Electronic Supplementary Material (ESI) for Dalton Transactions.

Tuning of azine derivatives for selective recognition of Ag^+ with *in vitro* tracking of endophytic bacteria in rice root tissue

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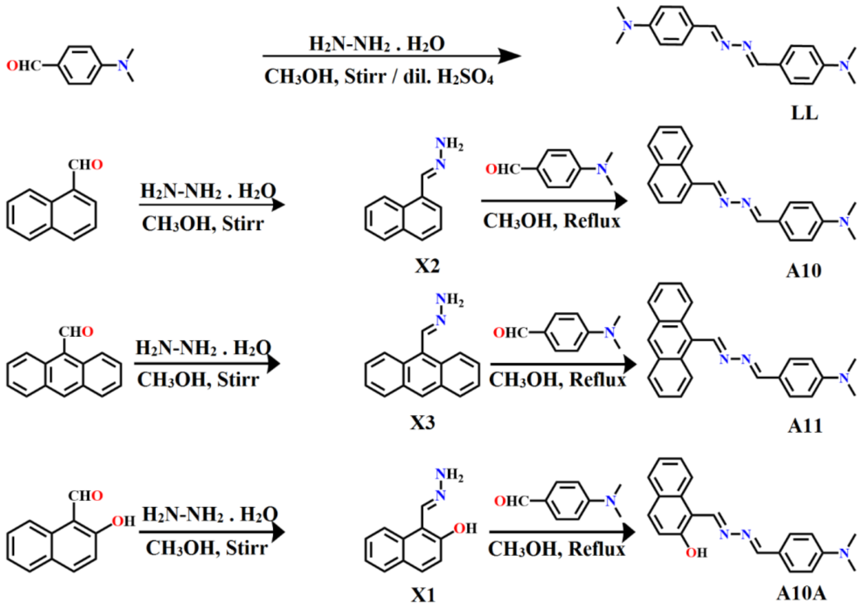

Scheme S1 Synthetic protocol of the probes

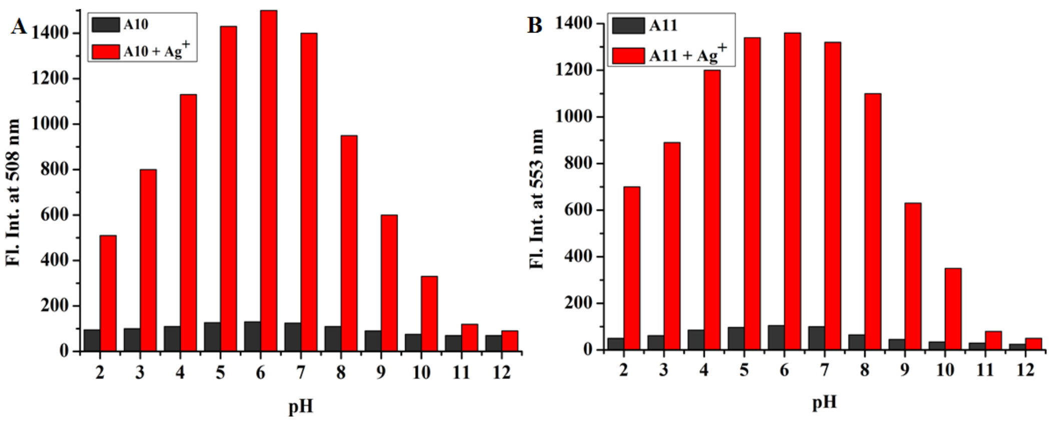

Fig.S1 Effect of pH on the emission intensities of (A) A10 **(**λ_{ex} = 410 nm; λ_{em} = 508 nm) and **(**B) A11 (λ_{ex} = 440 nm; λ_{em} = 553 nm) (20 µM) before and after addition Ag^+ (30 equiv.)

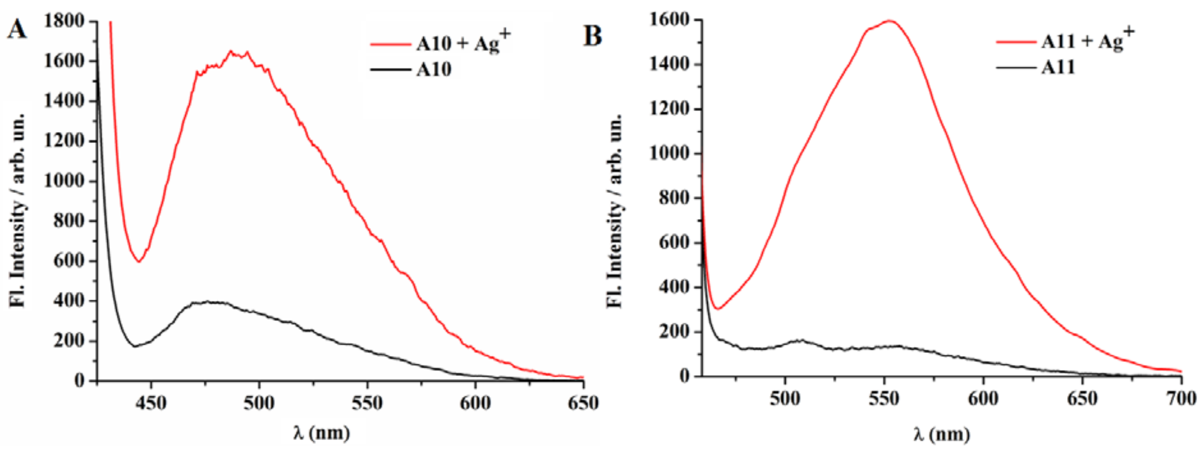

Fig.S2 Effect of Ag^+ (600 µM) on the emission spectrum of (A) A10 and (B) A11 (20 µM) in methanol

