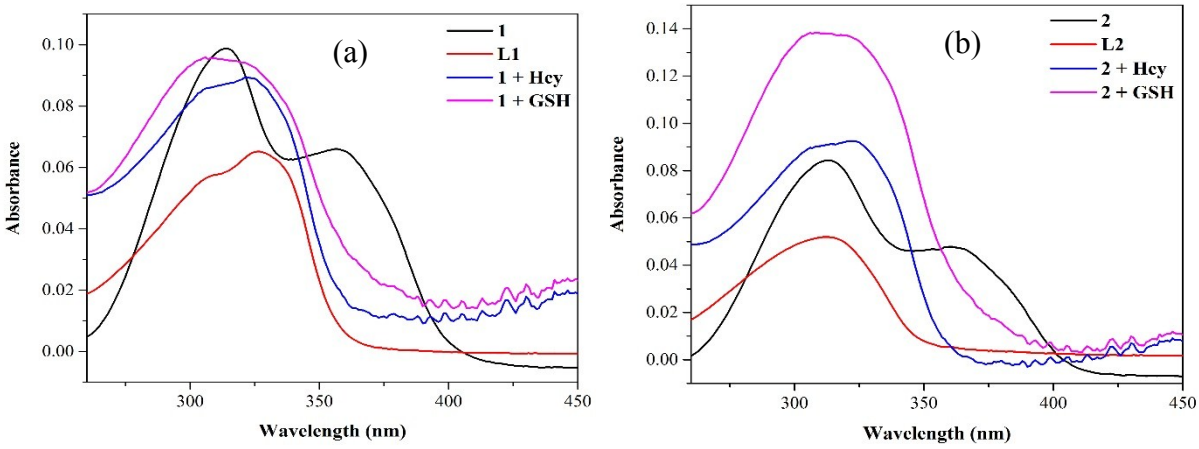


Figure S5. UV-Visible spectra of L1, **1**, **1** + Hcy and **1** + GSH (a) and L1, **2, 2** + Hcy and **2** + GSH (b) in HEPES buffer (pH 7.34) at 25°C. (5×10^{-6} M).

