Electronic Supplementary Information

A novel self-assembled supramolecular sensor based on thiophene functionalized imidazophenazine for dual-channel detection Ag^+ in aqueous solution

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Instruments and materials

^{1}H NMR and ^{13}C NMR spectra were carried out on a Mercury-400BB spectrometer at 600 MHz. Electrospray ionization mass spectra (ESI-MS) were measured on an Agilent 1100 LC-MSD-Trap-VL system. UV-visible spectra were recorded on a Shimadzu UV-2550 spectrometer. Photoluminescence spectra were performed on a Shimadzu RF-5301 fluorescence spectrophotometer. Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). The infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer. All cations, in terms of Fe^{3+}, Hg^{2+}, Ag^{+}, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+}, and Mg^{2+} were added in the form of perchlorate salts, which were purchased from Alfa-Aesar Chemical, and stored in a vacuum desiccator containing self-indicating silica and dried fully before using. All reagents were gained commercially for synthesis and without further purification during experiment progress. Double distilled water was used throughout the experiment.

Synthesis of sensors IM

2,3-Diamino-phenazine (0.42g, 2 mmol), 2-thiophene carboxaldehyde (0.22 g, 2 mmol) and catalytic amount of acetic acid (AcOH) were combined in hot absolute DMF (20 mL). The solution was stirred under reflux conditions for 8 h, after cooling to room temperature, the brown precipitate was filtrated, washed with hot absolute ethanol for three times, then recrystallized with DMF-H_2O to get yellow powdery product **S1** (0.52g) at yield of 82% (m.p. >300℃), ^{1}H NMR (DMSO-d_6, 600 MHz) δ:13.50 (s 1H), 8.44 (s 1H), 8.23 (s 2H), 8.15 (m 2H), 8.00-7.99 (d 1H), 7.90-7.88 (m

2H), 7.39-7.36 (m 1H), 6.25 (s 1H). ^{13}C NMR (151 MHz, DMSO-d_6), δ 155.63, 149.42, 142.34, 140.95, 132.92, 130.85 and 129.50. IR (KBr, cm^{-1}) v: 3428.85, 3200.52, 1655.37, 1589.50, 1565.35, 1505.34, 1427.05; ESI-MS m/z: [M - H^+] Calcd for $C_{17}H_{10}N_4S$ 301.06; Found 301.09.

General procedure for UV-vis and fluorescence spectra experiments

The solution of sensor **S1** (2.0×10^{-4} M) in DMSO was prepared and stored in dry atmosphere. The solution was used for all spectroscopic studies after appropriate dilution. The DMSO solutions of each cations (4×10^{-3} M) were prepared, via perchloratesalts of Fe^{3+}, Hg^{2+}, Ag^+, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+}, and Mg^{2+}. All the UV-vis experiments were carried out in DMSO/H_2O (v:v = 1:1, buffered with HEPES pH = 7.2) solution on a Shimadzu UV-2550 spectrometer. Any change in the UV-vis spectra of the synthesized compounds was recorded on addition of salts while keeping the ligand concentration constant (2.0×10^{-5} M) in all experiments. All the fluorescence spectra experiments were carried out in DMSO/H_2O (v:v = 1:1, buffered with HEPES pH = 7.2) solution on a Shimadzu RF-5301 spectrometer. The fluorescence spectra were obtained by excitation at 400 nm. Any change in the fluorescence spectra of the synthesized compounds was recorded upon the addition of salts while keeping the ligand concentration constant (2.0×10^{-5} M) in all experiments.

General procedure for ^{1}H NMR experiments

For ^{1}H NMR titrations, two stock solutions were prepared in DMSO-d_6, one containing the sensor only and the second containing an appropriate concentration of

the metal. Aliquots of the two solutions were mixed directly in NMR tube.

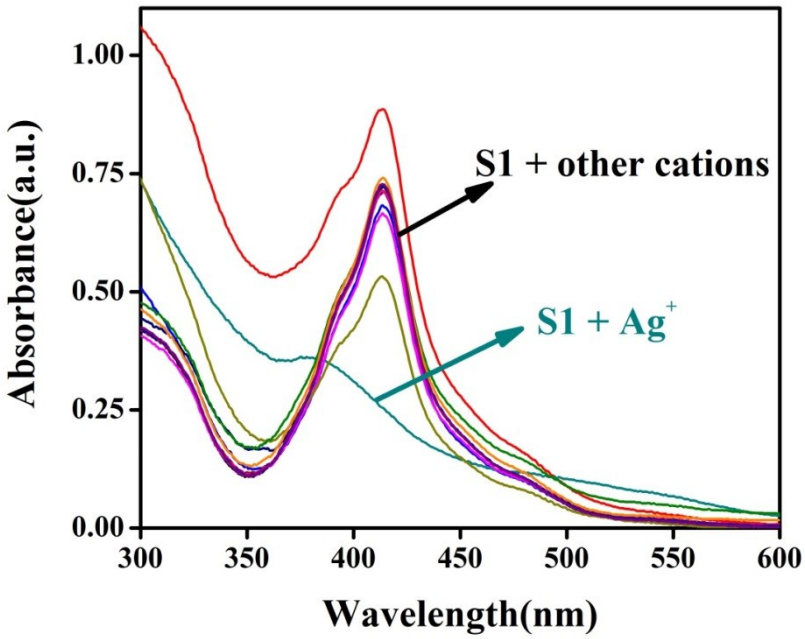

Fig. S1 UV–vis absorption and spectra of **S1** (20 μM) with metal ions (Fe^{3+}, Hg^{2+}, Ag^{+}, Ca^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+}, and Mg^{2+}) in the DMSO/H_2O (v:v = 1:1,buffered with HEPES pH = 7.2) solution in response to Ag^{+}(10 equiv.).

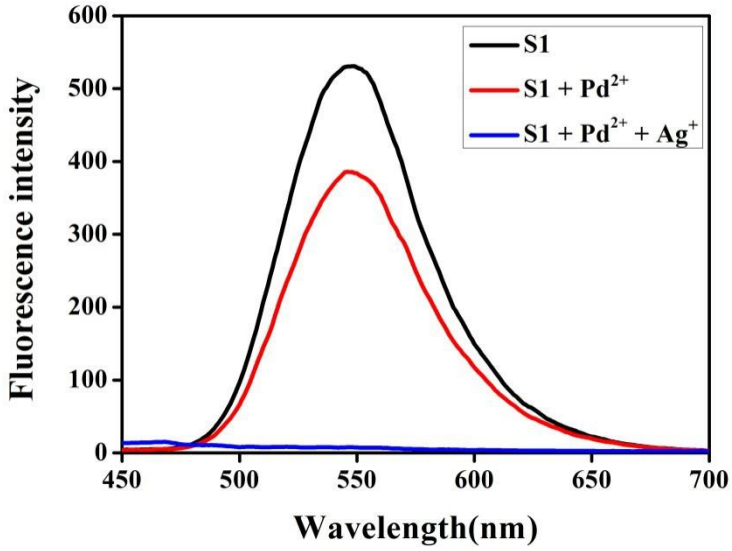

Fig. S2 Fluorescence spectra responses in DMSO/H_2O (v : v = 1 : 1, buffered with HEPES pH = 7.2) of **S1** (2.0×10^{-5} M) upon addition of Pd^{2+} (10 equiv.).