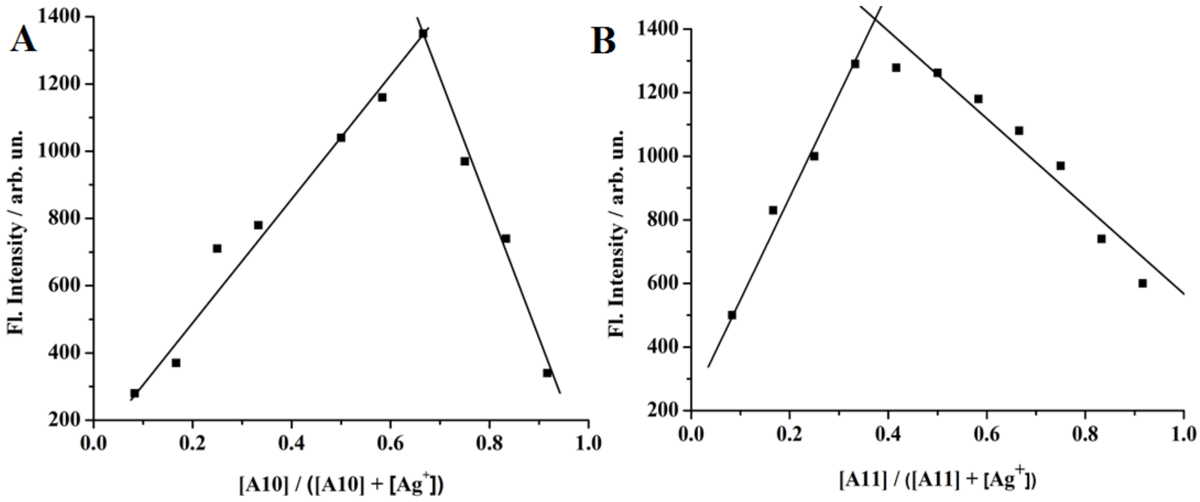

Fig.S3 Job's plot for determination of stoichiometry of the adduct of (A) A10 and (B) A11 with Ag^+

