Electronic Supplementary Material (ESI) for Analyst.

Supplementary Information (SI)

For

A new chromogenic and fluorescence chemosensor based on naphthol–bisthiazolopyridine hybrid: Fast response and selective detection of multiple targets, silver, cyanide, sulfide, hydrogen sulfide ions and gaseous H_2S

Maryam Kargar,[a] Hossein Reza Darabi,[a,*] Ali Sharifi,[a] Abdoljalil Mostashari[b]

Nano & Organic Synthesis Lab., Chemistry & Chemical Engineering Research Center of Iran, Pajoohesh Blvd., km 17, Karaj Hwy, Tehran 14968-13151, Iran. Tel.: +98 21 44787720; Fax: +98 21 44787762

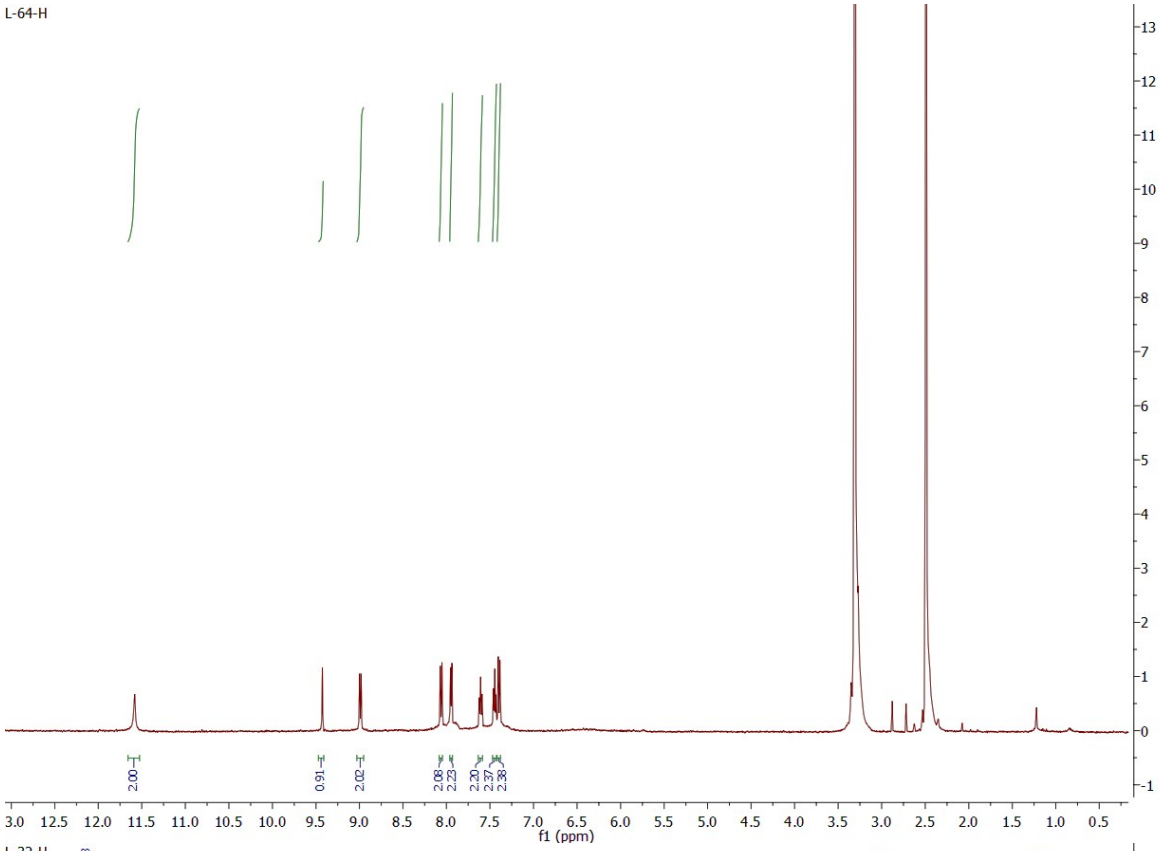
darabi@ccerci.ac.ir; r_darabi@yahoo.com

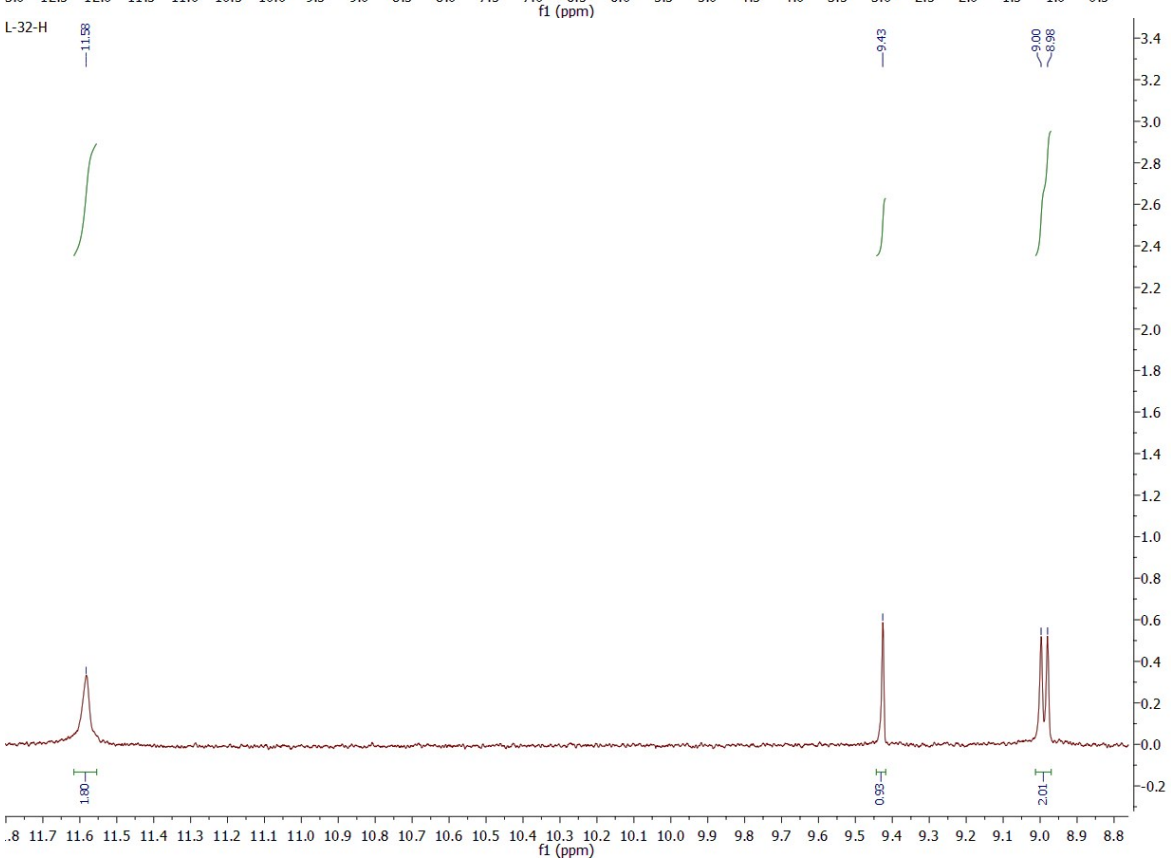
Table of contents

Synthesis and characterization of 1

We have recently introduced a new route to build bisthiazolopyridine skeleton in one-pot Willgerodt-Kindler reaction, using easily accessible starting materials [39]. In this study, we obtained product **1** from the reaction of 2,6-diaminopyridine with 2-hydroxy-1-naphtaldehyde and elemental sulfur at 110 °C in 15% yield. The product **1** was characterized by ^{1}H NMR, ^{13}C NMR, IR, and ESI-MS analysis (Fig. S1-S4). The high purity of **1** was confirmed using HPLC (Fig. S5).

The ^{1}H and ^{13}C NMR spectra of **1** are in accord with the symmetry of this molecule. The ^{1}H NMR spectra of compound **1** showed two singlets at 11.58 and 9.43 ppm related to hydrogen bonded OH groups and pyridine, respectively. The naphthyl protons appear as four doublets at 8.99, 8.06, 7.95 and 7.40 ppm, as well as two triplets at 7.61 and 7.45 ppm (Fig. S1). The number of observed carbons by ^{13}C NMR spectra of **1** is in agreement with the C_2-symmetric structure of **1** (Fig. S2). The mass spectrum of **1** showed a peak for the molecular ion at 477 m/z (Fig. S3).