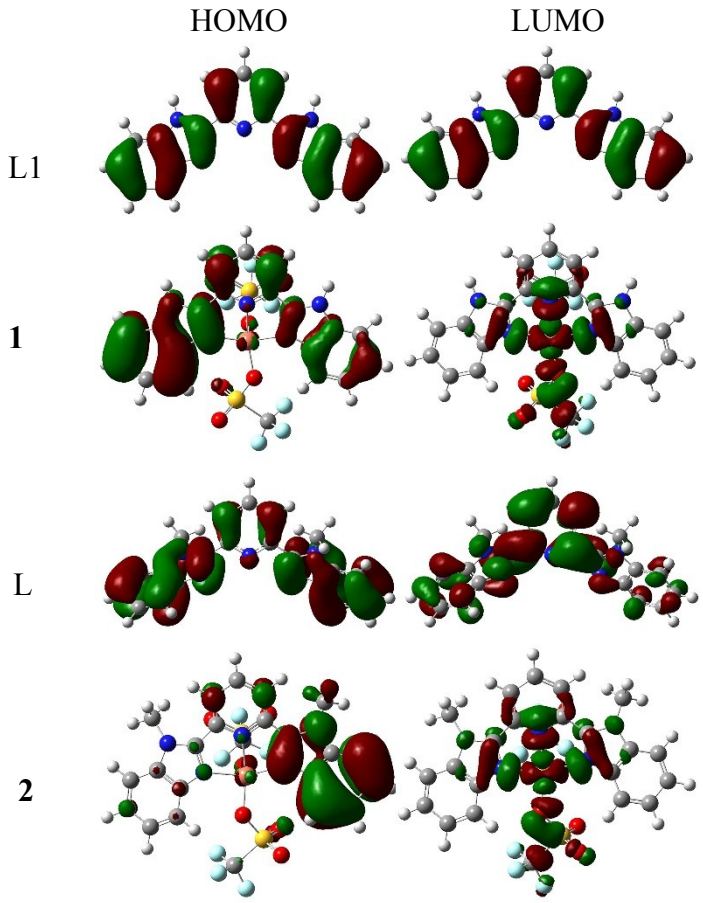
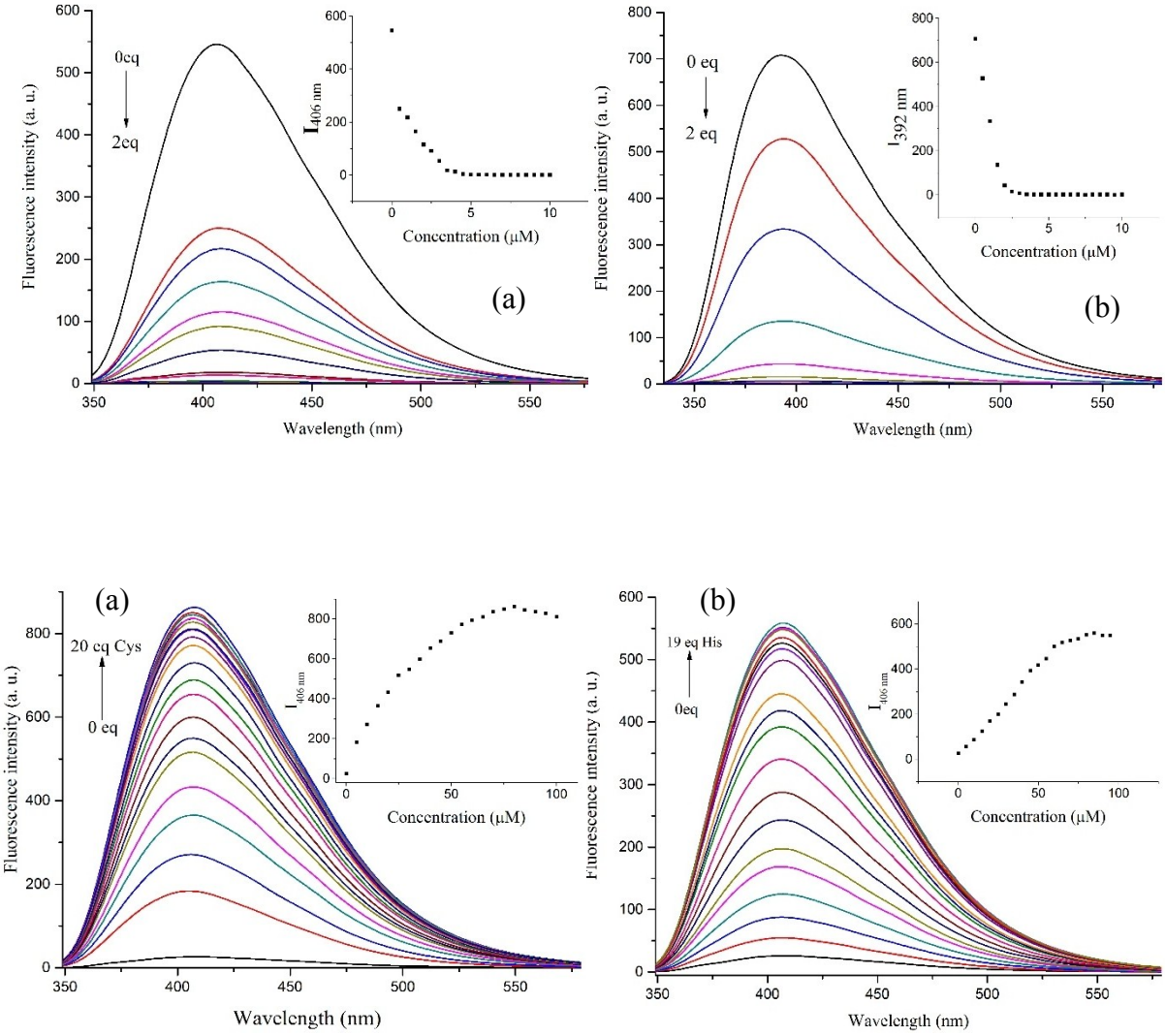


Figure S6. Frontier orbitals of L1, **1**, L2 and **2**; HOMO and LUMO are calculated using B3LYP 6-31G/LANL2DZ level.


0eq
2eq
Fluorescence intensity (a. u.)
Wavelength (nm)
$I_{406\ nm}$
Concentration (μM)
(a)
0 eq
2 eq
$I_{392\ nm}$
(b)
(a)
20 eq Cys
0 eq
(b)
19 eq His
0eq

[HEPES buffer, pH 7.34 ; λ_{exc}= 327 and 313 nm, slits: 5nm/5nm, time interval = 5 min].