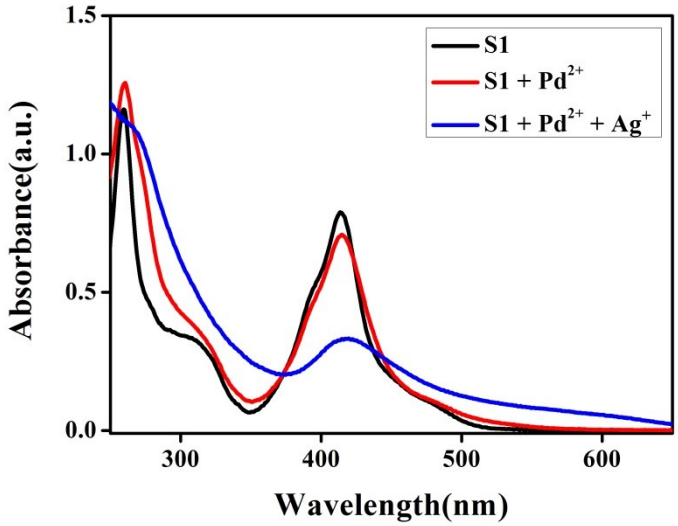

Fig. S3 UV–vis absorption and spectra of **S1** (20 μM) with Pd^{2+} ions in the DMSO/H_2O (v:v = 1:1,buffered with HEPES pH = 7.2) solution in response to Ag^{+} (10 equiv.).

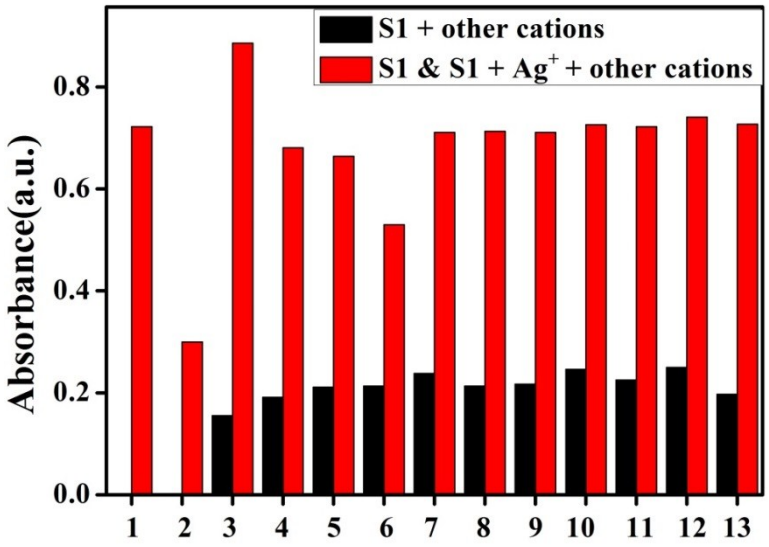

Fig. S4 UV–vis absorbance intensity of **S1** (20 μM) in response to Ag^{+} (10 equiv.) in the presence of various metal ions species in DMSO/H_2O (v:v = 1:1,buffered with HEPES pH = 7.2) solution. From 1 to 13: **S1**, **S1** + Ag^{+}, **S1** + Ag^{+} + Fe^{3+}, **S1** + Ag^{+} + Ca^{2+}, **S1** + Ag^{+} + Cu^{2+}, **S1** + Ag^{+} + Co^{2+}, **S1** + Ag^{+} + Ni^{2+}, **S1** + Ag^{+} + Cd^{2+}, **S1** + Ag^{+} + Pb^{2+}, **S1** + Ag^{+} + Zn^{2+}, **S1** + Ag^{+} + Hg^{2+}, **S1** + Ag^{+} + Cr^{3+}, **S1** + Ag^{+} + Mg^{2+}.

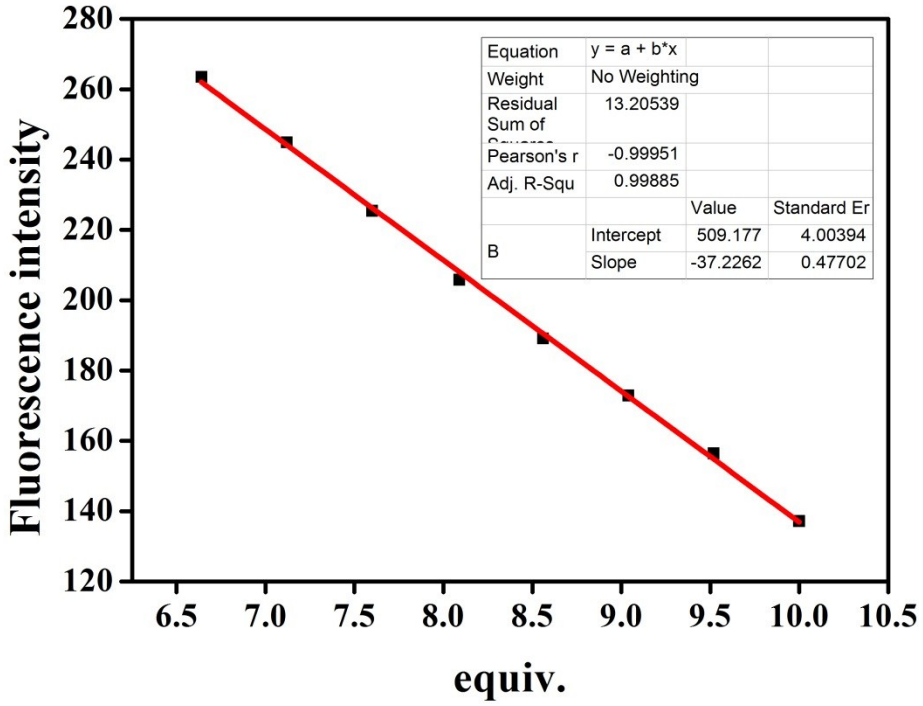

Fig. S5 Plot of the intensity at 365nm for a mixture of the sensor **S1** (20 μM) and Ag^+ in DMSO/H_2O (v:v = 1:1, buffered with HEPES pH = 7.2) in the range 0.00 to 42.24 μM. (λ_{ex} = 400 nm). The result of the analysis as follows:

Linear Equation: $Y = -37.2262 \times X + 509.177$ $R^2 = 0.99885$

$S = 37.2262 \times 10^6$ $\delta = \sqrt{\frac{\Sigma(A_0 - A_1)^2}{N-1}} = 0.1016 (N=20)$ $K = 3$

$LOD = K \times \delta / S = 8.18 \times 10^{-9}$ M

$\mathbf{A_0}$ is the absorbance intensity of **S1**; $\mathbf{A_1}$ is the average of the $\mathbf{A_0}$.

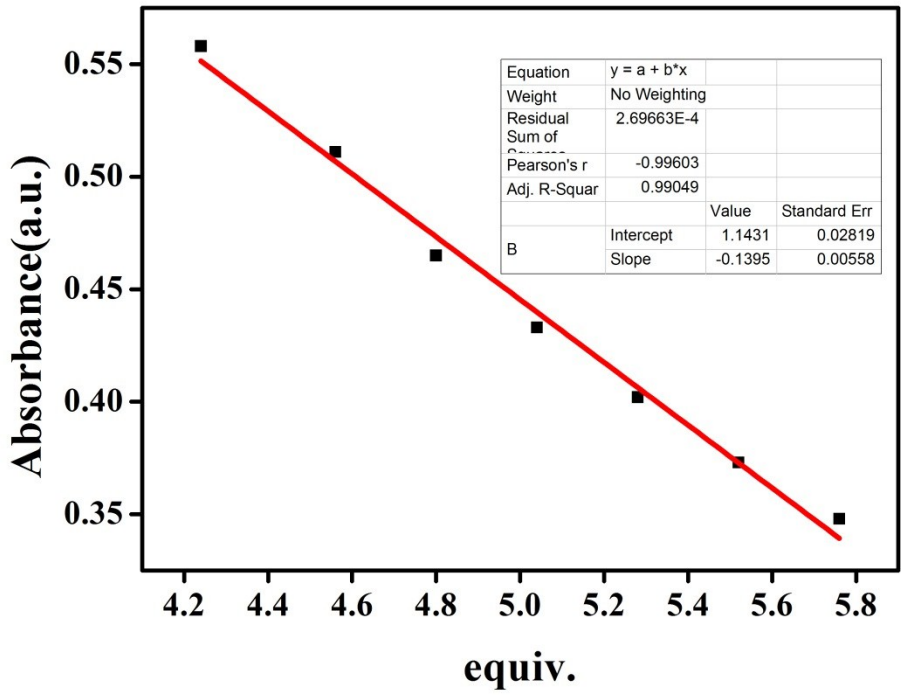

Fig. S6 Plot of the absorbance for a mixture of the sensor **S1** (20 μM) and Ag^+ in DMSO/H_2O (v:v = 1:1, buffered with HEPES pH = 7.2) in the range 0.00 to 40.32 μM. The result of the analysis as follows:

Linear Equation: $Y = -0.1395\times X + 1.1431$ $R^2 = 0.99603$

$S = 0.1395\times 10^6$ $\delta = \sqrt{\frac{\Sigma(A_0 - A_1)^2}{N-1}} = 0.040694 (N=20)$ $K = 3$

$LOD = K \times \delta / S = 8.75 \times 10^{-7}$ M

$\mathbf{A_0}$ is the absorbance intensity of **S1**; $\mathbf{A_1}$ is the average of the $\mathbf{A_0}$.

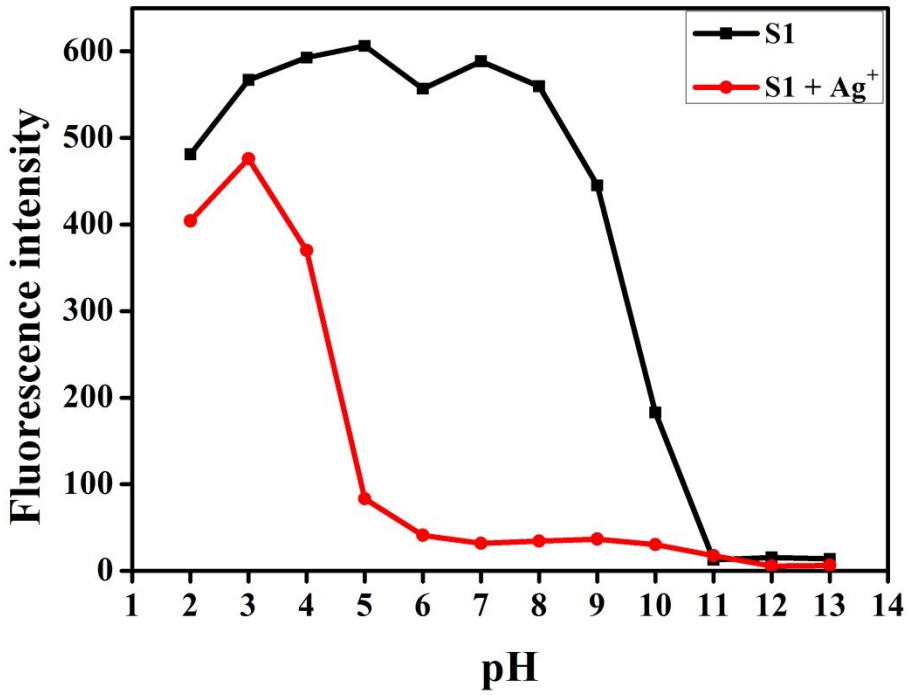

Fig. S7 The pH response of **S1** and **S1**-Ag^{+} in the DMSO/H_2O (v:v = 1:1, buffered with HEPES pH = 7.2) solution.

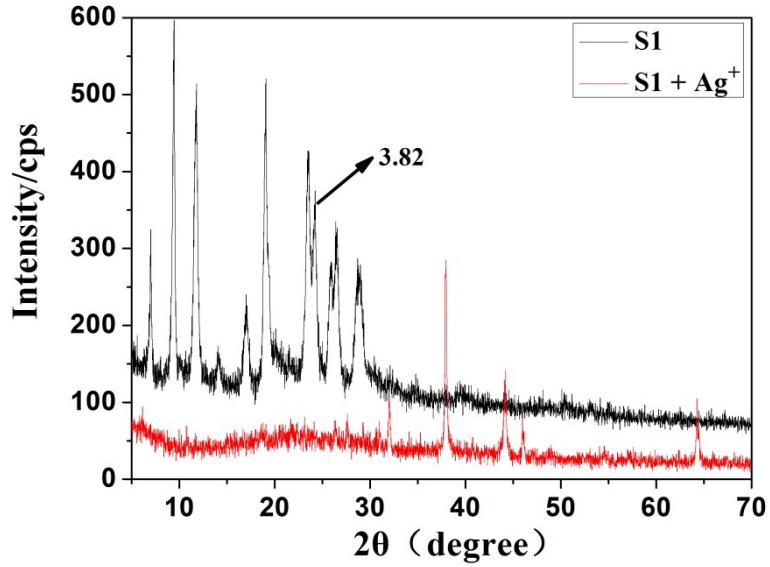

Fig. S8 XRD diagrams of **S1** and **S1-**Ag^{+}.

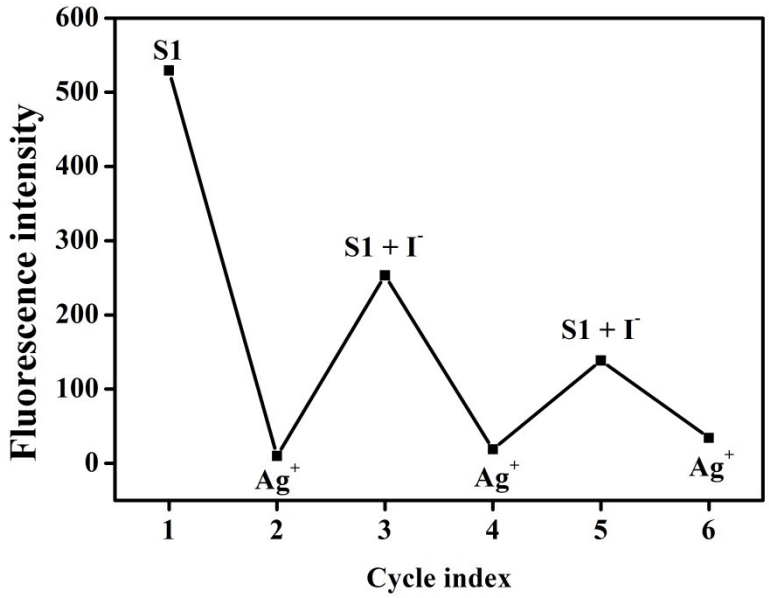

Fig. S9 Fluorescence intensity reversible switching cycles of the **S1** water solution (2.0×10^{-5} M) on alternate addition of Ag^+ and I^-.