L-64-H
2.00
0.91
2.02
2.08
2.23
2.20
2.37
2.38
f1 (ppm)


L-32-H
11.58
9.43
9.00
8.98
1.80
0.93
2.01
f1 (ppm)

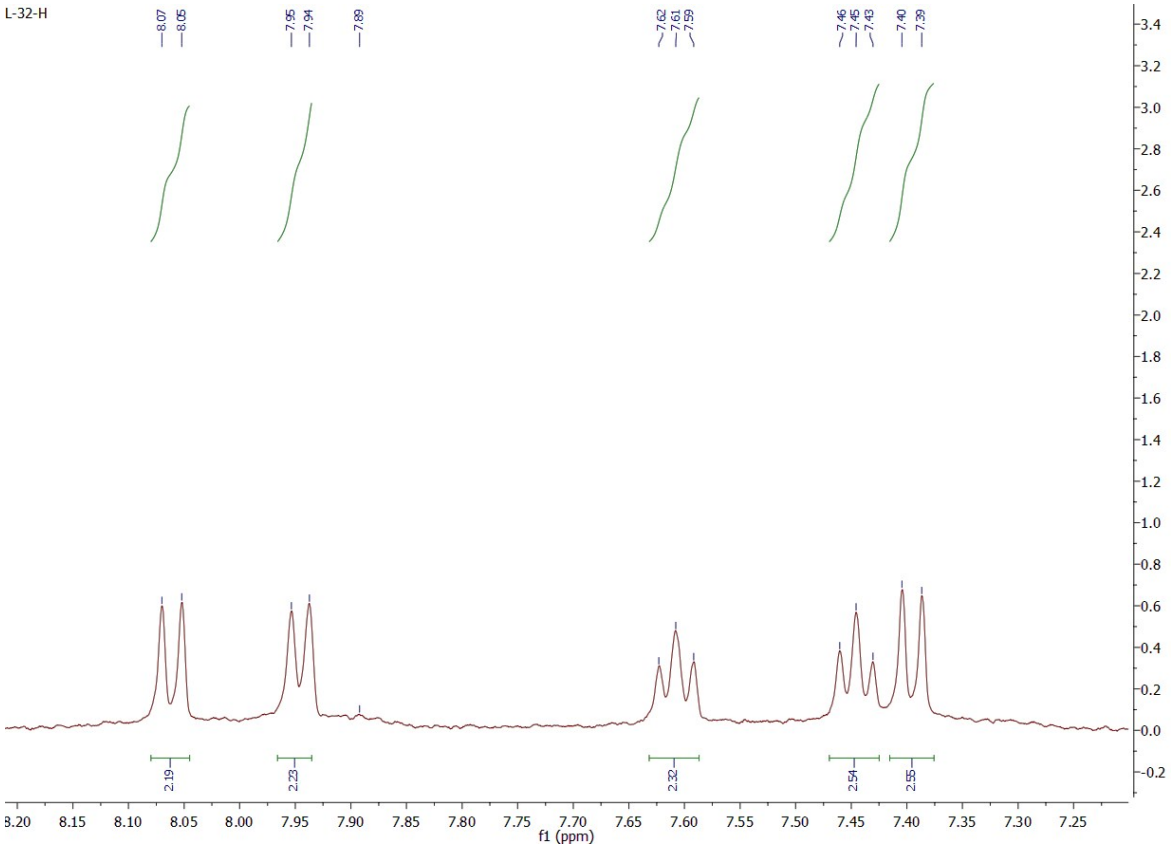


Figure S1. ^{1}H NMR of compound **1** and its expantion spectrum (DMSO-d_6, 500 MHz).

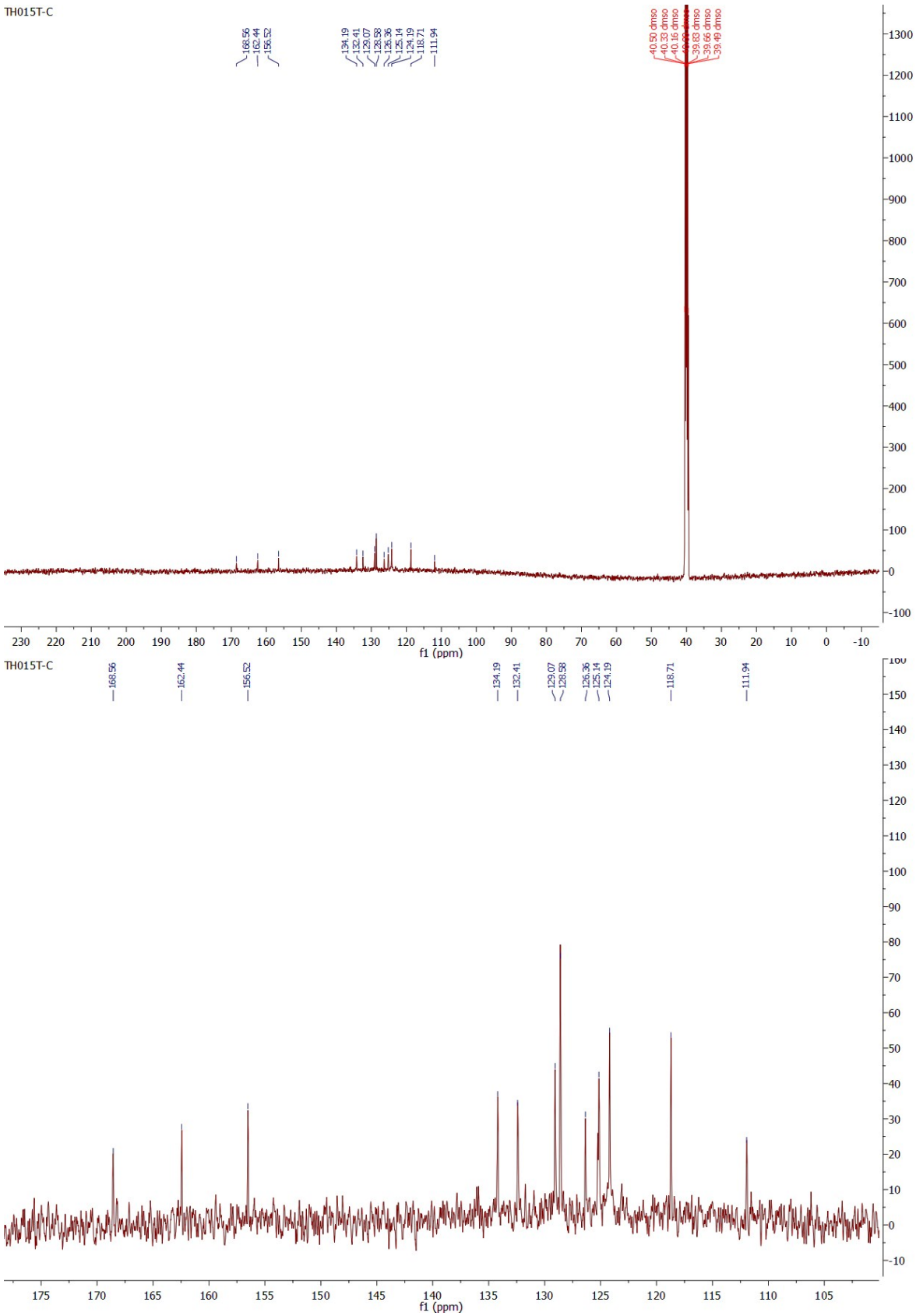


Figure S2. ^{13}C NMR spectrum of compound **1** (DMSO-d_6, 125 MHz).

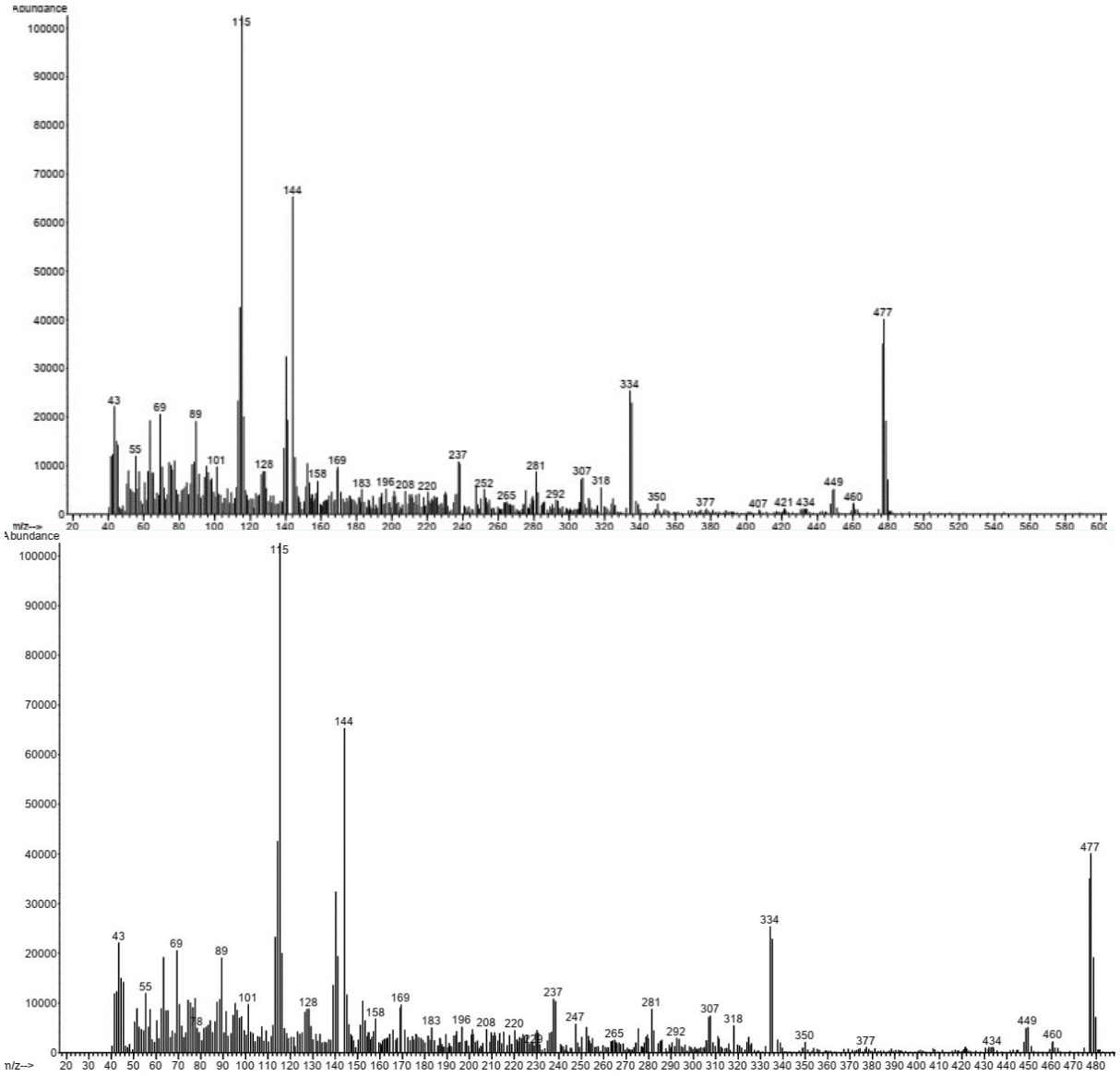


Figure S3. Mass spectrum of compound **1**.