Figure S8. Fluorescence intensity changes of **1** on adding Cys (a) and His (b); [HEPES buffer, pH 7.34 ; λ_{exc}= 327 nm, slits: 5nm/5nm, time interval = 5 min]

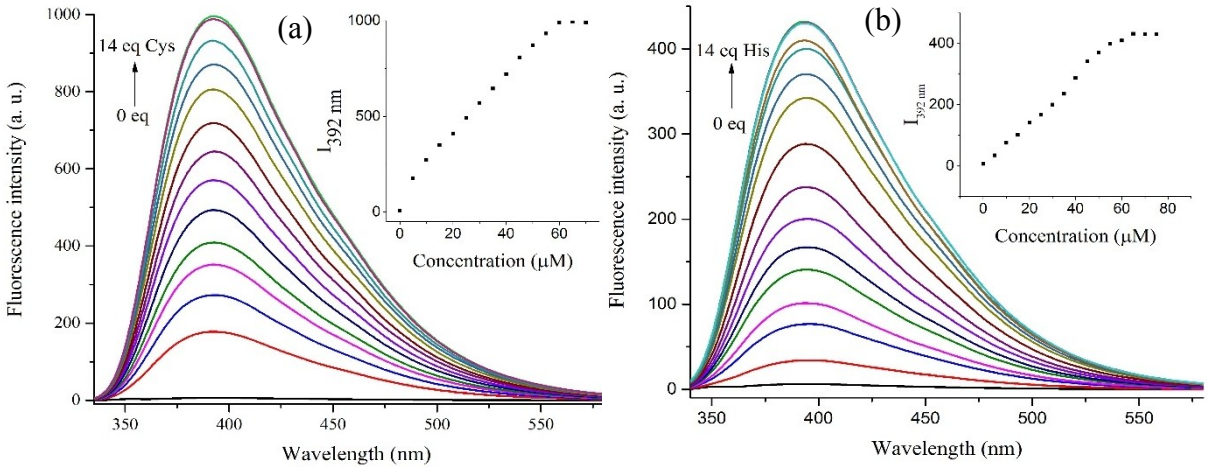
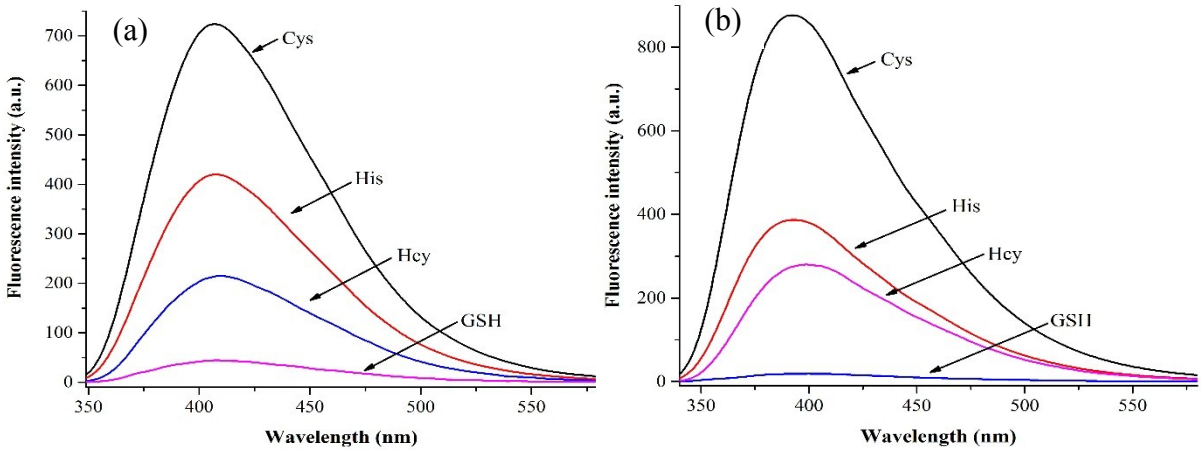


Figure S9. Fluorescence intensity changes of **2** on adding Cys (a) and His (b); [HEPES buffer, pH 7.34 ; λ_{exc}= 313 nm, slits: 5nm/5nm, time interval = 5 min]

Figure S10. Fluorescence intensity



comparison of **1**(a) and **2**(b) on adding Cys, His, Hcy and GSH in HEPES buffer, pH 7.34.