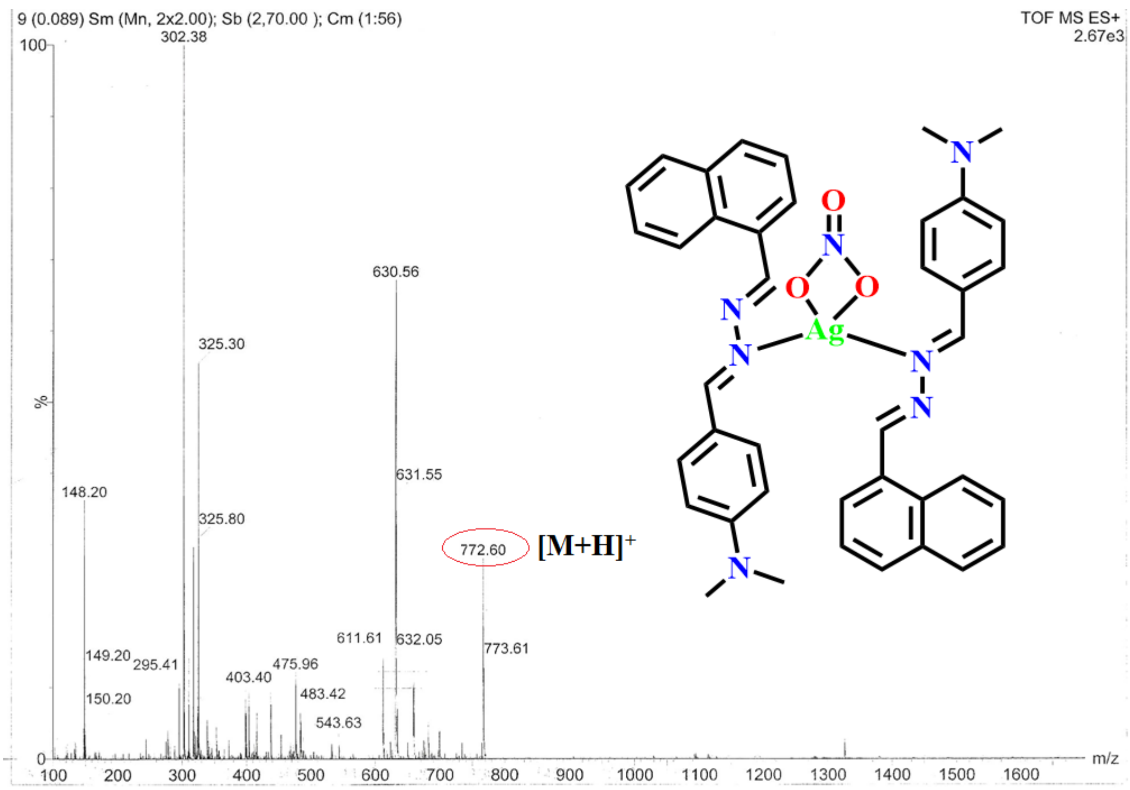

Fig.S4 ESI-MS spectrum of the Ag^+ complex of A10 in methanol

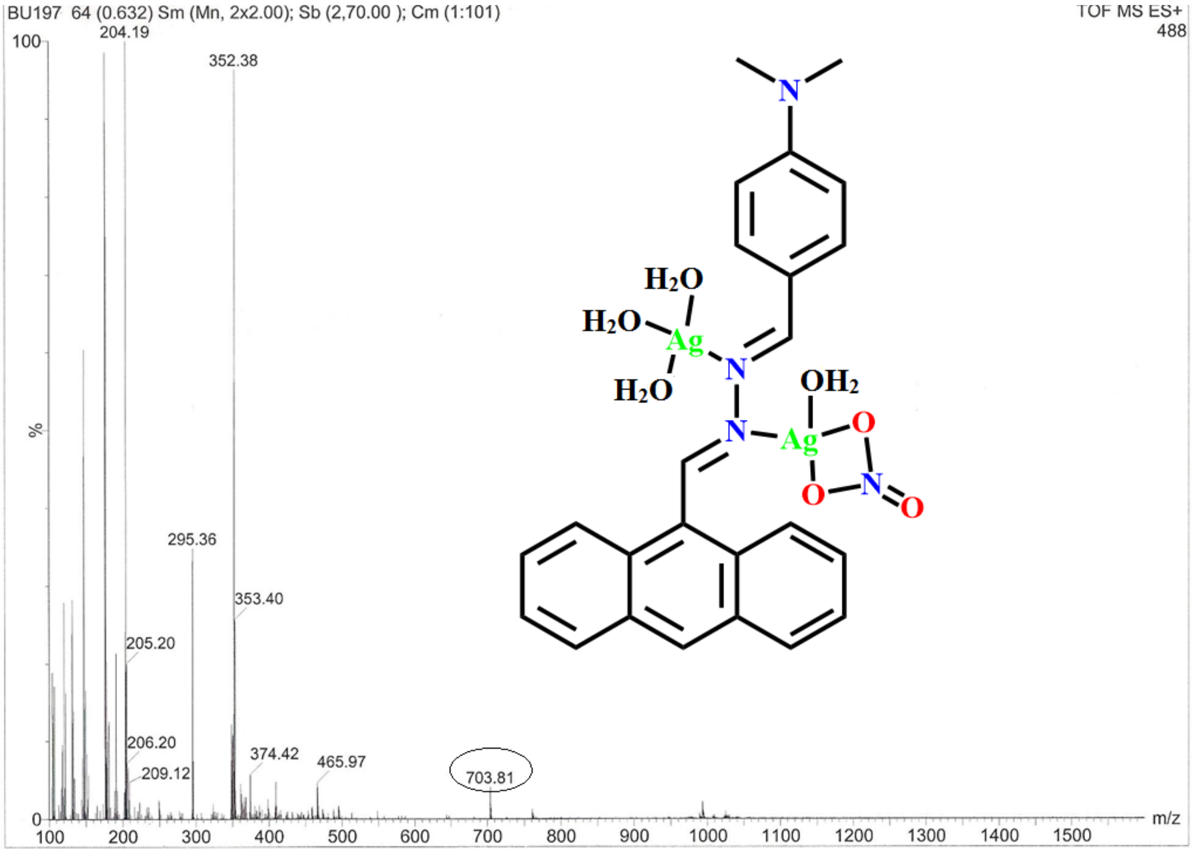

Fig.S5 ESI-MS spectrum of the Ag^+ complex of A11 in methanol

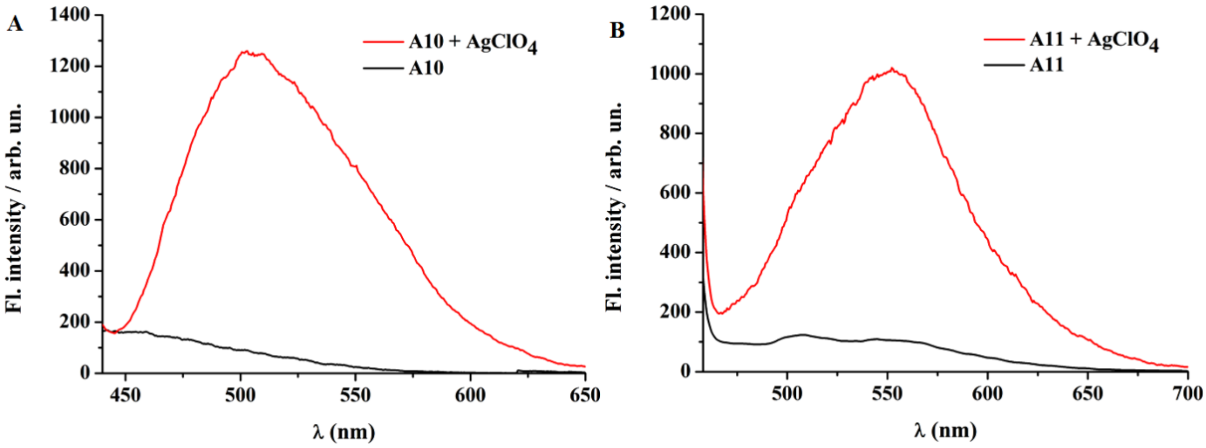

Fig.S6 Changes in the emission spectrum of (A) A10 and (B) A11 (20 μM in methanol-water (4: 1, v/v) upon addition of $AgClO_4$ (600 μM)

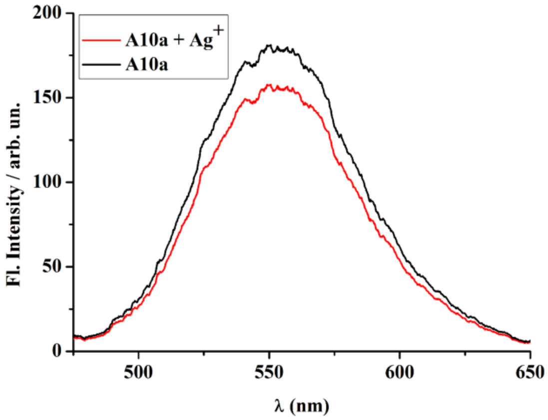

Fig.S7 Effect of Ag^{+} (100 µM) on the emission spectrum of A10a (10 µM, λ_{ex}, 445 nm; $\lambda_{em,}$ 535 nm) in methanol-water (4: 1, v/v)

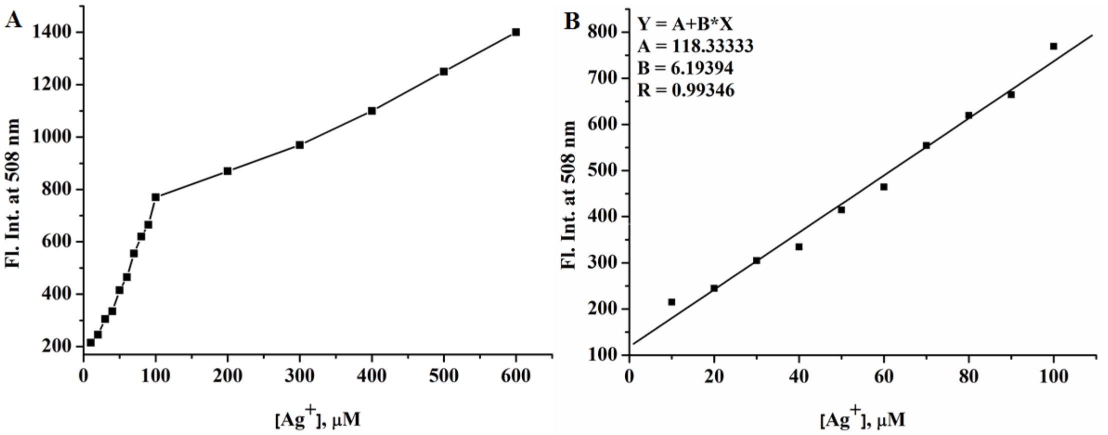

Fig.S8 Emission intensities of A10 (20 µM, methanol– water (4 : 1, v/v, 0.1 M HEPES buffer, pH 7.4, λ_{ex}, 410 nm; $\lambda_{em,}$ 508 nm) as a function of added Ag^{+} (0- 600 µM). Linear region of the plot (right)