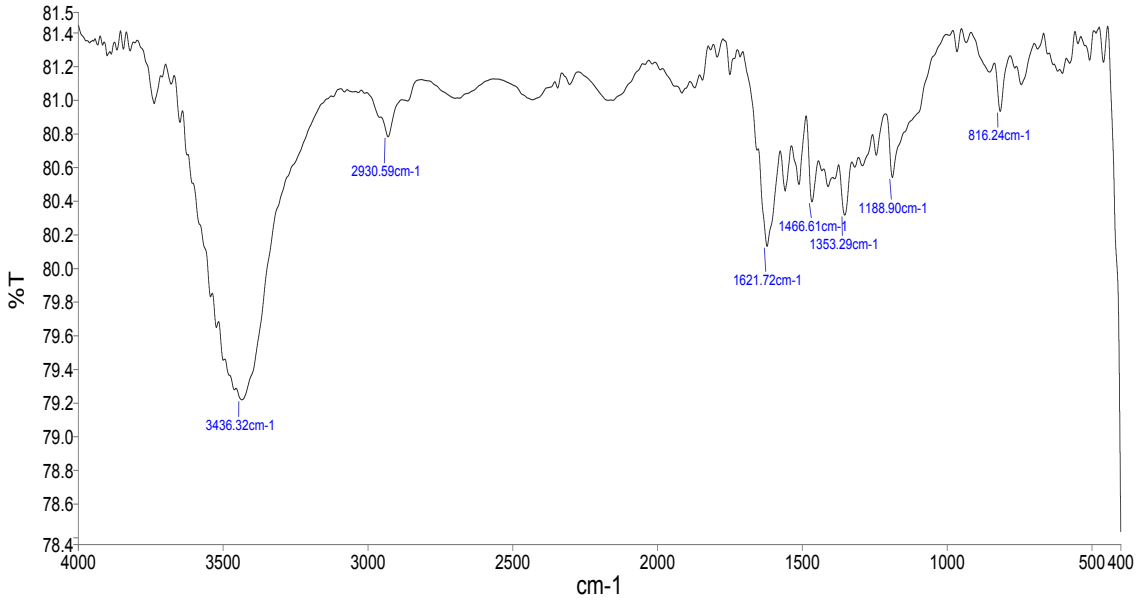
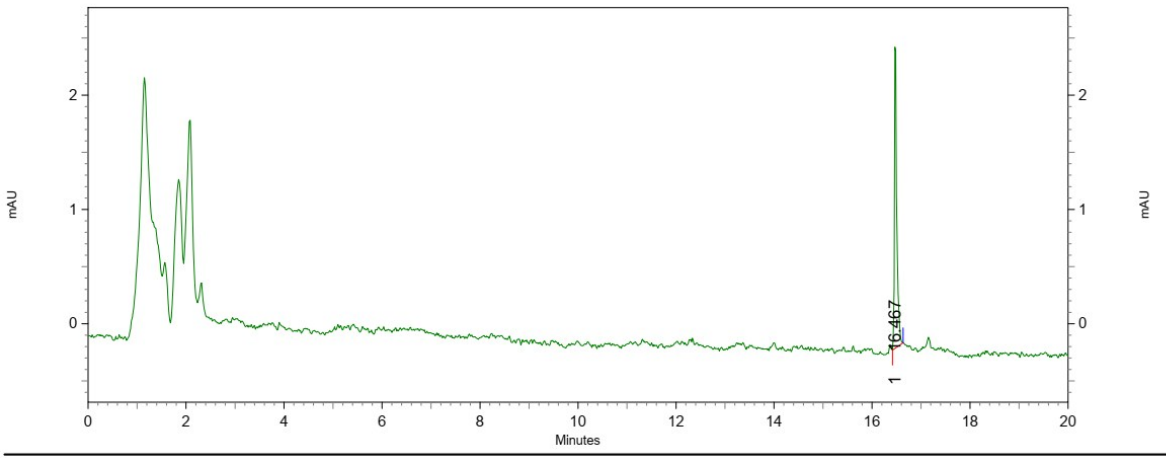


Figure S4. IR spectra of compound **1.**

```
 Sample ID:          kh.kargar-971102-sample 1-1
 Method File:        C:\EZChrom
Elite\Enterprise\Projects\Default\Method\A.Ahdeno-971115.met
 Run Time:           1/22/2019 1:47:50 PM
 User:               R.Hajipoor
 Method Create Date: 2/4/2019 11:58:03 AM
 Data File:          C:\EZChrom
Elite\Enterprise\Projects\Default\Data\Kh.kargar-971107\kh.kargar-971102-sample
1-1.dat
 Instrument :        HPLC (KNAUER - 101896)
 Software:           ChromGate Client/Server - Version 3.1.7
```

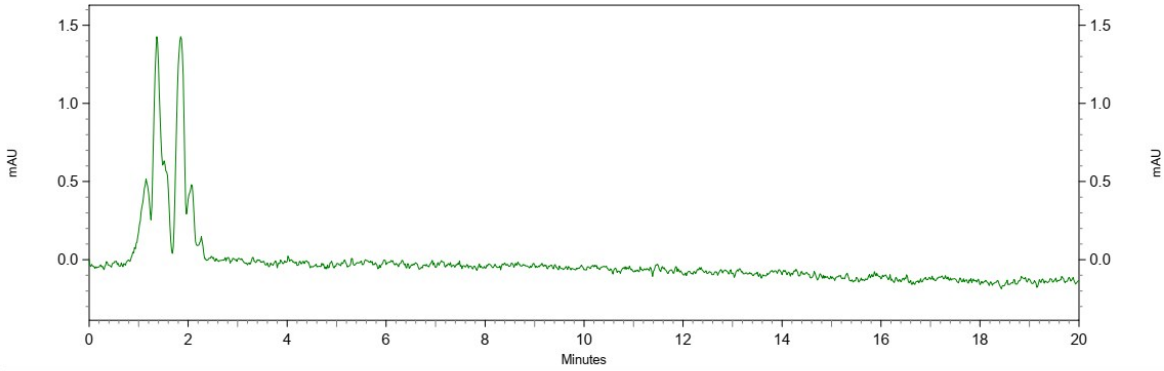


S 2500 Results

Pk #	Retention Time	Area	Area Percent	Height
1	16.467	9015	100.000	2637

Figure S5-a. HPLC of compound 1

```
 Sample ID:          kh.kargar-971102-blanck
 Method File:        C:\EZChrom
Elite\Enterprise\Projects\Default\Method\A.Ahdeno-971115.met
 Run Time:           1/22/2019 2:13:36 PM
 User:               R.Hajipoor
 Method Create Date: 2/4/2019 11:58:03 AM
 Data File:          C:\EZChrom
Elite\Enterprise\Projects\Default\Data\Kh.kargar-971107\kh.kargar-971102-blanck.dat
 Instrument :        HPLC (KNAUER - 101896)
 Software:           ChromGate Client/Server - Version 3.1.7
```