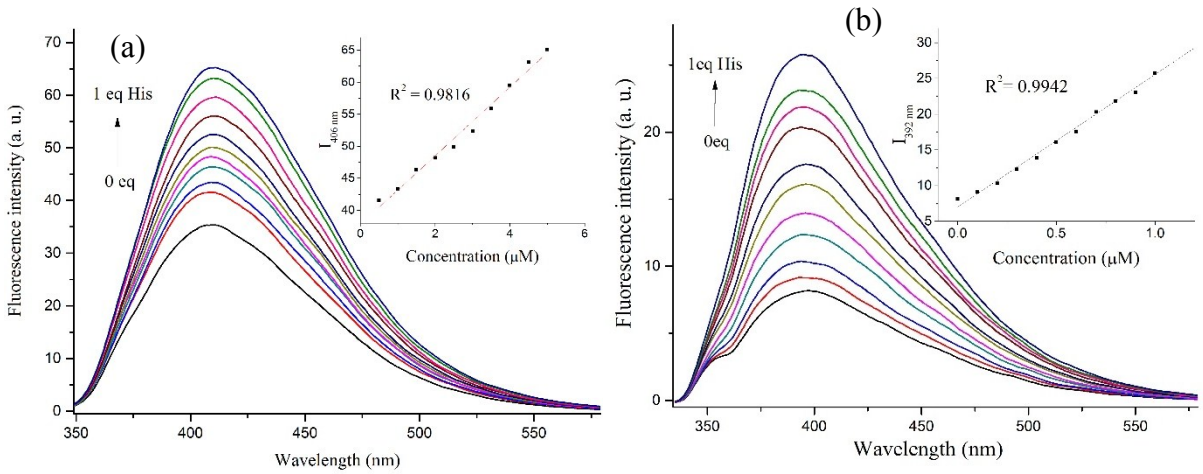
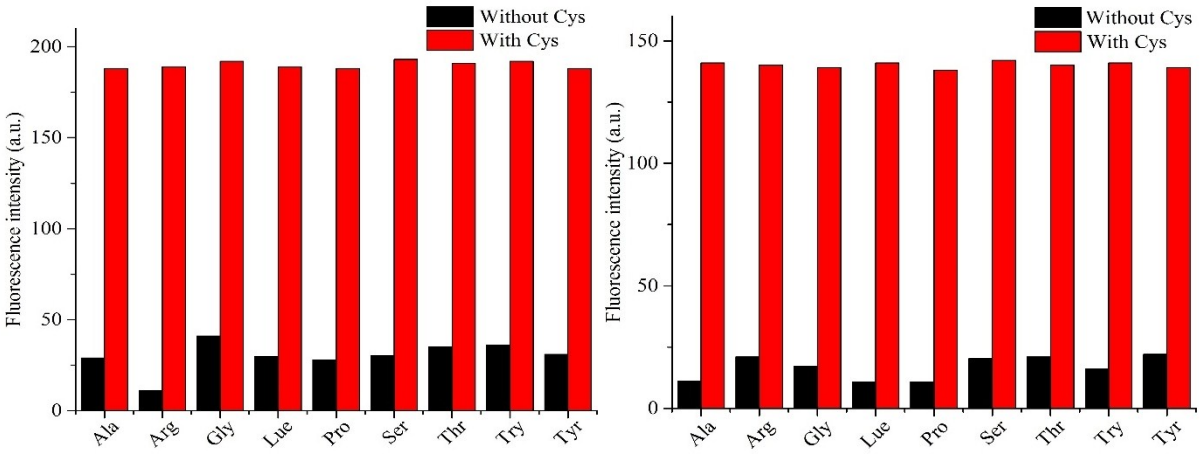


Figure S11. Fluorescence intensity changes of **1** (a) and **2** (b) upon addition of one equivalent of His (time interval = 5 min).


Without Cys
With Cys
Fluorescence intensity (a.u.)
0
50
100
150
200
Ala
Arg
Gly
Lue
Pro
Ser
Thr
Try
Tyr
Without Cys
With Cys
Fluorescence intensity (a.u.)
0
50
100
150
Ala
Arg
Gly
Lue
Pro
Ser
Thr
Try
Tyr

intensity changes **1** (a) and **2** (b) with and without of Cys.