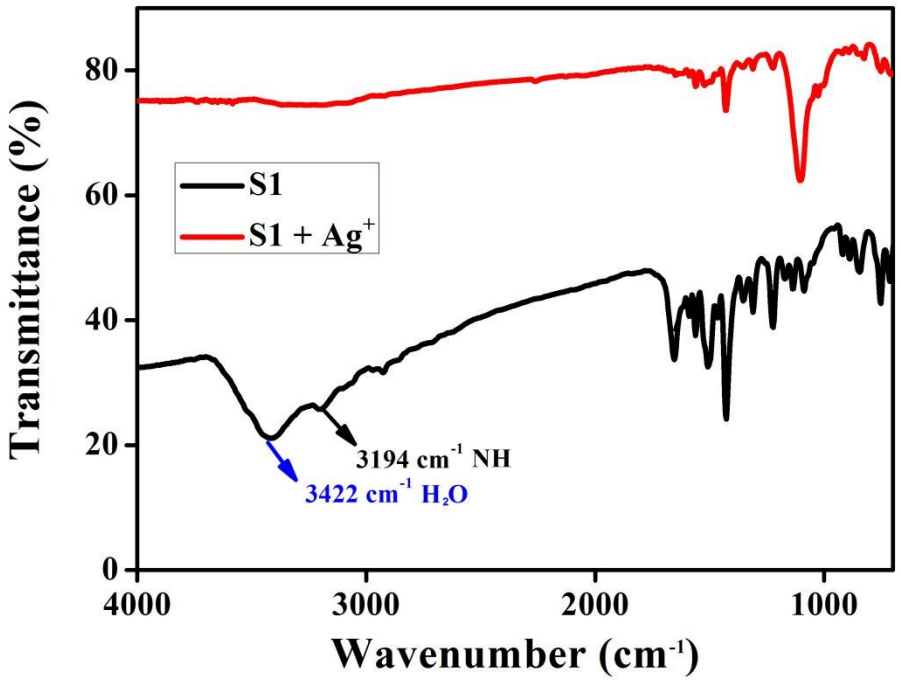

Fig. S10 FT-IR spectra of compound **S1** and **S1**-Ag^+.

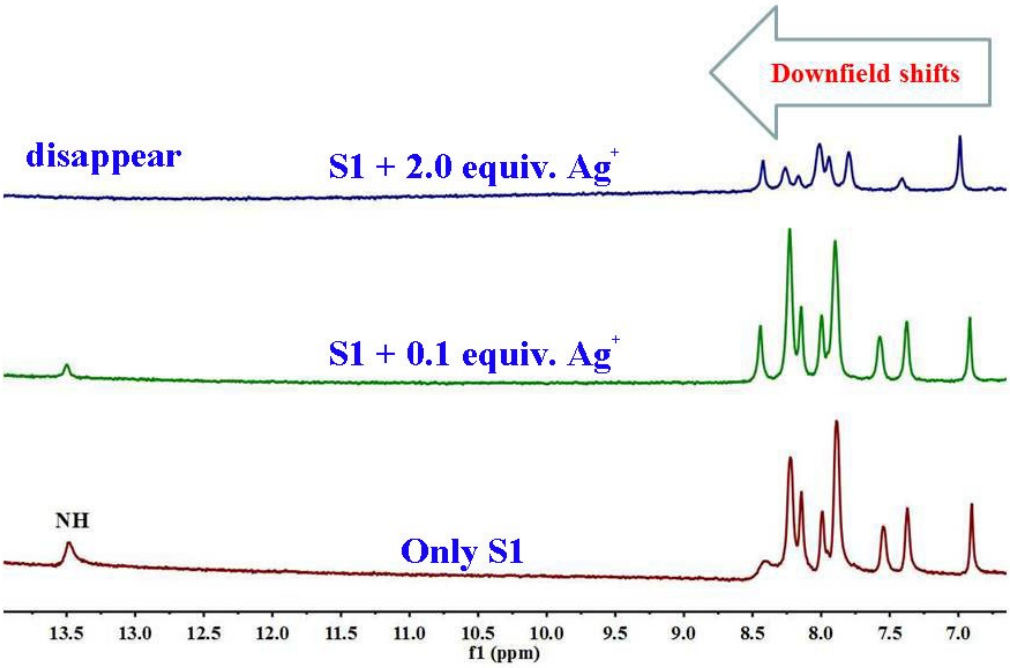

Fig. S11 ^{1}H NMR spectra (600 MHz, DMSO-d_6) of free **S1** and in the presence of Ag^+.

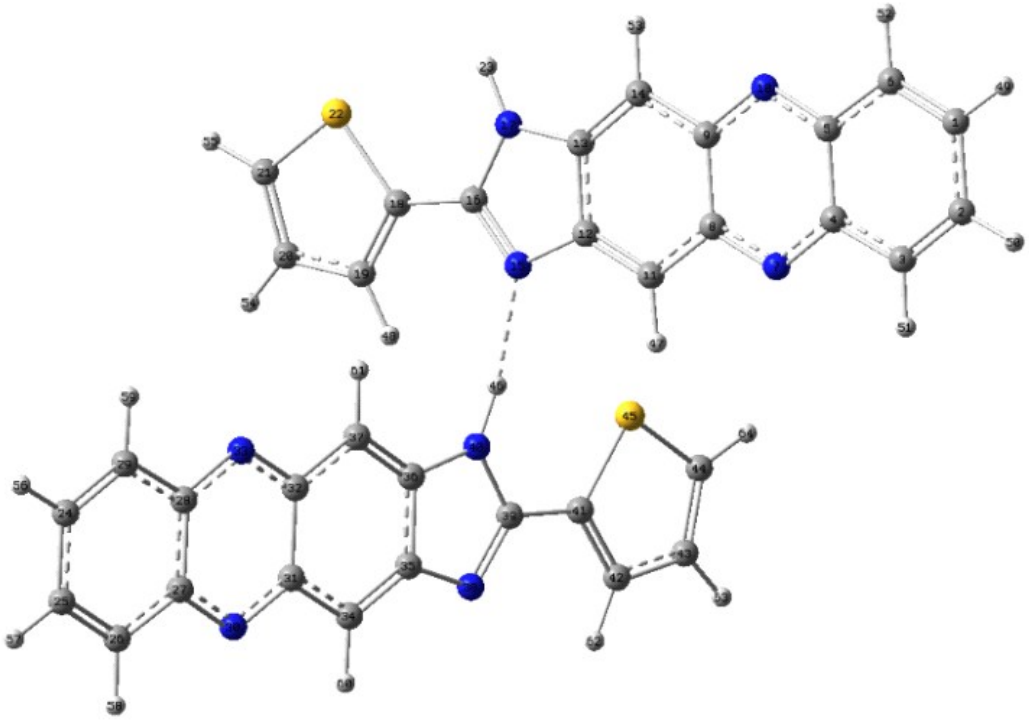

Fig. S12 Optimized structures of **IM**.

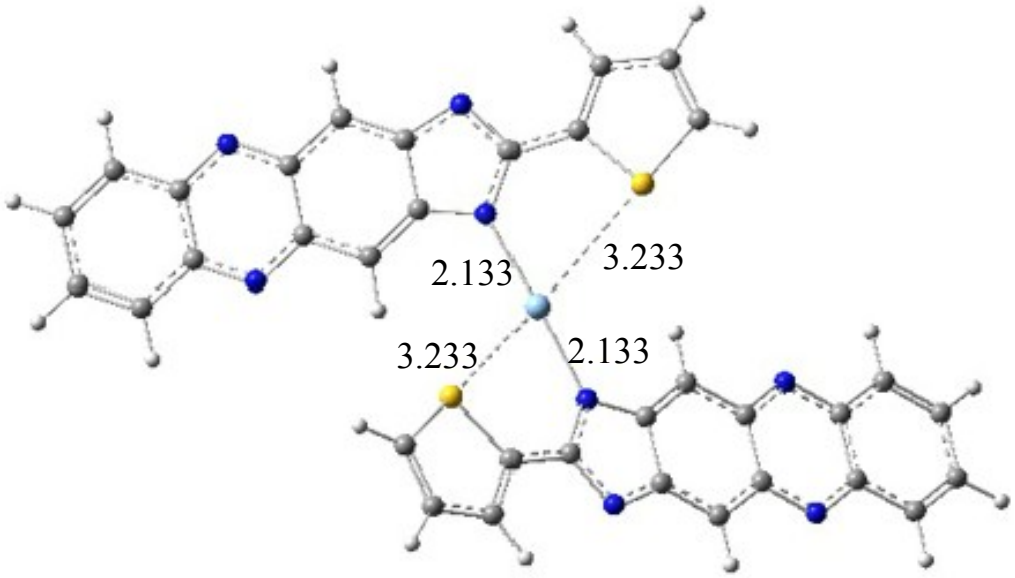

Fig. S13 Optimized structures of **IM**-Ag^+ complexes.