S 2500 Results

Pk #	Retention Time	Area	Area Percent	Height

Figure S5-b. Blank of HPLC of compound 1

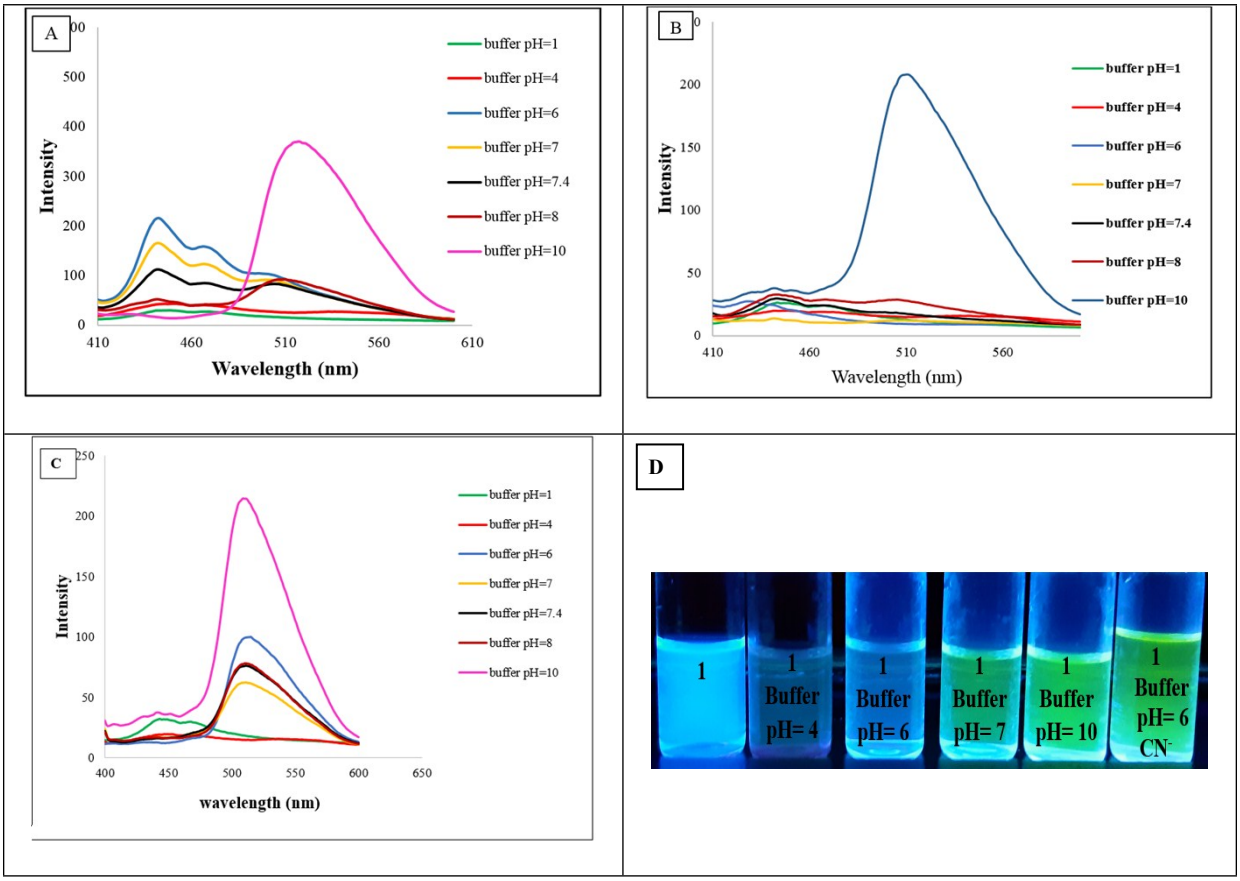


Figure S6. Fluoresence spectra of **1** (A) and **1•Ag**$^{+}$ (B) and addition of S^{2-} on **1•Ag**$^{+}$ (C) under various buffer solutions. Color images of pH-dependent response of **1** to CN^{-} from left: **1**, **1** in buffer pH 6, **1** in buffer pH 7, **1**+ CN^{-} in buffer pH 6 (D).

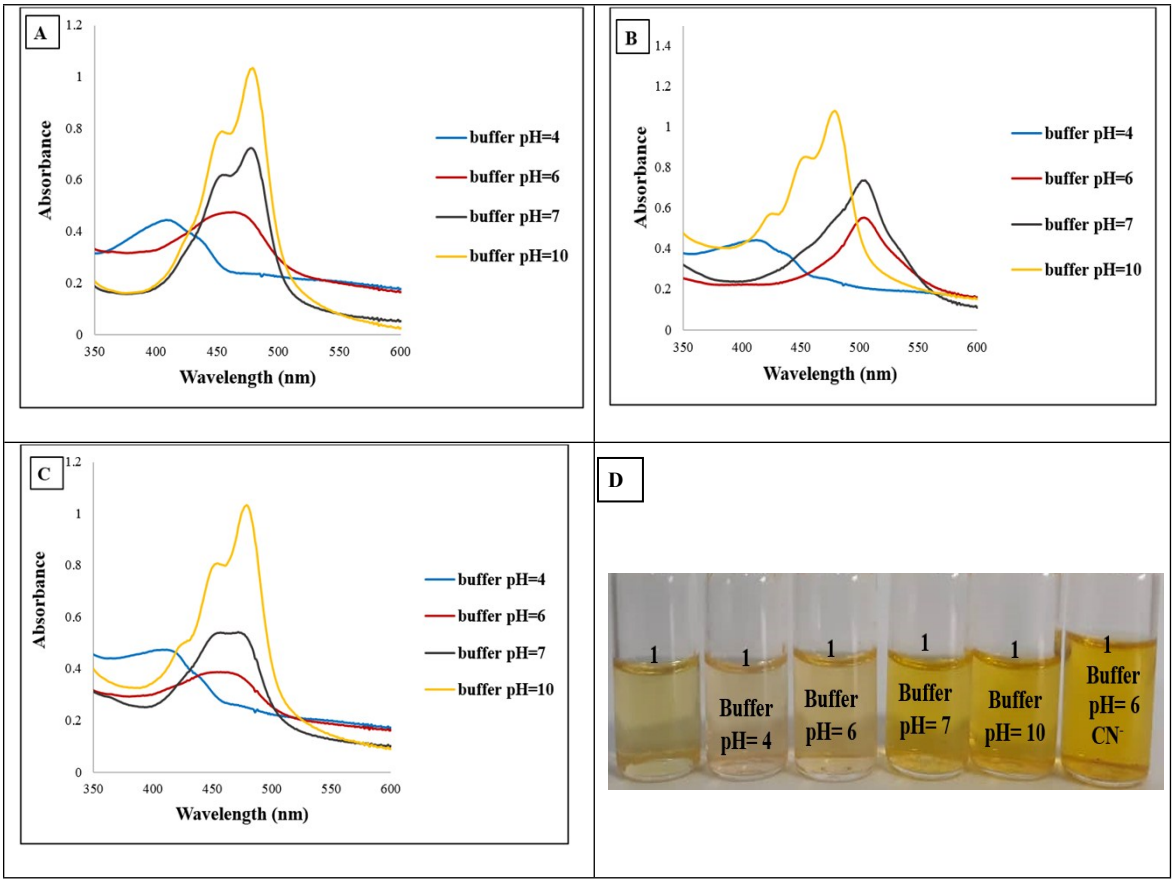


Figure S7. Absorbance spectra of **1** (A), **1•Ag**$^{+}$ (B), The effects of S^{2-} on **1•Ag**$^{+}$ under various buffer solutions (C), and color images of pH-dependent response of **1** to CN^{-} from left: **1**, **1** in buffer pH 6, **1** in buffer pH 7, **1**+ CN^{-} in buffer pH 6 (D).

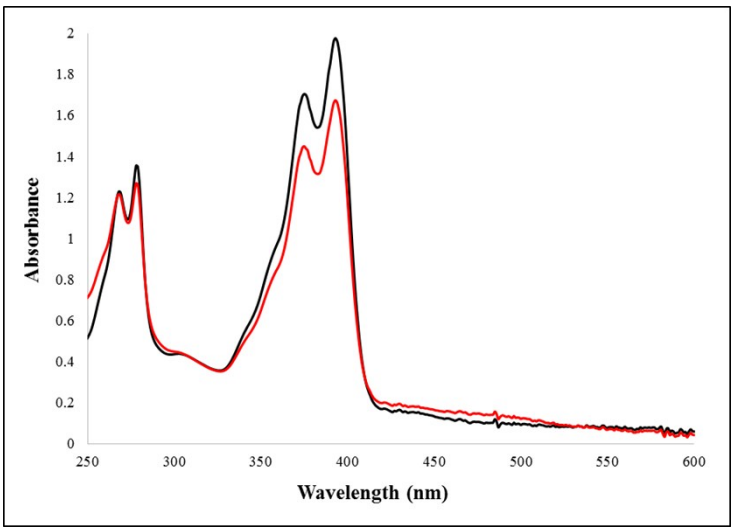


Figure S8. Absorbance of **2** with 1 equivalent of **Ag**$^{+}$.

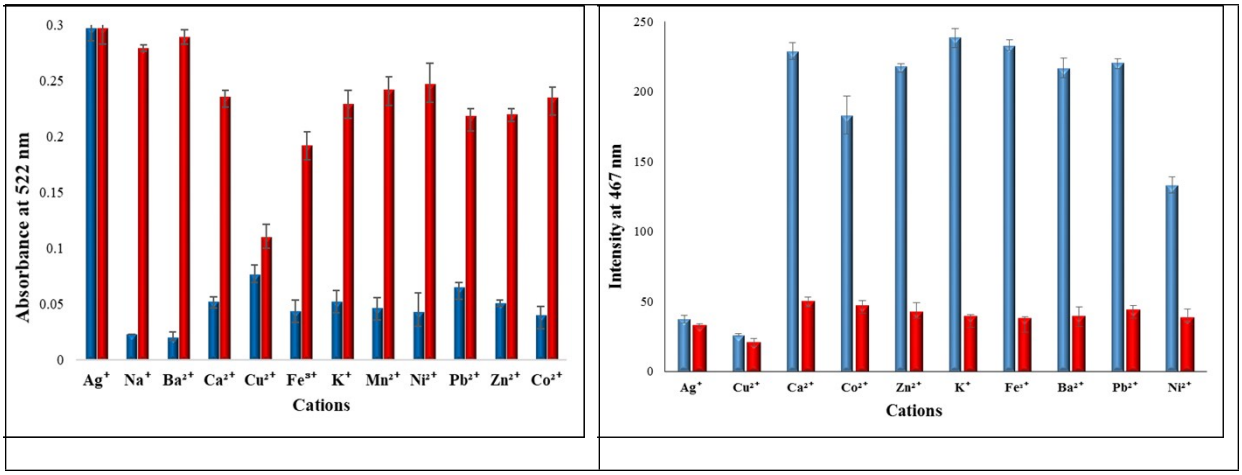


Fig. S9. Uv-vis (Left) and fluorescence (Right) response of **1** to various cations (1 equivalent of **1**) in MeOH/H_2O (8:2, v/v). The intensity of fluorescence emission of **1** (0.05 μmol) upon the addition of various metal ions (0.05 μmol). Blue bars represent the fluorescence intensity of **1** in the presence of different metal ions. Red bars represent the fluorescence intensity of **1** in the presence of Ag^+ and other metal ions.