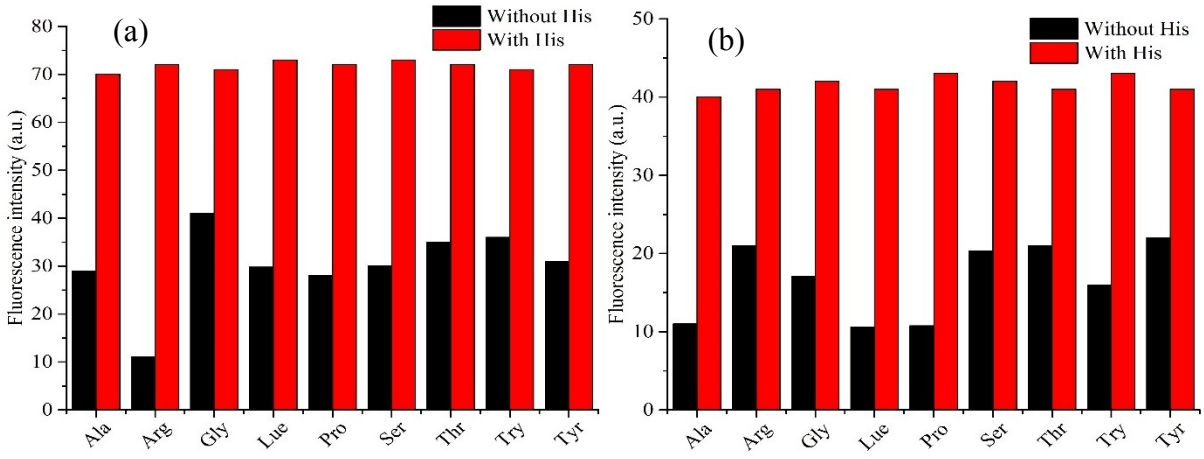
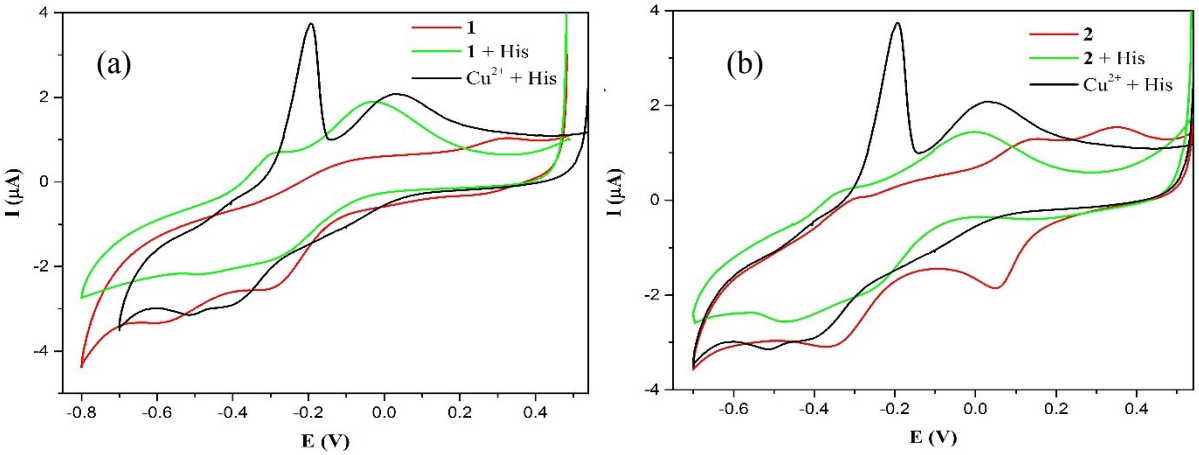


Figure S13. Bar diagram of a competitive binding experiment in **1** (a) and **2** (b) Fluorescence intensity changes **1** (a) and **2** (b) with and without of His.