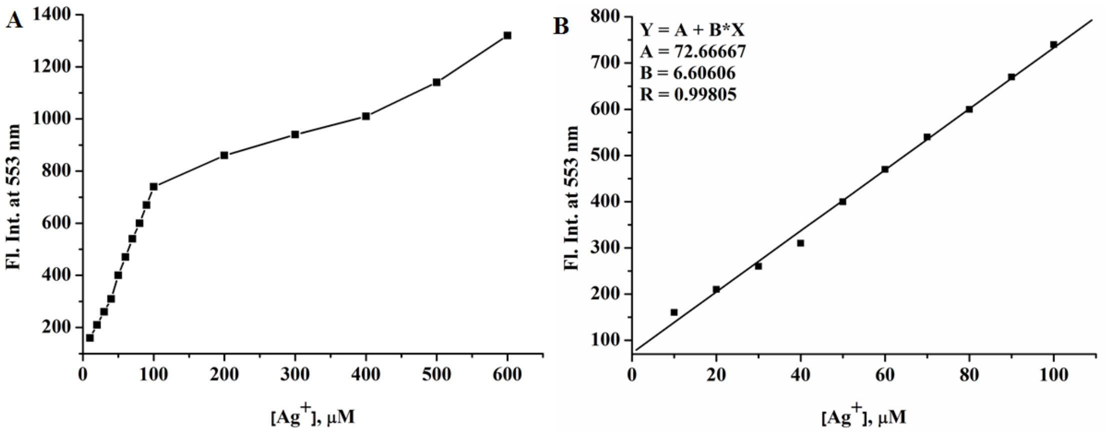

Fig.S9 Emission intensities of A11 (20 µM, methanol– water (4 : 1, v/v, 0.1 M HEPES buffer, pH 7.4, λ_{ex}, 440 nm; $\lambda_{em,}$ 553 nm) as a function of added Ag^{+} (0- 600 µM). Linear region of the plot (right)

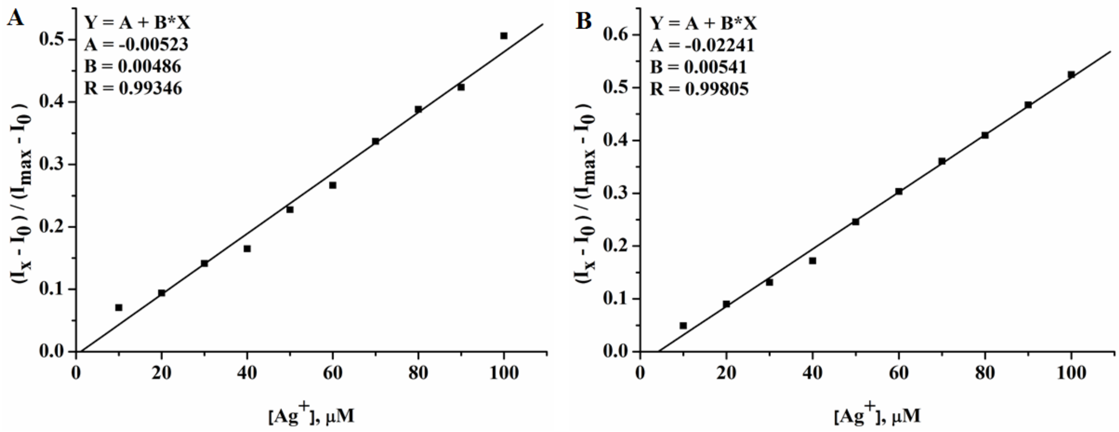

Fig.S10 Emission intensities of (A) A10 (20 μM, λ_{ex}, 410 nm; λ_{em}, 508 nm, from Fig. 6A); (B) A11 (20 μM, λ_{ex}, 440 nm; λ_{em}, 553 nm from Fig. 6B) as a function of added Ag^+ in methanol– water (4 : 1, v/v), 0.1 M HEPES buffer, pH 7.4

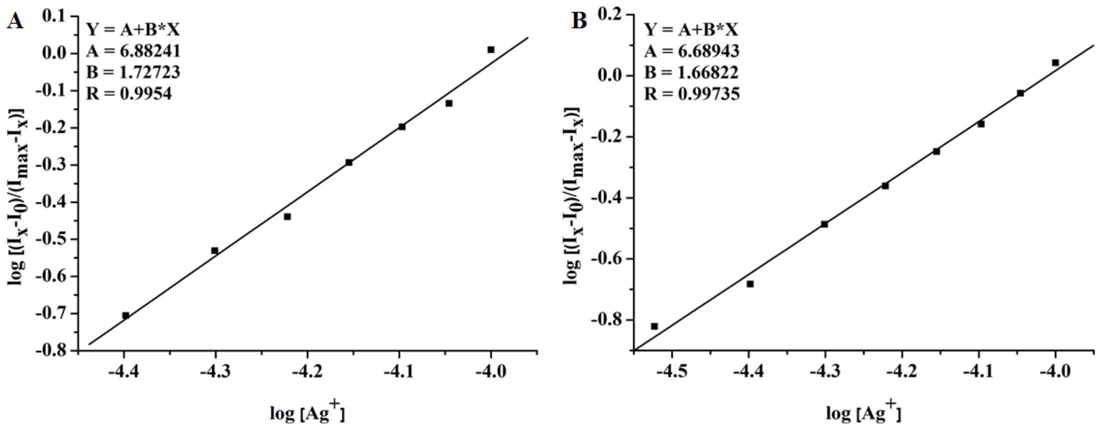

Fig.S11 Hill plot for determination of binding constant of (A) A10 and (B) A11 towards Ag^+ in 4:1 methanol-water (data used from Fig.6A and 6B)

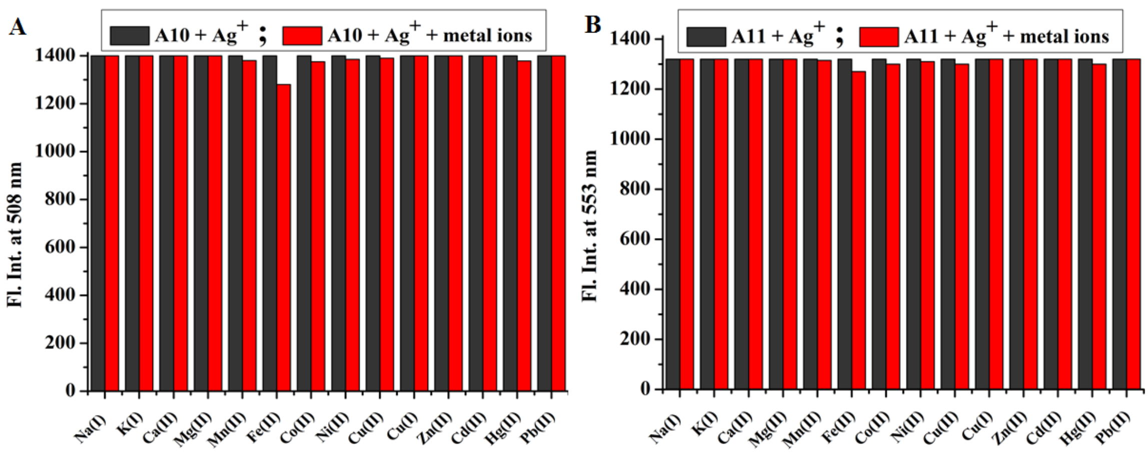

Fig.S12 Effect of common cations on the emission intensities of (A) [A10 + Ag^+] system (λ_{ex}, 410 nm; λ_{em}, 508 nm) and (B) [A11+Ag^+] system (λ_{ex}, 440 nm; λ_{em}, 553 nm) (methanol– water, 4 : 1, v/v, 0.1 M HEPES buffer, pH 7.4)