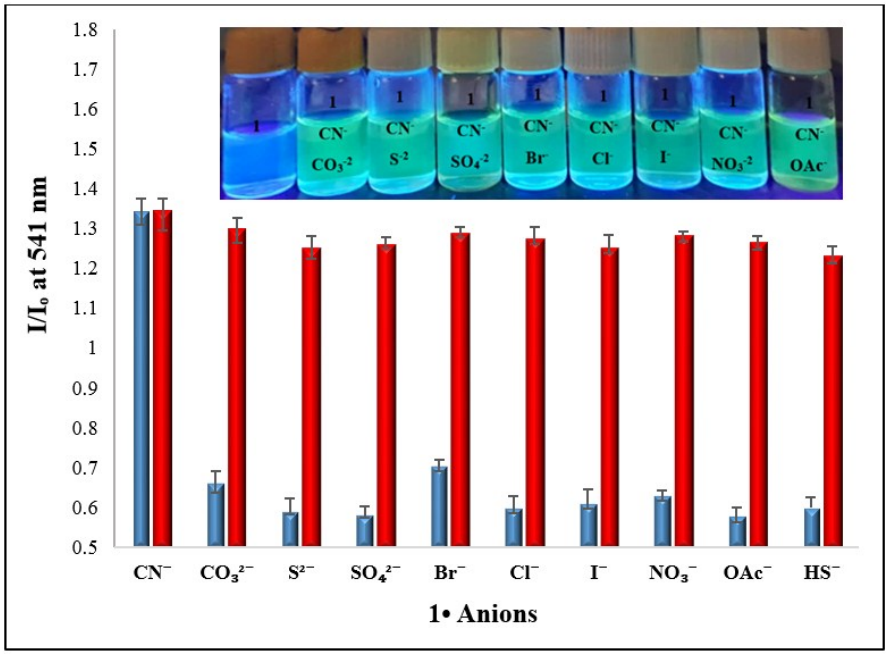


Figure S10. Fluorescence response of **1** to various anions in MeOH:H_2O (8:2). Inside image: Competitive selectivity of **1** toward CN^- in the presence of similar amounts of other anions under 366 nm UV light.

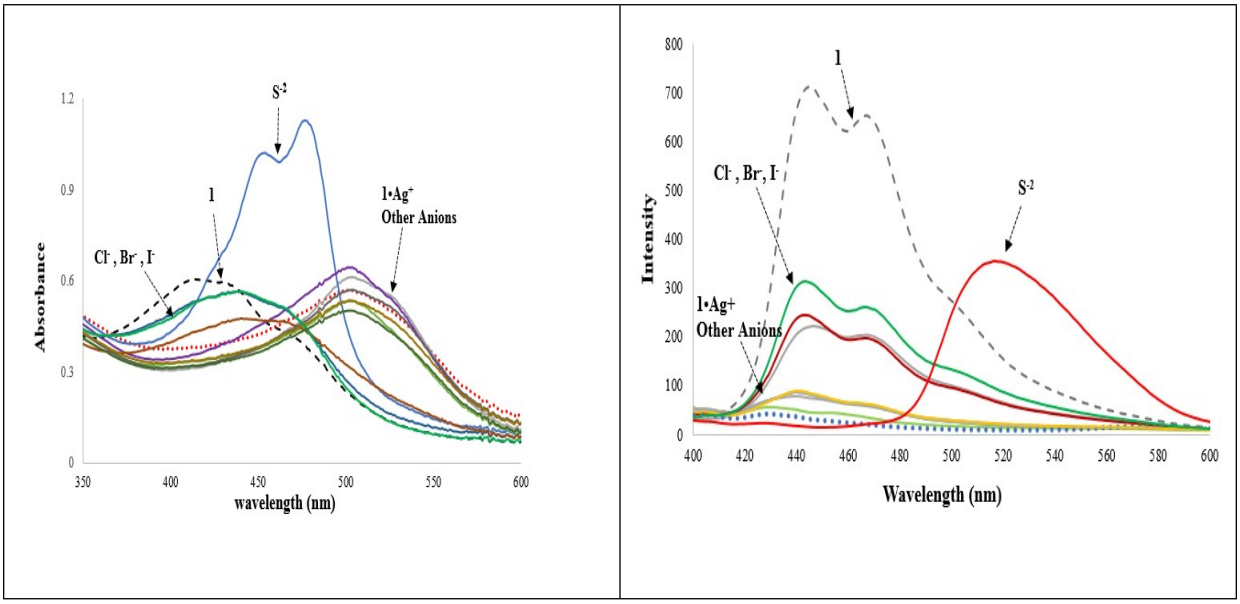


Fig. S11. Uv-vis (above) and Fluorescence (below) of sensor **1**•Ag^{+} with addition of 10 equiv. of anions.

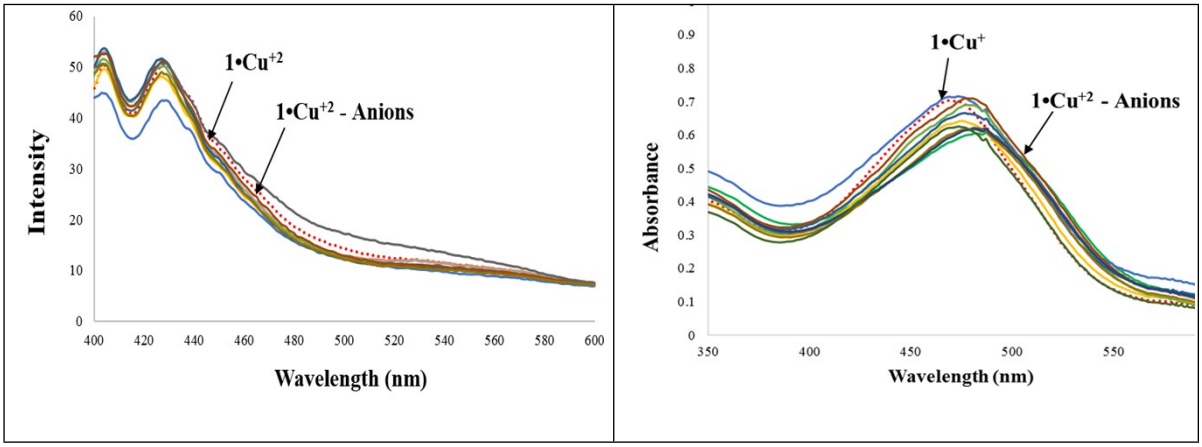


Figure S12. Fluorescence (left) and Uv-vis (right) of sensor **1•Cu^{+2}** with addition of 10 equiv. of various anions.

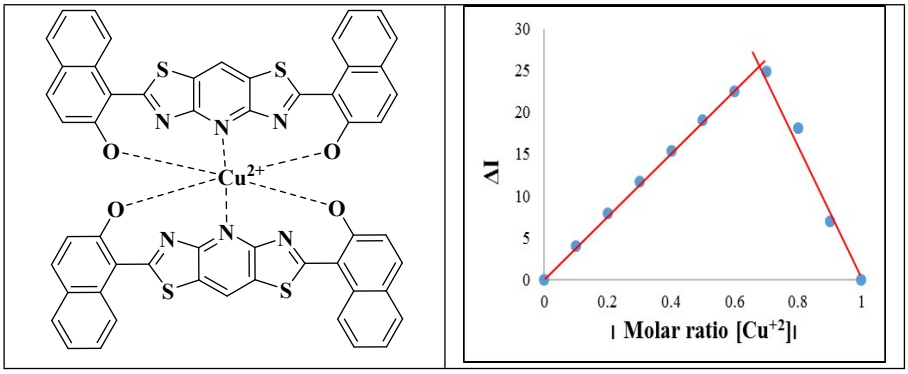


Figure S13. Proposed structure of **1•Cu^{+2}** (left) and Job plot for the binding of **1** and Cu^{+2}(right).

Table S1. Absorbance titration of **1** with various concentration of Ag^{+}.

V_0	V_t	C_0	C_t	eq	A_{505}	A/A_0	$A-A_0$
500	0	0.00005	0	0	0.163552284	1	0
500	10	4.9E-05	9.8E-06	0.2	0.177063942	1.082614	0.013512
500	30	4.72E-05	2.83E-05	0.6	0.254268646	1.554663	0.090716
500	40	4.63E-05	3.7E-05	0.8	0.306402683	1.873423	0.14285
500	50	4.55E-05	4.55E-05	1	0.354674129	2.168567	0.191122
500	60	4.46E-05	5.36E-05	1.2	0.393363953	2.405127	0.229812
500	70	4.39E-05	6.14E-05	1.4	0.433193207	2.648653	0.269641
500	80	4.31E-05	6.9E-05	1.6	0.470069408	2.874123	0.306517
500	90	4.24E-05	7.63E-05	1.8	0.480222225	2.9362	0.31667
500	100	4.17E-05	8.33E-05	2	0.48401022	2.959361	0.320458

Table S2. Fluoresence titration of **1** with various concentration of **Ag^{+}**.

V_0	V_t	C_0	C_t	eq	I_{460}	I/I_0	$I-I_0$
1050	0	0.00005	0	0	537.617	1	0
1050	10	4.95E-05	4.72E-06	0.095238	452.684	0.84202	84.933
1050	20	4.91E-05	9.35E-06	0.190476	379.442	0.705785	158.175
1050	30	4.86E-05	1.39E-05	0.285714	290.812	0.540928	246.805
1050	40	4.82E-05	1.83E-05	0.380952	204.968	0.381253	332.649
1050	50	4.77E-05	2.27E-05	0.47619	129.743	0.24133	407.874
1050	60	4.73E-05	2.7E-05	0.571429	83.6532	0.1556	453.9638
1050	70	4.69E-05	3.13E-05	0.666667	63.7446	0.118569	473.8724
1050	80	4.65E-05	3.54E-05	0.761905	45.0577	0.08381	492.5593
1050	90	4.61E-05	3.95E-05	0.857143	39.0141	0.072569	498.6029
1050	100	4.57E-05	4.35E-05	0.952381	35.5036	0.066039	502.1134
1050	110	4.53E-05	4.74E-05	1.047619	32.926	0.061244	504.691
1050	120	4.49E-05	5.13E-05	1.142857	31.7678	0.05909	505.8492

Table S3. Absorbance titration of **1•Ag**$^{+}$ with various concentration of **S**$^{-2}$.