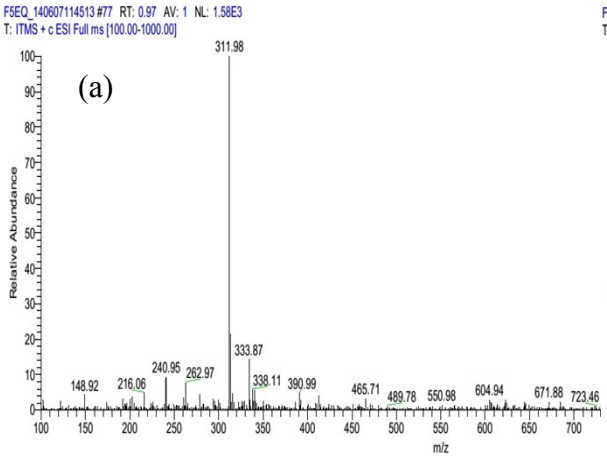
Table S1. Fluorescence quantum yield of L1 (5×10^{-6} M) and **1** + 20eq Cys (5×10^{-6} M) Fluorescence reference material: Quinine sulfate (5×10^{-6} M).

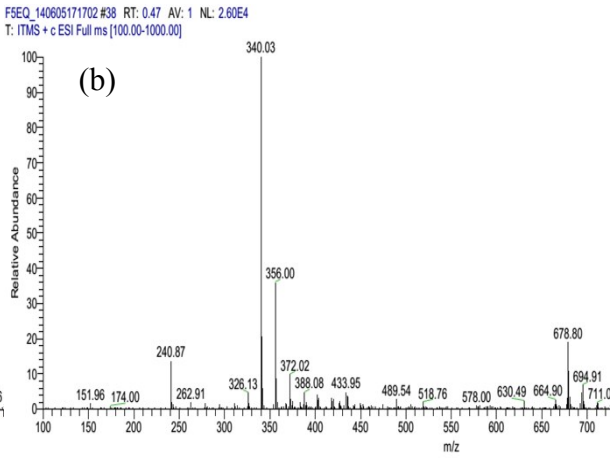
$$\mathbf{Y_u = Y_s \times (F_u/F_s) \times (A_s/A_u)}$$

	λ_{exc} (slits: 5/5 nm)	**F (Integral fluorescence intensity)**	**A (Absorbance)**	**Integration range**	**Y (Fluorescence quantum yield) %**
Quinine sulphate	327	49818.4013	0.024281	358-572	-
	313	56700.5571	0.02312	348-572	-
L1	327	9171.2794	0.054491	358-572	3.83
1 + Cys	327	16919.8431	0.026401	358-572	14.7
1 + His	327	4541.3758	0.019567	358-572	5
L2	313	17292.4863	0.040826	348-572	11.3
2 + Cys	313	27260.3246	0.031227	348-572	23
2 + His	313	10612.3526	0.029402	348-572	11.3


(a)
1
1 + His
Cu2+ + His
I (μA)
E (V)
(b)
2
2 + His
Cu2+ + His
I (μA)
E (V)

(pH 7.34) at 25°C [reference: saturated Ag/Ag^{+}; supporting electrolyte: 0.1M NaCl solution; scan rate: = 50 mV s^{-1}] (b).


F5EQ_140607114513 #77 RT: 0.97 AV: 1 NL: 1.58E3
T: ITMS + c ESI Full ms [100.00-1000.00]
(a)
311.98
333.87
240.95
262.97
148.92
216.06
338.11
390.99
465.71
489.78
550.98
604.94
671.88
723.46
Relative Abundance
m/z


F5EQ_140605171702 #38 RT: 0.47 AV: 1 NL: 2.60E4
T: ITMS + c ESI Full ms [100.00-1000.00]
(b)
340.03
356.00
240.87
372.02
678.80
694.91
151.96
174.00
262.91
326.13
388.08
433.95
489.54
518.76
578.00
630.49
664.90
Relative Abundance
m/z