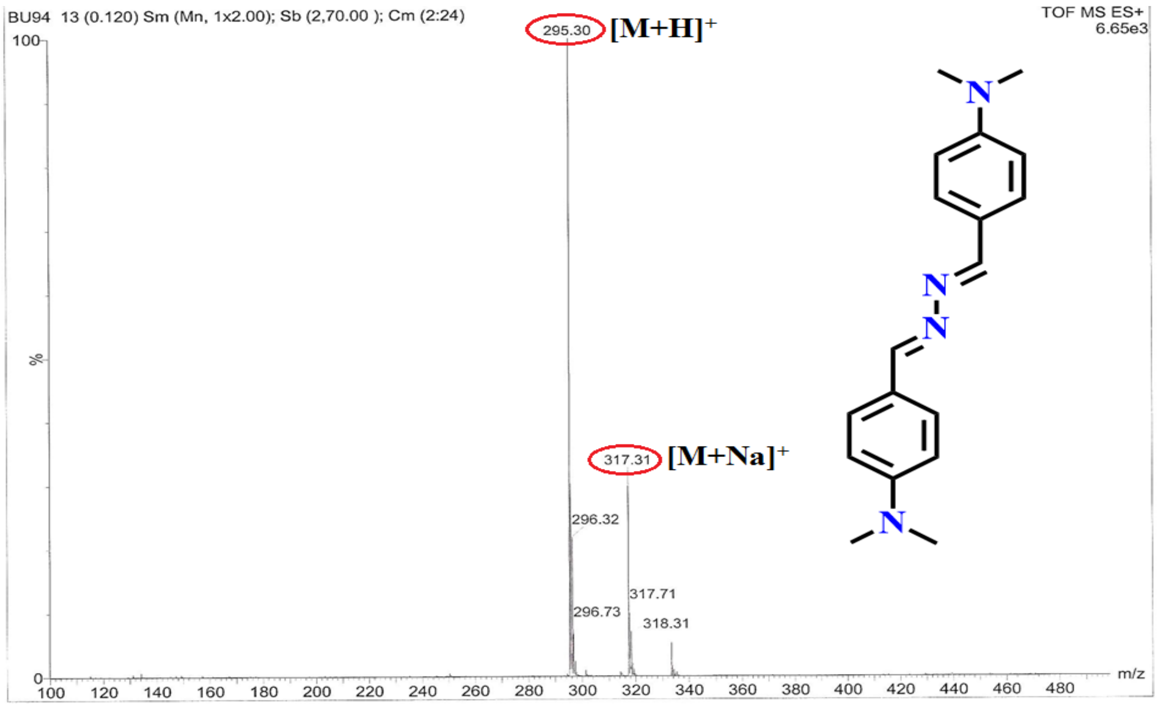

Fig.S13 Mass spectrum of LL

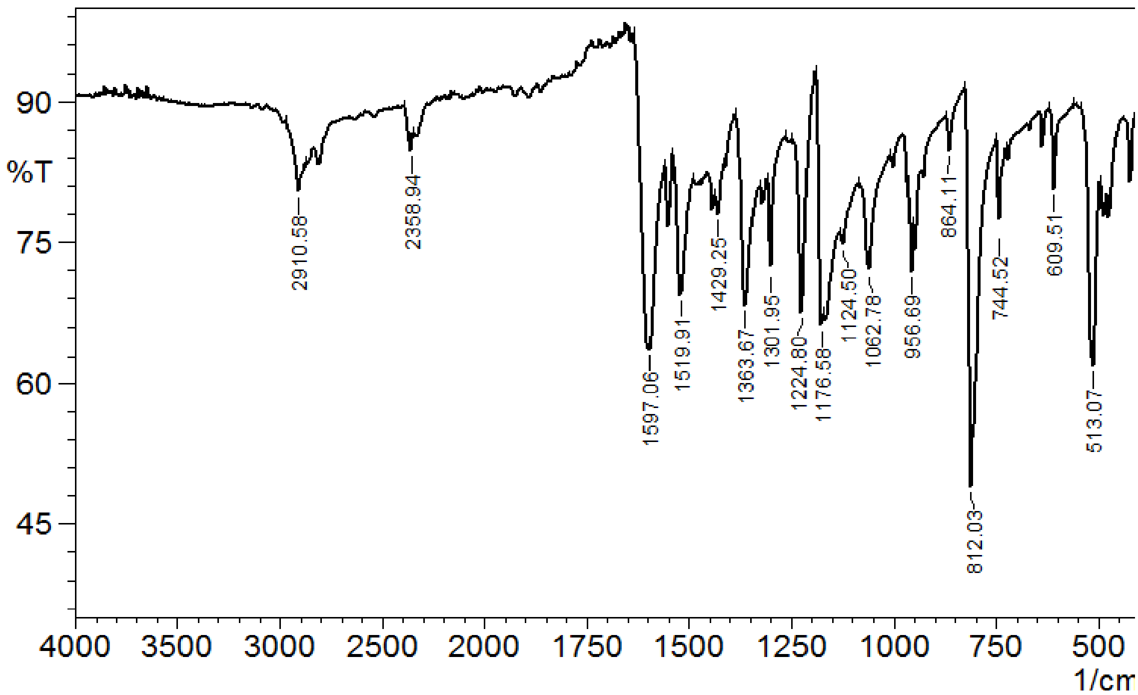

Fig.S14 FTIR spectrum of LL

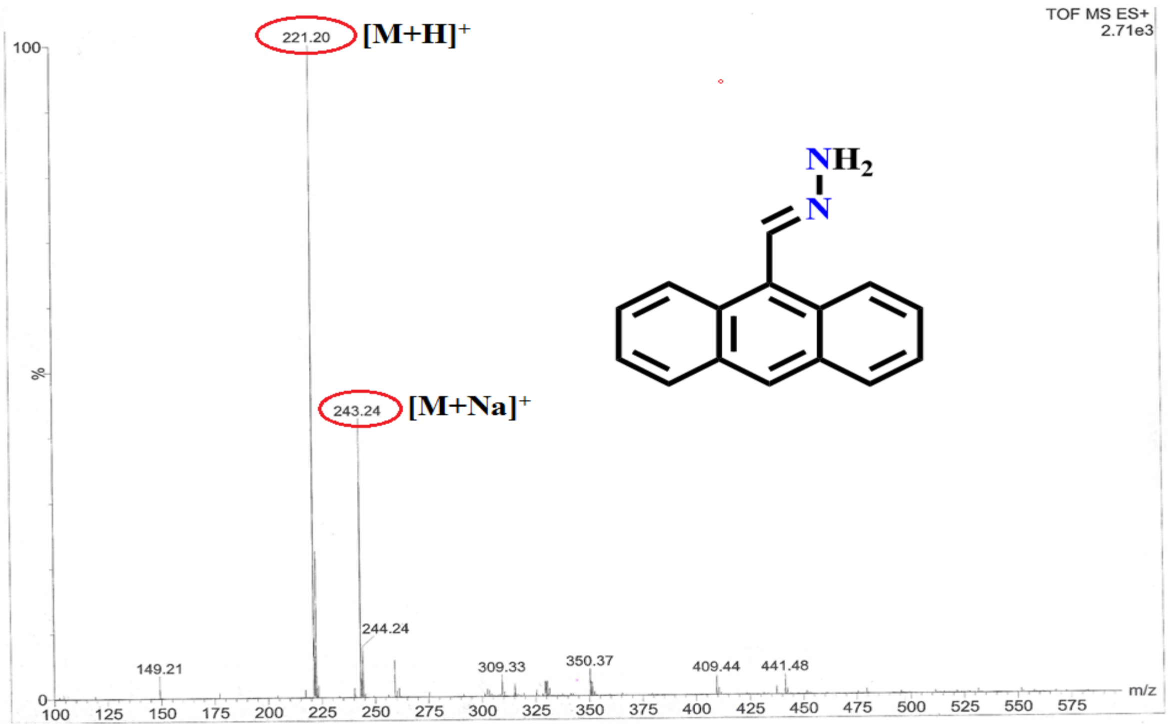