Table S1 Fluorescent sensors reported for the detection of Ag^+.

References	Reproducibility	LOD (M)	Solvent	Selectivity
[1]	No	4.0×10^{-9}	Ethanol	Ag^+
[2]	No	5.0×10^{-8}	DMSO/H_2O (v/v, 9:1)	Ag^+
[3]	No	6.20×10^{-6}	CH3CN/H_2O (v/v, 1:1)	Ag^+
[4]	No	6.0×10^{-7}	H_2O	Ag^+
[5]	More than 3 times	7.73×10^{-8}	DMSO/H_2O (v/v, 1:1)	Ag^+
This work	3 times	8.18×10^{-9}	DMSO/H_2O (v/v, 1:1)	Ag^+

Table S2 DFT computed selected bond lengths for **IM**.

Chemical bond	**Bond length/(10^{-10} m)**	**Chemical bond**	**Bond length/(10^{-10} m)**	**Chemical bond**	**Bond length/(10^{-10} m)**	**Chemical bond**	**Bond length/(10^{-10} m)**
R(1,2)	1.418	R(1,6)	1.3779	R(1,46)	1.0851	R(2,3)	1.3843
R(2,47)	1.0856	R(3,4)	1.4138	R(3,48)	1.0848	R(4,5)	1.4441
R(4,7)	1.3562	R(5,6)	1.4253	R(5,10)	1.3431	R(6,49)	1.0849
R(7,8)	1.3286	R(8,9)	1.4607	R(8,11)	1.4407	R(9,10)	1.3428
R(9,14)	1.4177	R(11,12)	1.3706	R(11,50)	1.0854	R(12,13)	1.4499
R(12,15)	1.3826	R(13,14)	1.3976	R(13,17)	1.3471	R(14,51)	1.0845
R(15,16)	1.3617	R(15,45)	2.1266	R(16,17)	1.3639	R(16,18)	1.4403
R(18,19)	1.3854	R(18,22)	1.7527	R(19,20)	1.4143	R(19,52)	1.0842
R(20,21)	1.3775	R(20,53)	1.0833	R(21,22)	1.7194	R(21,54)	1.0819
R(23,24)	1.4183	R(23,28)	1.384	R(23,55)	1.0856	R(24,25)	1.3777
R(24,56)	1.0851	R(25,26)	1.4255	R(25,57)	1.0849	R(26,27)	1.4443
R(26,29)	1.3429	R(27,28)	1.4141	R(27,32)	1.3558	R(28,58)	1.0848
R(29,30)	1.3431	R(30,31)	1.4606	R(30,33)	1.4175	R(31,32)	1.3288
R(31,36)	1.4404	R(33,34)	1.3978	R(33,59)	1.0845	R(34,35)	1.45
R(34,37)	1.348	R(35,36)	1.3703	R(35,39)	1.3827	R(36,60)	1.0855
R(37,38)	1.3635	R(38,39)	1.3616	R(38,40)	1.4405	R(39,45)	2.1278
R(40,41)	1.3845	R(40,44)	1.7497	R(41,42)	1.4162	R(41,61)	1.0826
R(42,43)	1.3728	R(42,62)	1.0833	R(43,44)	1.7311	R(43,63)	1.0815

Table S3 DFT computed selected bond angles for **IM**.

Bond angle	Angle/°	Bond angle	Angle/°	Bond angle	Angle/°
A(2,1,6)	120.4738	A(2,1,46)	119.4293	A(6,1,46)	120.0969
A(1,2,3)	121.0959	A(1,2,47)	119.2574	A(3,2,47)	119.6468
A(2,3,4)	119.9675	A(2,3,48)	121.8157	A(4,3,48)	118.2168
A(3,4,5)	119.1093	A(3,4,7)	119.5132	A(5,4,7)	121.3775
A(4,5,6)	119.4099	A(4,5,10)	121.3586	A(6,5,10)	119.2316
A(1,6,5)	119.9436	A(1,6,49)	122.1907	A(5,6,49)	117.8657
A(4,7,8)	117.3548	A(7,8,9)	121.2693	A(7,8,11)	118.4534
A(9,8,11)	120.2773	A(8,9,10)	121.3611	A(8,9,14)	120.1786
A(10,9,14)	118.4603	A(5,10,9)	117.2787	A(8,11,12)	118.167
A(8,11,50)	118.0939	A(12,11,50)	123.7391	A(11,12,13)	121.6983
A(11,12,15)	131.6499	A(13,12,15)	106.6509	A(12,13,14)	121.4714
A(12,13,17)	109.497	A(14,13,17)	129.0317	A(9,14,13)	118.2069
A(9,14,51)	119.7279	A(13,14,51)	122.0652	A(12,15,16)	104.6061
A(12,15,45)	123.3185	A(16,15,45)	131.9418	A(15,16,17)	114.8109
A(15,16,18)	125.8876	A(17,16,18)	119.2997	A(13,17,16)	104.4332
A(16,18,19)	130.7173	A(16,18,22)	118.5193	A(19,18,22)	110.7562
A(18,19,20)	113.106	A(18,19,52)	123.5561	A(20,19,52)	123.3256
A(19,20,21)	112.3134	A(19,20,53)	124.1256	A(21,20,53)	123.5597
A(20,21,22)	112.6167	A(20,21,54)	127.5504	A(22,21,54)	119.8325
A(18,22,21)	91.2064	A(24,23,28)	121.087	A(24,23,55)	119.2573
A(28,23,55)	119.6557	A(23,24,25)	120.4884	A(23,24,56)	119.4189
A(25,24,56)	120.0927	A(24,25,26)	119.9515	A(24,25,57)	122.1853
A(26,25,57)	117.8631	A(25,26,27)	119.3859	A(25,26,29)	119.2394
A(27,26,29)	121.3747	A(26,27,28)	119.118	A(26,27,32)	121.3678
A(28,27,32)	119.5142	A(23,28,27)	119.9692	A(23,28,58)	121.8264
A(27,28,58)	118.2045	A(26,29,30)	117.2841	A(29,30,31)	121.3258
A(29,30,33)	118.475	A(31,30,33)	120.1992	A(30,31,32)	121.2971
A(30,31,36)	120.244	A(32,31,36)	118.4588	A(27,32,31)	117.3504
A(30,33,34)	118.2557	A(30,33,59)	119.677	A(34,33,59)	122.0672
A(33,34,35)	121.3536	A(33,34,37)	128.9537	A(35,34,37)	109.6926
A(34,35,36)	121.7814	A(34,35,39)	106.5054	A(36,35,39)	131.7126
A(31,36,35)	118.1654	A(31,36,60)	118.0518	A(35,36,60)	123.7822
A(34,37,38)	104.2122	A(37,38,39)	114.9622	A(37,38,40)	119.5105
A(39,38,40)	125.527	A(35,39,38)	104.6272	A(35,39,45)	123.9543
A(38,39,45)	131.4119	A(38,40,41)	125.4435	A(38,40,44)	123.8537
A(41,40,44)	110.7025	A(40,41,42)	113.1482	A(40,41,61)	121.7707
A(42,41,61)	125.0811	A(41,42,43)	112.7268	A(41,42,62)	124.038
A(43,42,62)	123.2352	A(42,43,44)	112.0393	A(42,43,63)	128.3543
A(44,43,63)	119.6058	A(40,44,43)	91.3831		

Table S4 DFT computed selected bond lengths for **IM**-Ag^{+}.