V_0	V_t	C_0	C_t	eq	A_{481}	A/A_0	$A-A_0$
1100	0	0.00005	0	0	0.629088	1	0
1100	50	4.78E-05	0.000435	9.090909	1.426494	2.267557	0.797406
1100	60	4.74E-05	0.000517	10.90909	1.68086	2.671898	1.051772
1100	70	4.7E-05	0.000598	12.72727	1.90112	3.022024	1.272032
1100	80	4.66E-05	0.000678	14.54545	1.971163	3.133365	1.342075
1100	90	4.62E-05	0.000756	16.36364	1.997812	3.175726	1.368724
1100	100	4.58E-05	0.000833	18.18182	2.011443	3.197393	1.382355
1100	110	4.55E-05	0.000909	20	2.024318	3.21786	1.39523
1100	120	4.51E-05	0.000984	21.81818	2.024366	3.217936	1.395278
1100	130	4.47E-05	0.001057	23.63636	2.018826	3.20913	1.389738
1100	140	4.44E-05	0.001129	25.45455	2.00231	3.182875	1.373221

Table S4. Fluoresence titration of **1•Ag**$^{+}$ with various concentration of **S**$^{-2}$.

V_0	V_t	C_0	C_t	eq	I_{518}	I/I_0	$I-I_0$
1000	0	0.00005	0	0	10.3136	1	0
1000	30	4.85E-05	0.000291	6	209.224	20.28622	198.9104
1000	40	4.81E-05	0.000385	8	301.766	29.25904	291.4524
1000	50	4.76E-05	0.000476	10	354.259	34.34872	343.9454
1000	70	4.67E-05	0.000654	14	397.374	38.52913	387.0604
1000	80	4.63E-05	0.000741	16	401.252	38.90513	390.9384
1000	90	4.59E-05	0.000826	18	408.392	39.59742	398.0784
1000	100	4.55E-05	0.000909	20	410.822	39.83304	400.5084

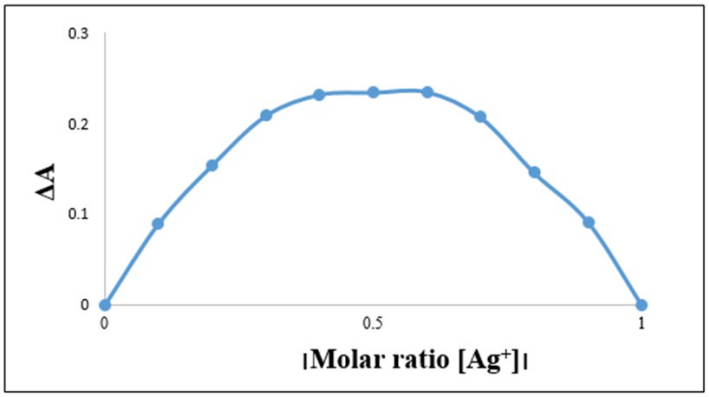


Figure S14. Job plot for the binding of **1** and Ag^{+}.

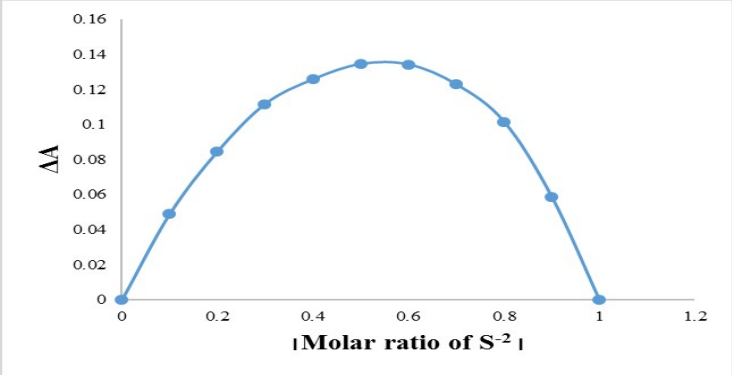


Figure S15. Job plot for the binding of **1•Ag**$^{+}$ and S^{-2}.

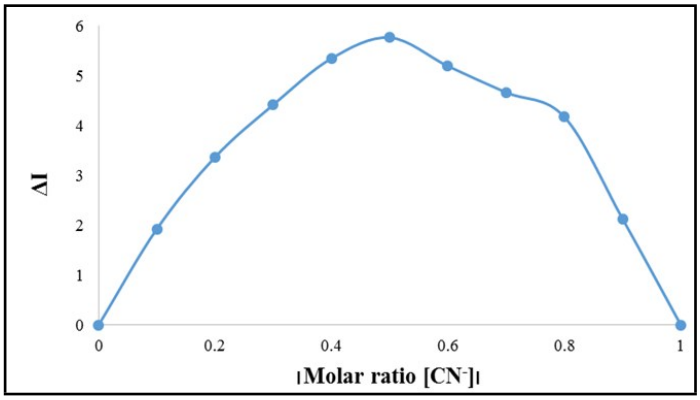


Figure S16. Job plot for the binding of **1** and CN^{-}.

Table S5. Absorbance titration of **1** with various concentration of **CN**$^{-}$.

V_0	V_t	C_0	C_t	eq	A_{400}	A/A_0	$A-A_0$
1000	0	0.00005	0	0	0.613093	1	0
1000	10	4.95E-05	9.9E-06	0.2	0.51695	0.843183	0.096143
1000	20	4.9E-05	1.96E-05	0.4	0.457039	0.745465	0.156054
1000	30	4.85E-05	2.91E-05	0.6	0.431294	0.703473	0.181799
1000	40	4.81E-05	3.85E-05	0.8	0.390916	0.637613	0.222177
1000	60	4.72E-05	5.66E-05	1.2	0.379062	0.618277	0.234032
1000	70	4.67E-05	6.54E-05	1.4	0.341403	0.556852	0.271691
1000	80	4.63E-05	7.41E-05	1.6	0.326983	0.533334	0.28611
1000	90	4.59E-05	8.26E-05	1.8	0.332743	0.542728	0.28035
1000	100	4.55E-05	9.09E-05	2	0.315424	0.51448	0.297669
1000	110	4.5E-05	9.91E-05	2.2	0.304735	0.497045	0.308359
1000	120	4.46E-05	0.000107	2.4	0.301956	0.492513	0.311137
1000	130	4.42E-05	0.000115	2.6	0.294907	0.481014	0.318187
1000	140	4.39E-05	0.000123	2.8	0.280305	0.457199	0.332788
1000	150	4.35E-05	0.00013	3	0.27594	0.450079	0.337153
1000	200	4.17E-05	0.000167	4	0.271052	0.442105	0.342041

Table S6. Fluoresence titration of **1** with various concentration of $\mathbf{CN^-}$.

V0	Vt	C0	Ct	eq	I447	I/I0	I-I0
2000	0	0.00005	0	0	204.663	1	0
2000	20	4.9505E-05	9.9E-05	2	187.983	0.9185	-16.68
2000	40	4.90196E-05	0.000196	4	171.303	0.837	-33.36
2000	60	4.85437E-05	0.000291	6	156.765	0.765966	-47.898
2000	80	4.80769E-05	0.000385	8	145.227	0.709591	-59.436
2000	100	4.7619E-05	0.000476	10	131.689	0.643443	-72.974
2000	130	4.69484E-05	0.00061	13	117.43	0.573772	-87.233
2000	150	4.65116E-05	0.000698	15	106.774	0.521706	-97.889
2000	200	4.54545E-05	0.000909	20	83.859	0.409742	-120.804

Table S7. Absorbance titration of $\mathbf{1{\bullet}Ag^+}$ with various concentration of $\mathbf{HS^-}$.

V_0	V_t	C_0	C_t	eq	A_{530}	A/A_0	$A-A_0$
600	0	0.00005	0	0	0.456097	1	0
600	20	4.84E-05	0.000161	3.333333	0.434968	0.953674	-0.02113
600	30	4.76E-05	0.000238	5	0.398087	0.872813	-0.05801
600	40	4.69E-05	0.000313	6.666667	0.288653	0.632877	-0.16744
600	50	4.62E-05	0.000385	8.333333	0.243876	0.534702	-0.21222
600	60	4.55E-05	0.000455	10	0.205042	0.449558	-0.25105
600	80	4.41E-05	0.000588	13.33333	0.162808	0.356959	-0.29329
600	100	4.29E-05	0.000714	16.66667	0.145211	0.318377	-0.31089

Table S8. Fluoresence titration of $\mathbf{1{\bullet}Ag^+}$ with various concentration of $\mathbf{HS^-}$.

V_0	V_t	C_0	C_t	eq	I_{447}	I/I_0	$I-I_0$
1100	0	0.00005	0	0	13.1849	1	0
1100	20	4.91E-05	0.000179	3.636364	22.0246	1.670441	8.8397
1100	30	4.87E-05	0.000265	5.454545	27.7724	2.106379	14.5875
1100	50	4.78E-05	0.000435	9.090909	41.8718	3.175739	28.6869
1100	60	4.74E-05	0.000517	10.90909	45.35	3.439541	32.1651
1100	70	4.7E-05	0.000598	12.72727	48.4412	3.673991	35.2563
1100	80	4.66E-05	0.000678	14.54545	51.2282	3.885369	38.0433
1100	90	4.62E-05	0.000756	16.36364	53.8082	4.081047	40.6233
1100	100	4.58E-05	0.000833	18.18182	55.3848	4.200623	42.1999
1100	110	4.55E-05	0.000909	20	57.0521	4.327079	43.8672
1100	120	4.51E-05	0.000984	21.81818	58.7024	4.452245	45.5175
1100	160	4.37E-05	0.00127	29.09091	60.6556	4.600384	47.4707
1100	180	4.3E-05	0.001406	32.72727	59.3916	4.504517	46.2067

Table S9. Fluoresence titration of **1•Ag^{+}** with various concentration of **S^{-2}** in PBS buffer solution at pH 7.4.