Fig.S15 Mass spectrum of X3

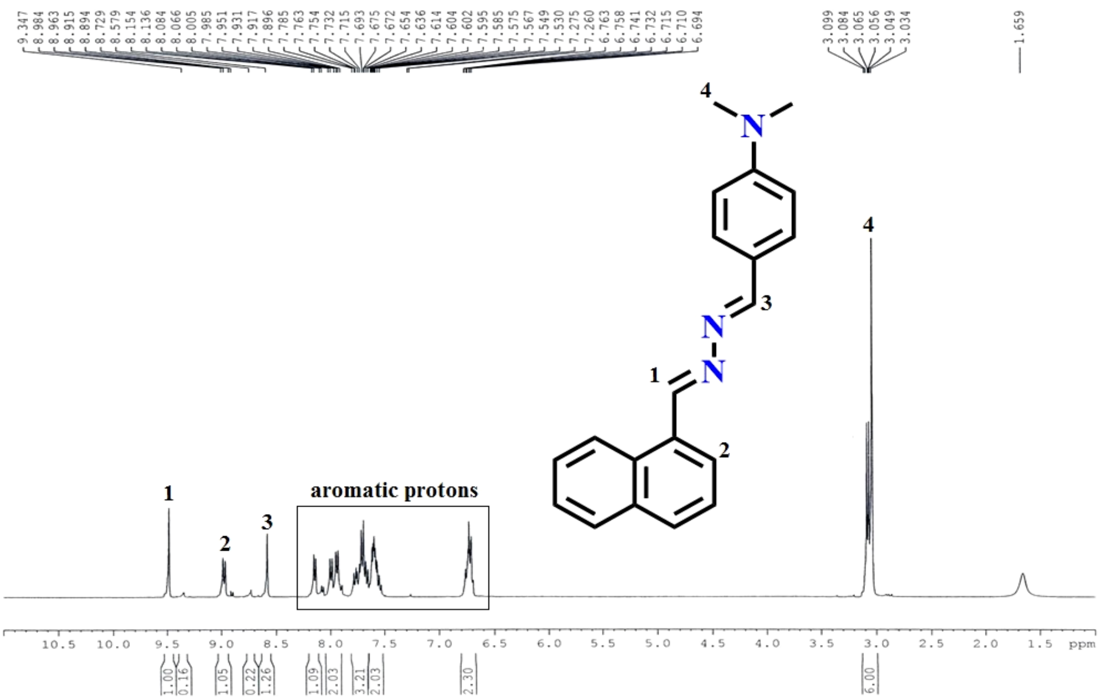

Fig.S16 ^{1}H NMR spectrum of A10 in $CDCl_3$

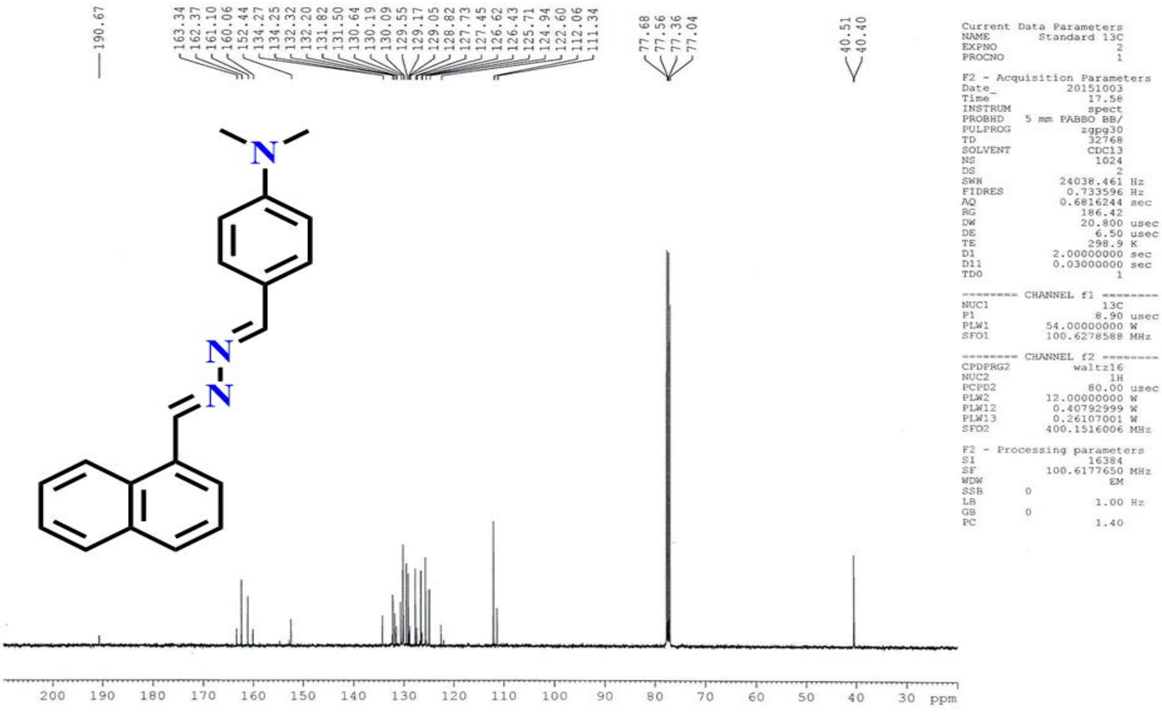

Fig.S17 ^{13}C NMR spectrum of A10 in $CDCl_3$