Chemical bond	Bond length/(10^{-10} m)	Chemical bond	Bond length/(10^{-10} m)	Chemical bond	Bond length/(10^{-10} m)	Chemical bond	Bond length/(10^{-10} m)
R(1,2)	1.4298	R(1,6)	1.3688	R(1,49)	1.0859	R(2,3)	1.3684
R(2,50)	1.0859	R(3,4)	1.4303	R(3,51)	1.085	R(4,5)	1.448
R(4,7)	1.3383	R(5,6)	1.4295	R(5,10)	1.3396	R(6,52)	1.085
R(7,8)	1.346	R(8,9)	1.4591	R(8,11)	1.4221	R(9,10)	1.3446
R(9,14)	1.424	R(11,12)	1.3758	R(11,47)	1.0836	R(12,13)	1.441
R(12,15)	1.3906	R(13,14)	1.3701	R(13,17)	1.3855	R(14,53)	1.0841
R(15,16)	1.321	R(15,46)	1.9384	R(16,17)	1.3821	R(16,18)	1.4476
R(17,23)	1.0082	R(18,19)	1.3784	R(18,22)	1.7527	R(19,20)	1.4198
R(19,48)	1.0825	R(20,21)	1.3697	R(20,54)	1.0832	R(21,22)	1.7302
R(21,55)	1.0809	R(24,25)	1.4289	R(24,29)	1.3694	R(24,56)	1.0862
R(25,26)	1.3691	R(25,57)	1.0861	R(26,27)	1.4301	R(26,58)	1.0852
R(27,28)	1.4461	R(27,30)	1.3395	R(28,29)	1.4295	R(28,33)	1.3406
R(29,59)	1.0853	R(30,31)	1.3463	R(31,32)	1.4626	R(31,34)	1.4212
R(32,33)	1.3448	R(32,37)	1.4232	R(34,35)	1.3773	R(34,60)	1.0836
R(35,36)	1.4462	R(35,38)	1.3839	R(36,37)	1.3721	R(36,40)	1.3824
R(37,61)	1.0838	R(38,39)	1.3188	R(39,40)	1.3859	R(39,41)	1.4503
R(40,46)	1.0288	R(41,42)	1.3778	R(41,45)	1.7514	R(42,43)	1.4199
R(42,62)	1.0826	R(43,44)	1.3702	R(43,63)	1.0837	R(44,45)	1.7318
R(44,64)	1.081	R(45,48)	4.0556				

Table S5 DFT computed selected bond angles for **IM**-Ag^+.

Bond angle	Angle/°	Bond angle	Angle/°	Bond angle	Angle/°
A(2,1,6)	120.87	A(2,1,49)	119.107	A(6,1,49)	120.0231
A(1,2,3)	120.8081	A(1,2,50)	119.1266	A(3,2,50)	120.0653
A(2,3,4)	120.1969	A(2,3,51)	122.2527	A(4,3,51)	117.5504
A(3,4,5)	118.9809	A(3,4,7)	119.4579	A(5,4,7)	121.5612
A(4,5,6)	118.9472	A(4,5,10)	121.528	A(6,5,10)	119.5248
A(1,6,5)	120.1969	A(1,6,52)	122.198	A(5,6,52)	117.6051
A(4,7,8)	117.4115	A(7,8,9)	120.9677	A(7,8,11)	118.5821
A(9,8,11)	120.4501	A(8,9,10)	121.2359	A(8,9,14)	120.2297
A(10,9,14)	118.5343	A(5,10,9)	117.2956	A(8,11,12)	118.2261
A(8,11,47)	119.0823	A(12,11,47)	122.6915	A(11,12,13)	120.6005
A(11,12,15)	129.824	A(13,12,15)	109.5753	A(12,13,14)	123.442
A(12,13,17)	104.1446	A(14,13,17)	132.4135	A(9,14,13)	117.0514
A(9,14,53)	118.9015	A(13,14,53)	124.0471	A(12,15,16)	105.9652
A(12,15,46)	121.9964	A(16,15,46)	131.7492	A(15,16,17)	112.3494
A(15,16,18)	125.0787	A(17,16,18)	122.5718	A(13,17,16)	107.9649
A(13,17,23)	125.9329	A(16,17,23)	126.0436	A(16,18,19)	127.2922
A(16,18,22)	122.0369	A(19,18,22)	110.6704	A(18,19,20)	113.0751
A(18,19,48)	122.6835	A(20,19,48)	124.241	A(19,20,21)	112.953
A(19,20,54)	123.7593	A(21,20,54)	123.2877	A(20,21,22)	111.8319
A(20,21,55)	128.5624	A(22,21,55)	119.6037	A(18,22,21)	91.4686
A(25,24,29)	120.7728	A(25,24,56)	119.1753	A(29,24,56)	120.0519
A(24,25,26)	120.7258	A(24,25,57)	119.1876	A(26,25,57)	120.0865
A(25,26,27)	120.3313	A(25,26,58)	122.1797	A(27,26,58)	117.489
A(26,27,28)	118.9304	A(26,27,30)	119.4809	A(28,27,30)	121.5887
A(27,28,29)	118.9098	A(27,28,33)	121.5622	A(29,28,33)	119.528
A(24,29,28)	120.3298	A(24,29,59)	122.1423	A(28,29,59)	117.5279
A(27,30,31)	117.4489	A(30,31,32)	118.7364	A(32,31,34)	120.3548
A(31,32,33)	121.1345	A(31,32,37)	120.2248	A(33,32,37)	118.6406
A(28,33,32)	117.3567	A(31,34,35)	118.4641	A(31,34,60)	119.2495
A(35,34,60)	122.2863	A(34,35,36)	120.4561	A(34,35,38)	129.7226
A(36,35,38)	109.8212	A(35,36,37)	123.2686	A(35,36,40)	104.6125
A(37,36,40)	132.1185	A(32,37,36)	117.2315	A(32,37,61)	119.0431
A(36,37,61)	123.7253	A(35,38,39)	105.176	A(38,39,40)	113.6767
A(38,39,41)	122.8132	A(40,39,41)	123.5097	A(36,40,39)	106.7119
A(36,40,46)	124.5837	A(39,40,46)	128.6451	A(39,41,42)	125.5604
A(39,41,45)	123.685	A(42,41,45)	110.7545	A(41,42,43)	113.1554
A(41,42,62)	121.5211	A(43,42,62)	125.3234	A(42,43,44)	112.7957
A(42,43,63)	123.9038	A(44,43,63)	123.3004	A(43,44,45)	111.9142
A(43,44,64)	128.4471	A(45,44,64)	119.6387	A(41,45,44)	91.3801
A(41,45,48)	79.3565	A(44,45,48)	145.0939		