V_0	V_t	C_0	C_t	Eq	$I_{(510)}$	I/I_0	$I-I_0$
1150	0	0.001304	0	0	40.3182	1	0
1150	10	0.001293	8.62E-05	0.066667	61.1557	1.516826	20.8375
1150	20	0.001282	0.000171	0.133333	72.7132	1.803483	32.395
1150	30	0.001271	0.000254	0.2	84.1091	2.086132	43.7909
1150	40	0.001261	0.000336	0.266667	101.683	2.522012	61.3648
1150	50	0.00125	0.000417	0.333333	119.375	2.960822	79.0568
1150	60	0.00124	0.000496	0.4	129.997	3.224276	89.6788
1150	90	0.00121	0.000726	0.6	177.863	4.411482	137.5448
1150	100	0.0012	0.0008	0.666667	191.01	4.737563	150.6918
1150	110	0.00119	0.000873	0.733333	197.458	4.89749	157.1398
1150	120	0.001181	0.000945	0.8	216.446	5.368444	176.1278
1150	130	0.001172	0.001016	0.866667	223.655	5.547247	183.3368
1150	140	0.001163	0.001085	0.933333	238.716	5.9208	198.3978
1150	150	0.001154	0.001154	1	257.648	6.390365	217.3298
1150	160	0.001145	0.001221	1.066667	276.475	6.857325	236.1568

Table S10. Fluoresence titration of **1•Ag^{+}** with various concentration of **HS^{-}** in PBS buffer solution at pH 7.4.

V_0	V_t	C_0	C_t	Eq	$I_{(510)}$	I/I_0	$I-I_0$
1100	0	0.00005	0	0	44.3014	1	0
1100	40	4.82E-05	0.000351	7.272727	52.542	1.186012	8.2406
1100	50	4.78E-05	0.000435	9.090909	53.3121	1.203395	9.0107
1100	60	4.74E-05	0.000517	10.90909	55.2092	1.246218	10.9078
1100	70	4.7E-05	0.000598	12.72727	58.5696	1.322071	14.2682
1100	90	4.62E-05	0.000756	16.36364	61.4954	1.388114	17.194
1100	100	4.58E-05	0.000833	18.18182	61.9905	1.39929	17.6891
1100	110	4.55E-05	0.000909	20	63.8552	1.441381	19.5538
1100	120	4.51E-05	0.000984	21.81818	63.9912	1.444451	19.6898
1100	130	4.47E-05	0.001057	23.63636	64.4144	1.454004	20.113
1100	140	4.44E-05	0.001129	25.45455	65.7096	1.48324	21.4082
1100	150	0.000044	0.0012	27.27273	66.4397	1.49972	22.1383
1100	160	4.37E-05	0.00127	29.09091	66.8775	1.509602	22.5761
1100	170	4.33E-05	0.001339	30.90909	67.6349	1.526699	23.3335
1100	180	4.3E-05	0.001406	32.72727	68.9433	1.556233	24.6419

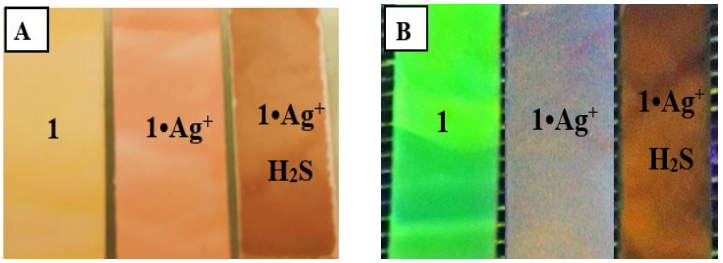


Figure S17. portable kit of Ag^+, H_2S : The naked eye (**A**, under visible light) and fluorescence (**B**, under 366 nm UV light)

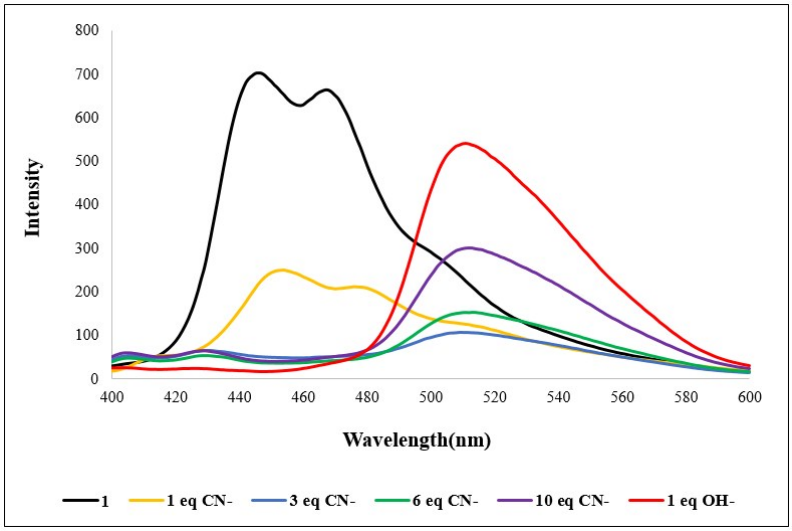


Figure S18. The comparison of Fluoresence spectra of **1** under addition of OH^- and CN^- ions in non-buffered solution at pH = 6.

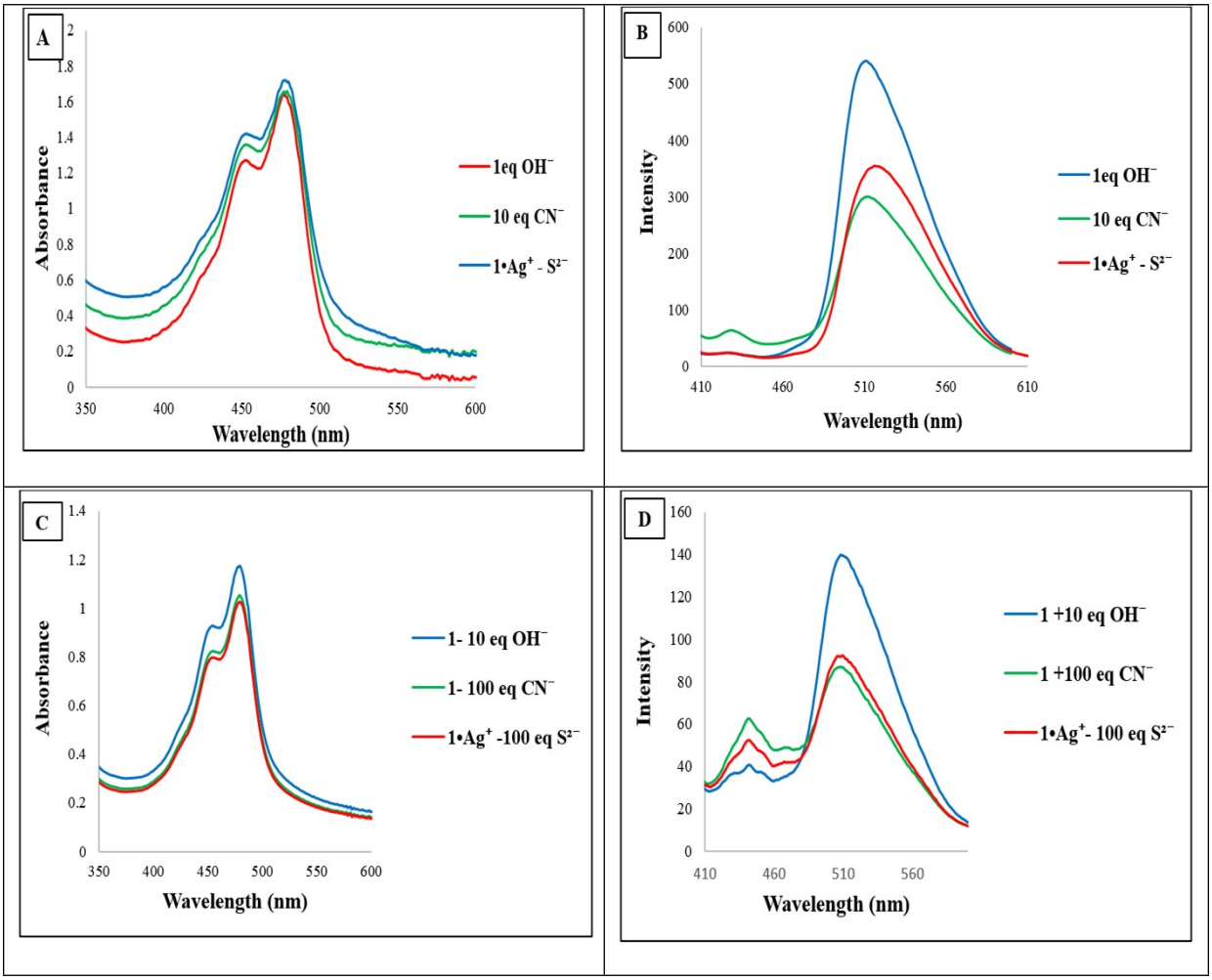


Figure S19. The comparison of UV-Vis and Fluoresence spectra of **1** under addition of OH^- and CN^- ions and **1•Ag**$^+$ under addition of S^{-2} in non-buffered solution at pH = 6.