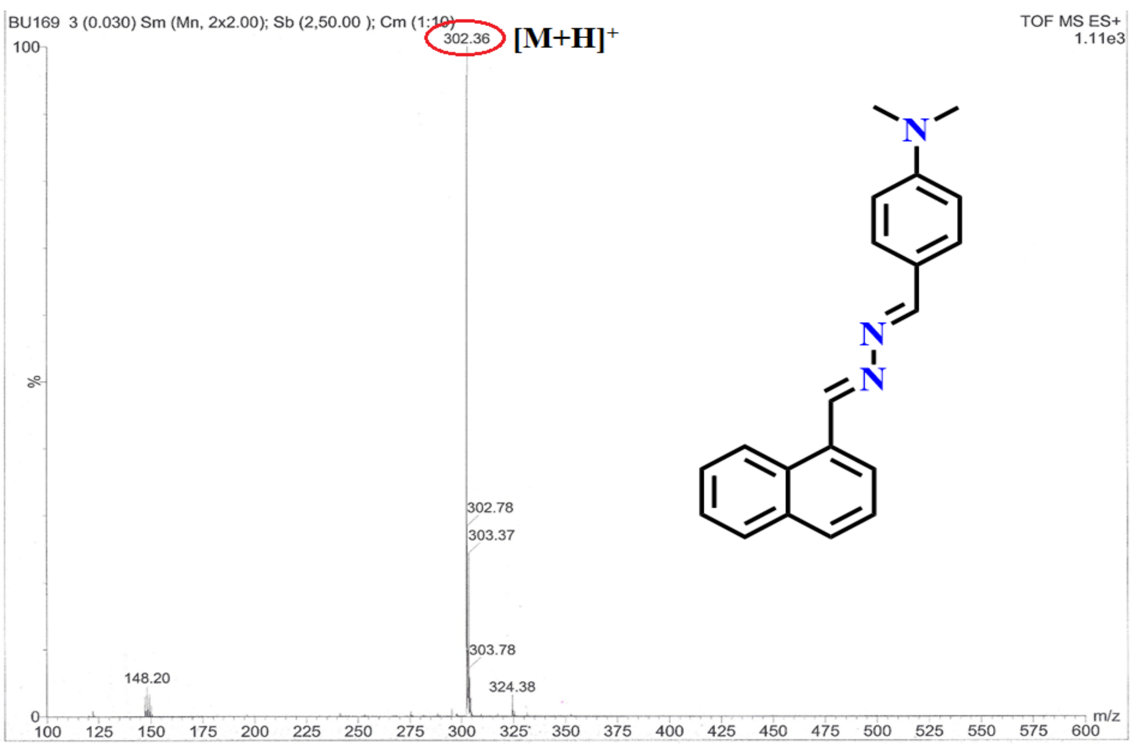

Fig.S18 Mass spectrum of A10

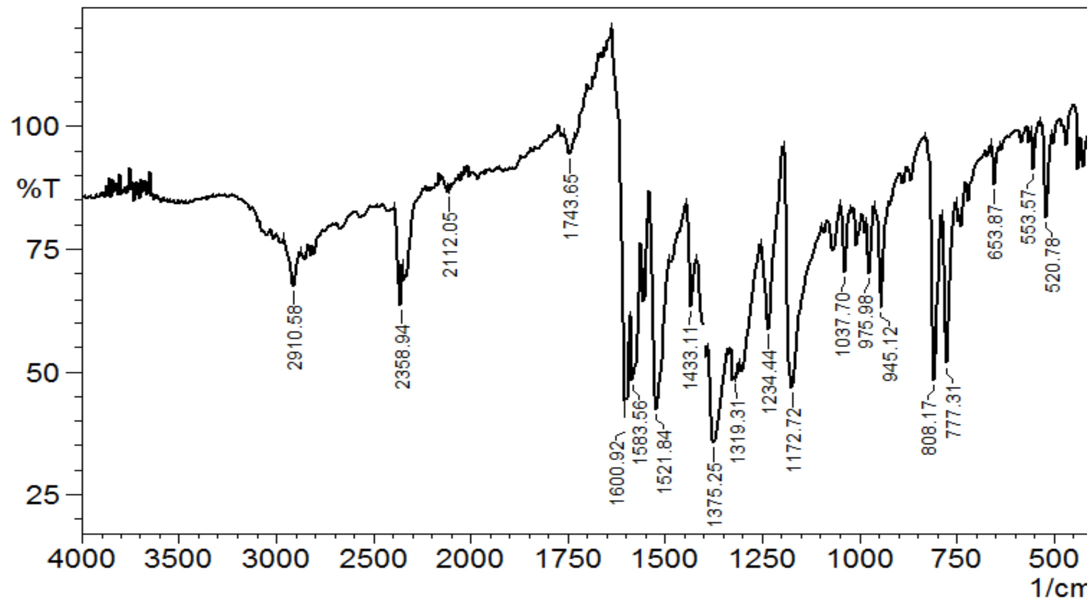

Fig.S19 FTIR spectrum of A10

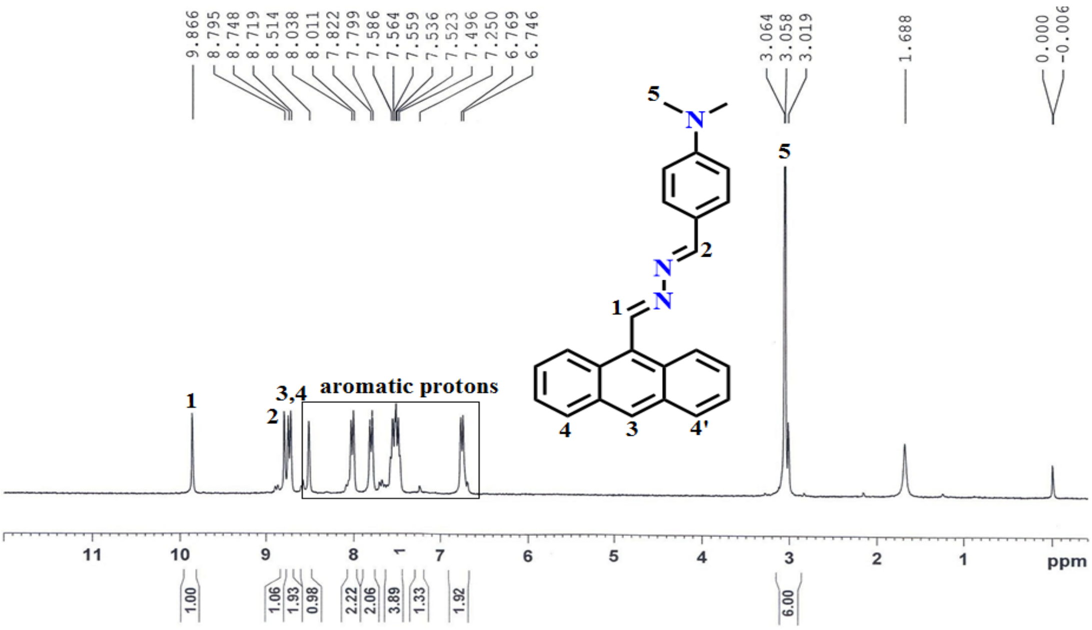