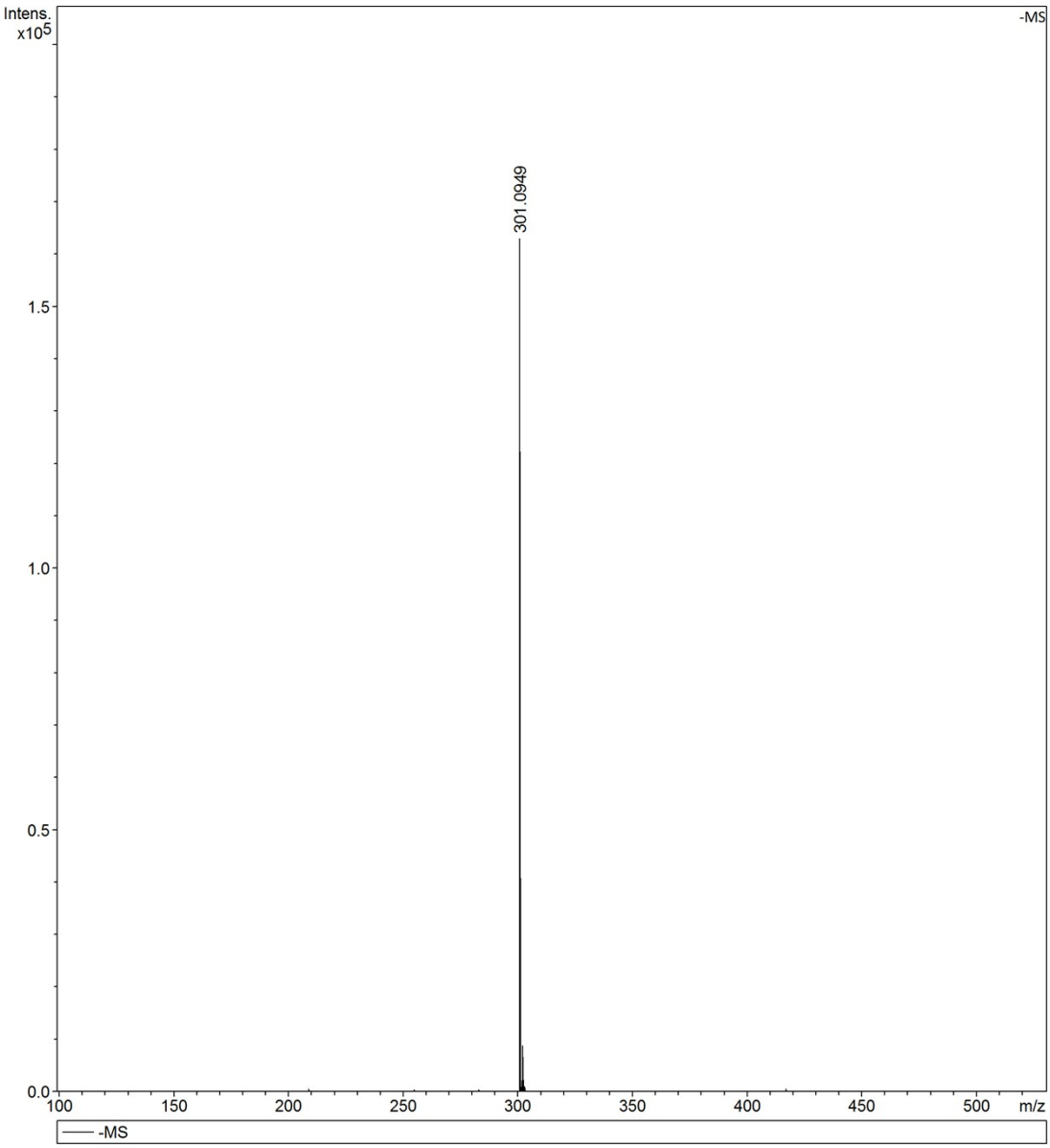

Fig. S14 ESI-MS spectrum of **IM**.

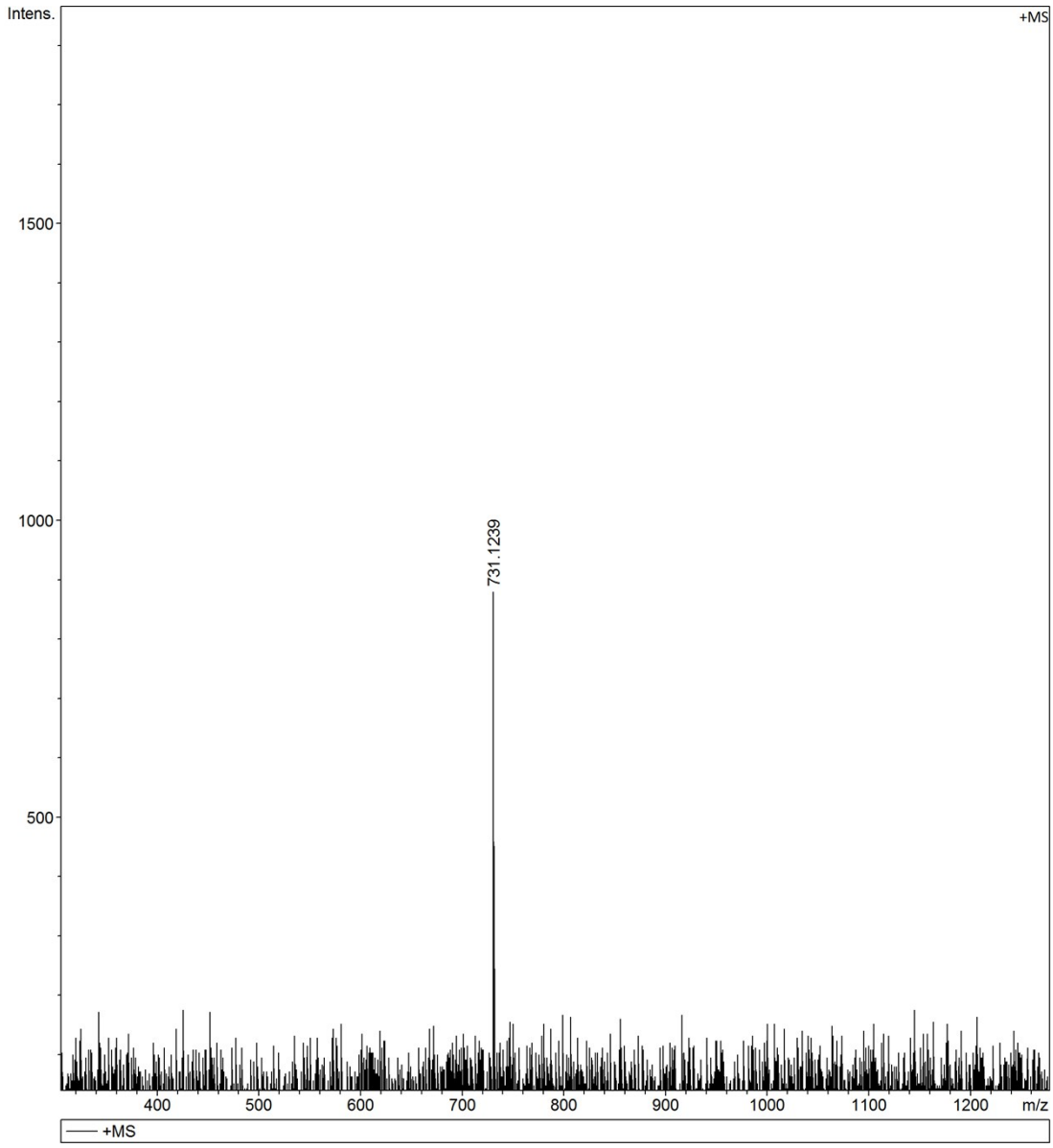

Fig. S15 ESI-MS spectrum of **IM**-Ag^{+}.