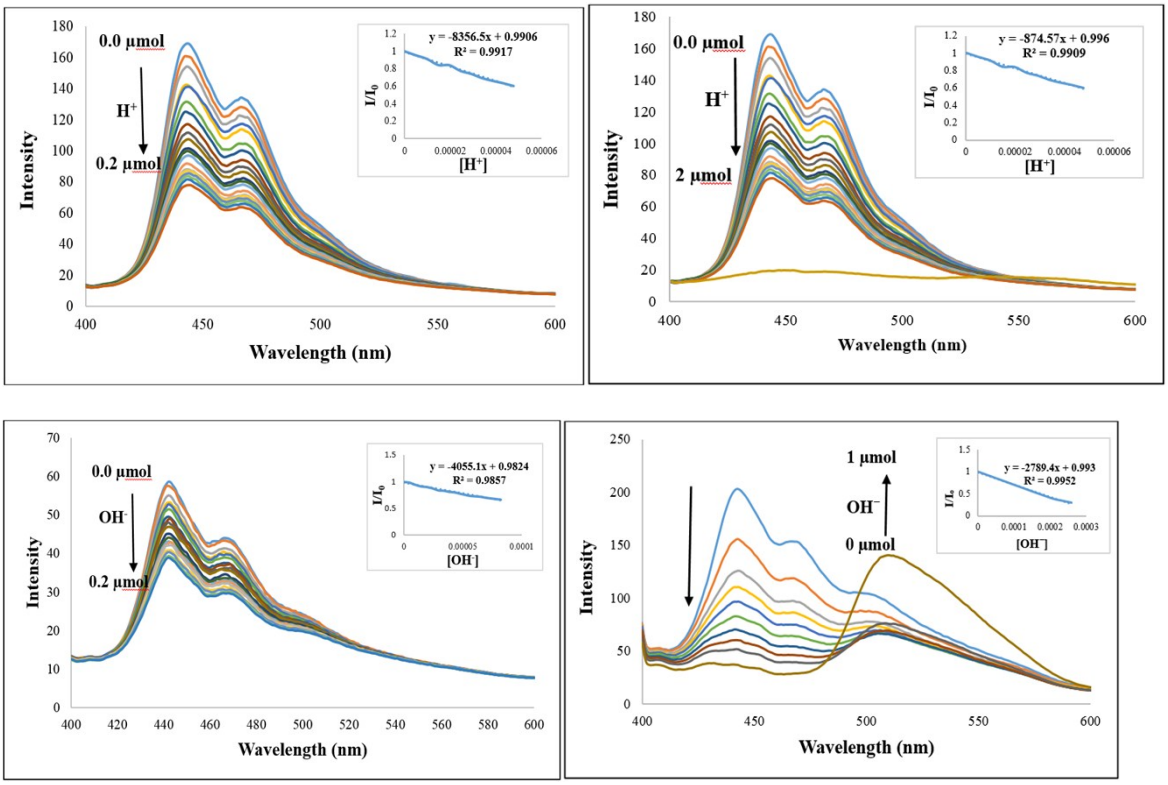


Figure S20. The titration of buffer solution **1** (pH 7) under addition of (above) 1 and 10 eqiv. of HCl (below) 1 and 10 eqiv. NaOH.

Table S11. Comparison of 1 with other probes for detection of silver ions

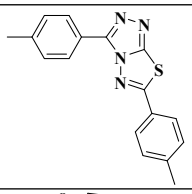
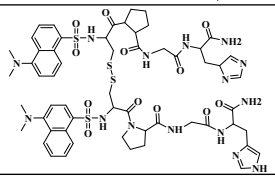
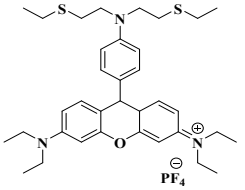
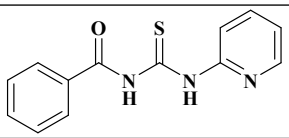
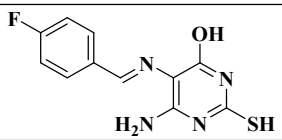
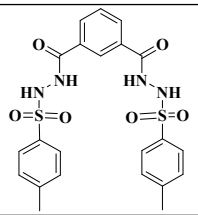
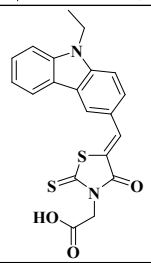
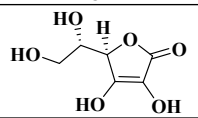
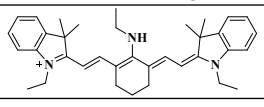
Chemical Structure	Method	Sensing ions	Solvent medium	LOD	Reference Number
	**Fluorescent**	**Ag^+ Cysteine**	**THF/H_2O**	**2.87×10^9 M**	**9**
	**Fluorescent**	**Ag^+**	**H_2O**	**17.4nM**	**10**
	**Fluorescent**	**Ag^+**	**EtOH**	**10^{-7}M**	**11**
	**Fluorescent**	**Ag^+**	**MeOH/H_2O 8:2**	**3.67 µM (Ag^+) 0.69 nM (Hg^{+2})**	**12**
	**Fluorescent**	**Ag^+**	**DMF/H_2O 50:50**	**1.12 µM**	**13**
	**uv-vis**	**Ag^+**	**H_2O**	**2.43 µM**	**14**
	**Fluorescent**	**Ag^+**	**CH_3CN, H_2O 1:9**	**12.8×10^{-9} M**	**15**
	**UV-Vis**	**Ag^+**	**H_2O**	**0.85 µM**	**16**
	**Fluorescent**	**Ag^+**	**(EtOH/PBS) 1:9**	**0.03 µM**	**17**

Table S12. Comparison of **1** with other probes for detection of cyanide ions *via* deprotonation.

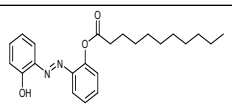
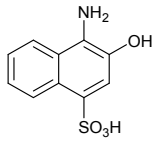
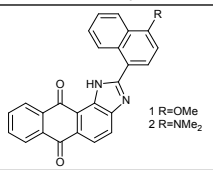
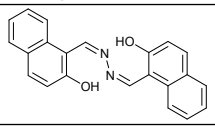
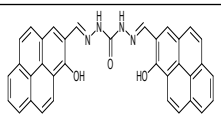
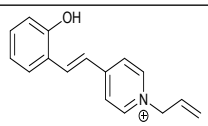
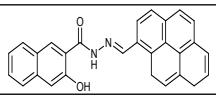
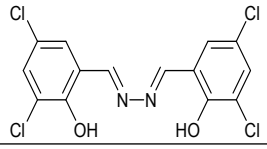
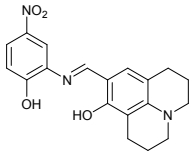
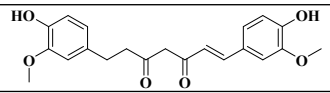
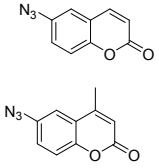
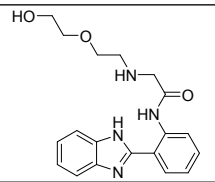
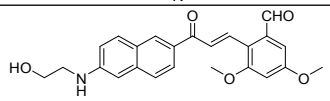
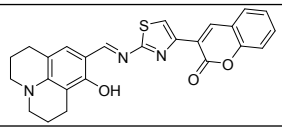
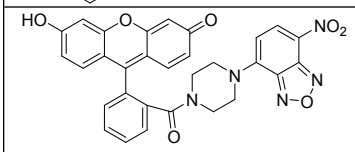
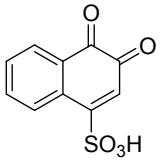
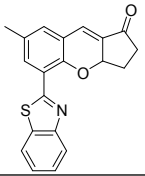
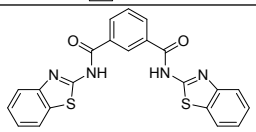
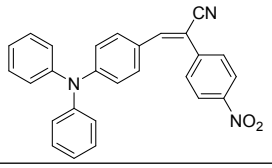
Chemical Structure	Method	Sensing ions	Solvent medium	LOD	Reference Number
	Fluorescent UV-Vis	CN-, HCO3-, CO32- the weak selectivity and weak sensitivity	H2O–MeOH (v/v,2/5)	-	18
	Fluorescent UV-Vis	Cyanide	H2O	0.32 µmol	19
	UV-Vis	Fluoride & Cyanide	CH3CN–H2O (9:1)	17.7 µmol	20
	Fluorescent UV-Vis	CN Job (2:1)	DMSO/H2O (9:1)	0.4 µmol	21
	Fluorescent UV-Vis	cyanide	CH3CN-DMSO-H2O (94:1:5)	0.25 µmol	22
	UV-Vis	cyanide	CH3CN–H2O (95 : 5)	8 µmol	23
	UV-Vis	cyanide	CH3CN - buffer (1:1)	1.2 µmol	24
	UV-Vis	cyanide Job (1:1)	CH3CN/bis-tris buffer solution (3:7)	210 mM	25
	UV-Vis	cyanide Job (1:1) Intereferes in organic media		105 mM	26

Table S13. Comparison of **1** with other probes for detection of sulfide ions

Chemical Structure	Method	Sensing ions	Solvent medium	LOD	Reference Number
	**UV-Vis**	**S^{2-}**	**buffer (pH 9)**	**0.4 ng ml^{-1}**	**27**
	**Fluorescent**	**H_2S**	**PBS buffer**	**0.25 µM**	**28**
	**Fluorescent On-Off-On**	**CuS**	**H_2O**	**1.35×10^{-6} M**	**29**
	**Fluorescent**	**Na_2S, H_2S**	**HEPES buffer (pH 7.4)**	**50 nM**	**30**
	**Fluorescent UV-Vis**	**Cu2S**	**HEPES buffer, pH 7.4**	**11.4 µM**	**31**
	**Fluorescent on**	**H_2S**	**aqueous buffer and in vivo**	**0.057 mM**	**32**
	**UV-Vis**	**H_2S**	**H_2O**	**0.16mg/L**	**33**
	**Fluorescent on**	**H_2S**	**PBS buffer pH 7.4**	**41 nM**	**34**
	**Fluorescent UV-Vis**	**H_2S Na_2S**	**H_2O**	**1.17 mM 1.28 mM**	**35**
	**Fluorescent UV-Vis**	**H_2S**	**PBS buffer pH 7.4**	**6.87 mM**	**36**