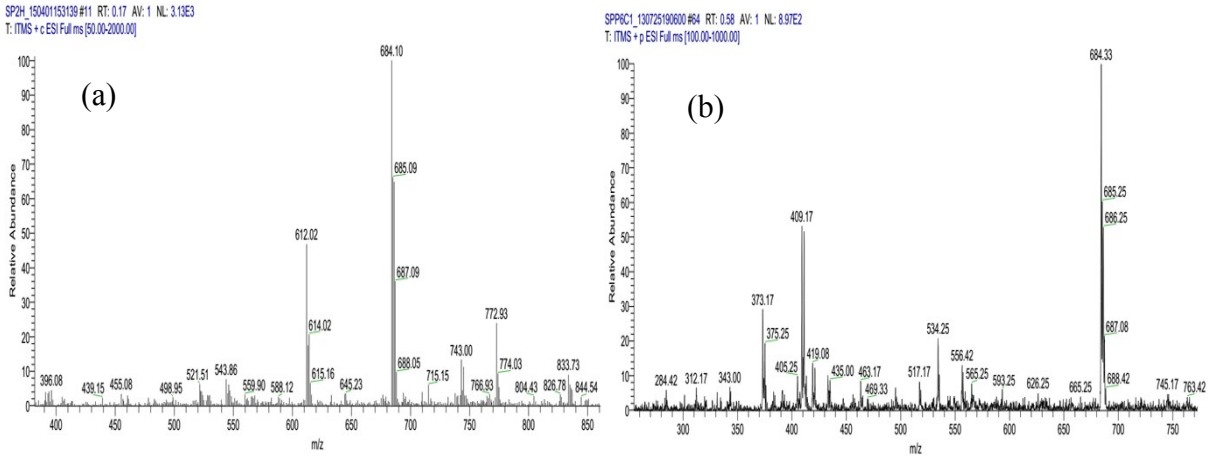
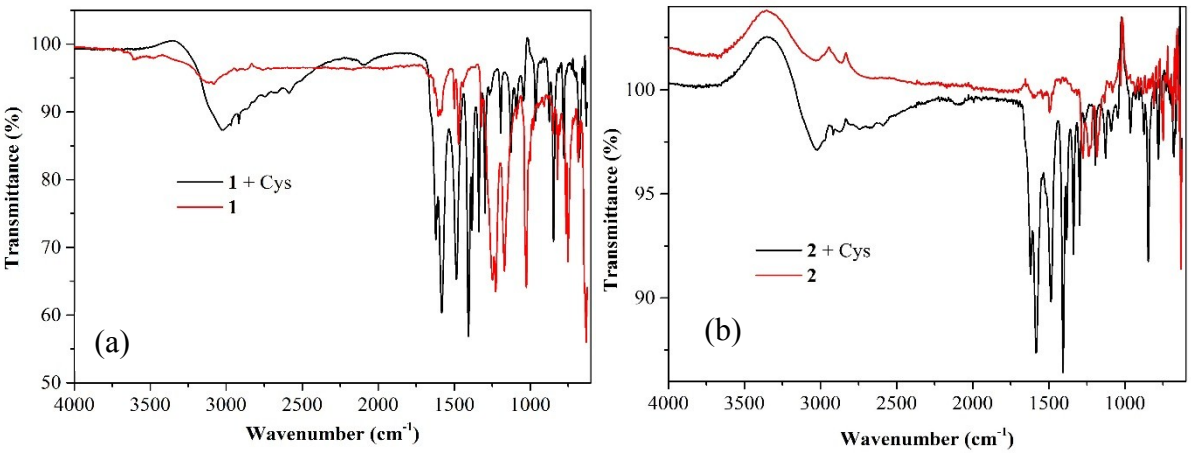

SP2H_1504015313 9 #11 RT: 0.17 AV: 1 NL: 3.13E3
T: ITMS + c ESI Full ms [50.00-2000.00]
(a)
Relative Abundance
m/z
684.10
685.09
687.09
612.02
614.02
772.93
743.00
774.03
833.73
396.08
439.15
455.08
498.95
521.51
543.86
559.90
588.12
615.16
645.23
688.05
715.15
766.93
804.43
826.78
844.54
SPP6C1_1307251906 00 #64 RT: 0.58 AV: 1 NL: 8.97E2
T: ITMS + p ESI Full ms [100.00-1000.00]
(b)
Relative Abundance
m/z
684.33
685.25
686.25
409.17
373.17
375.25
534.25
419.08
556.42
405.25
435.00
463.17
517.17
565.25
593.25
626.25
665.25
687.08
688.42
745.17
763.42
284.42
312.17
343.00
469.33

Figure S16. ESI-Mass spectra of **1** + His (a) and **2** + His (b).


Transmittance (%)
Wavenumber (cm-1)
1 + Cys
1
(a)
2 + Cys
2
(b)

+ Cys (black) (b).