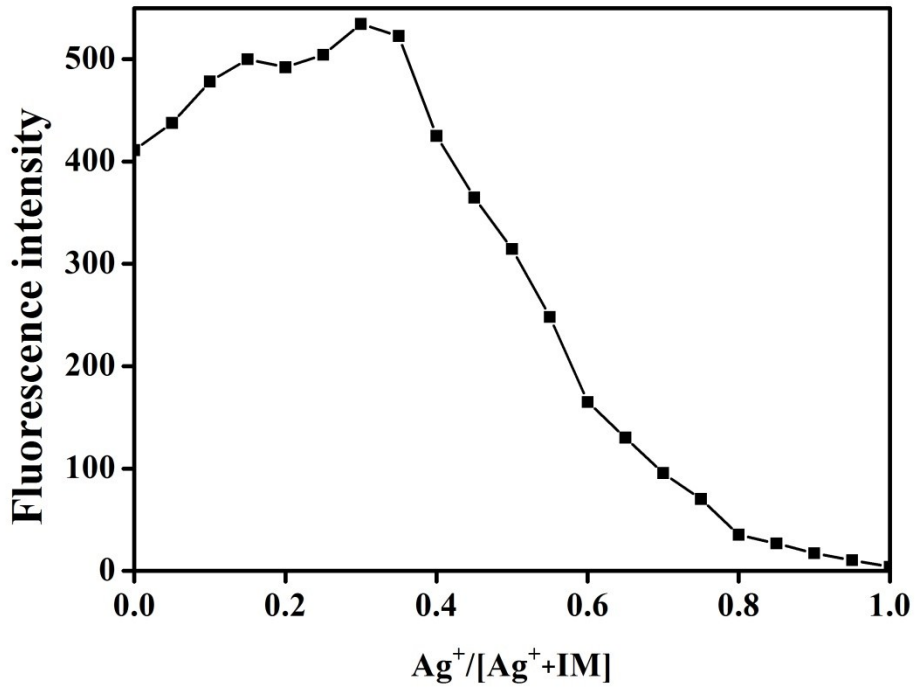

Fig. S16 The Job's plot examined between Ag^+ and **IM**, indicating the 2 : 1 stoichiometry, which was carried out by fluorescence spectra (λex = 400 nm).

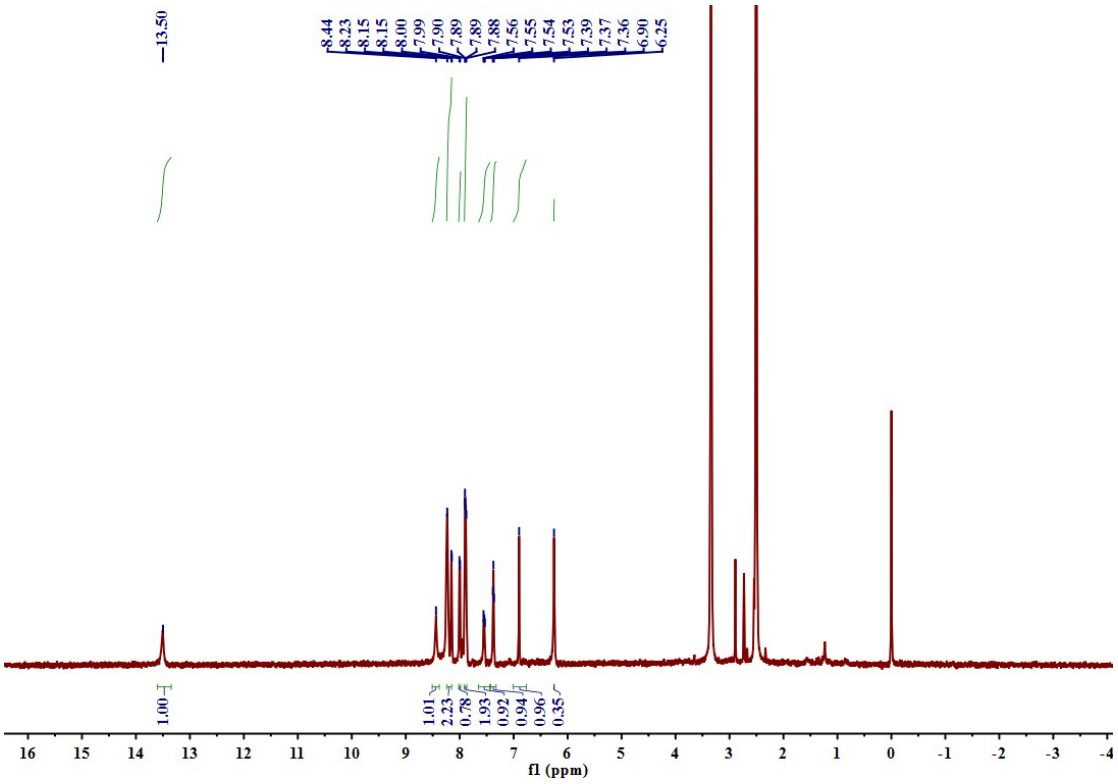

Fig. S17 ^1H NMR spectra of compound **IM**.

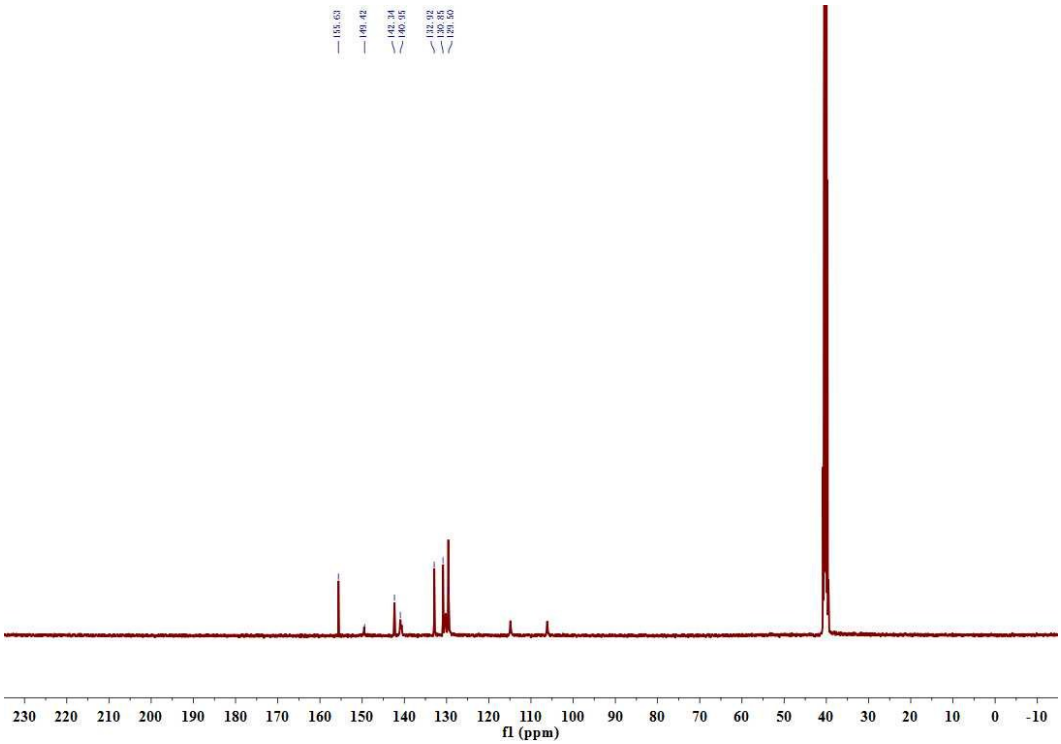

Fig. S18 ^{13}C NMR spectra of compound **IM**.

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