Fig.S20 ^{1}H NMR spectrum of A11 in $CDCl_3$

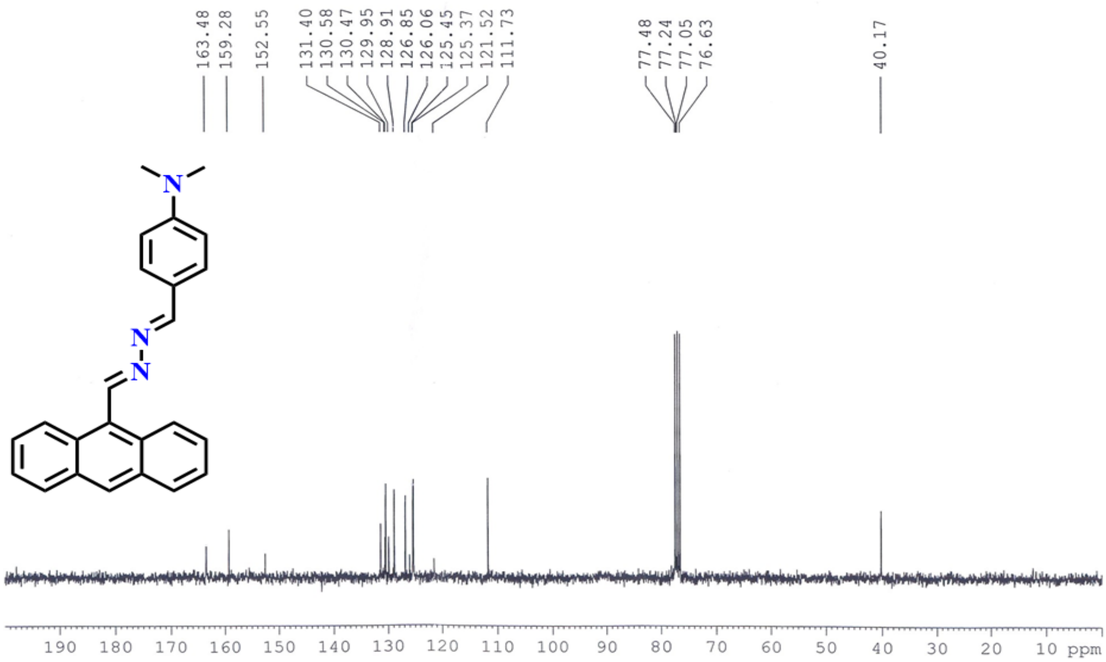

Fig.S21 ^{13}C NMR spectrum of A11 in $CDCl_3$

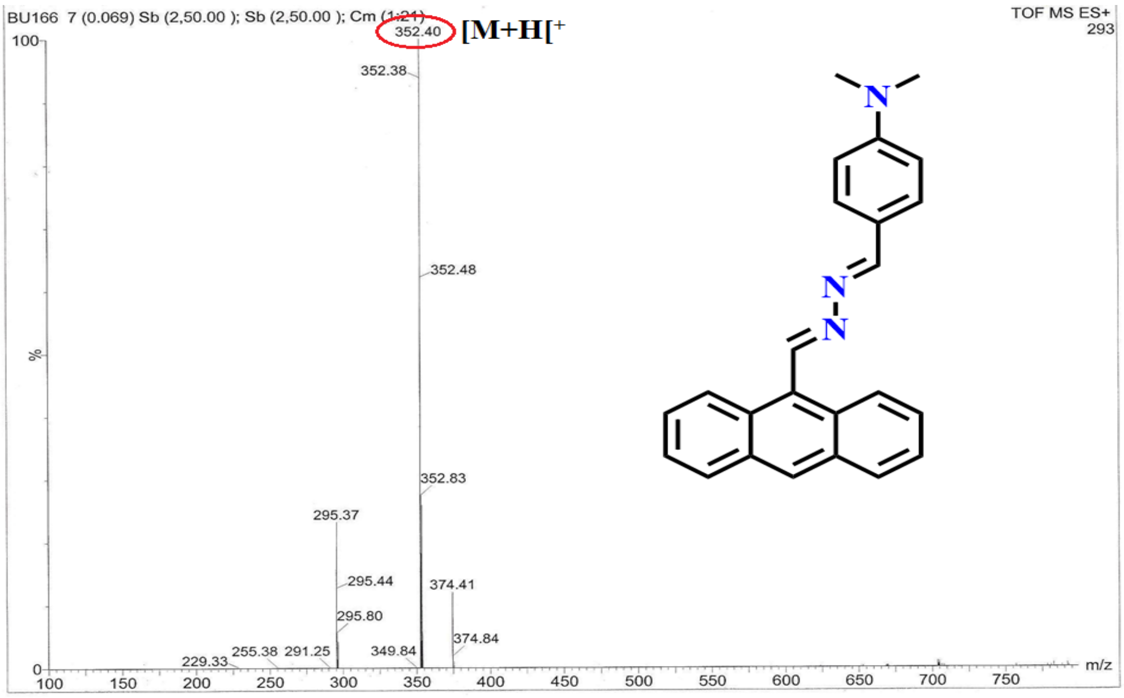

Fig.S22 Mass spectrum of A11

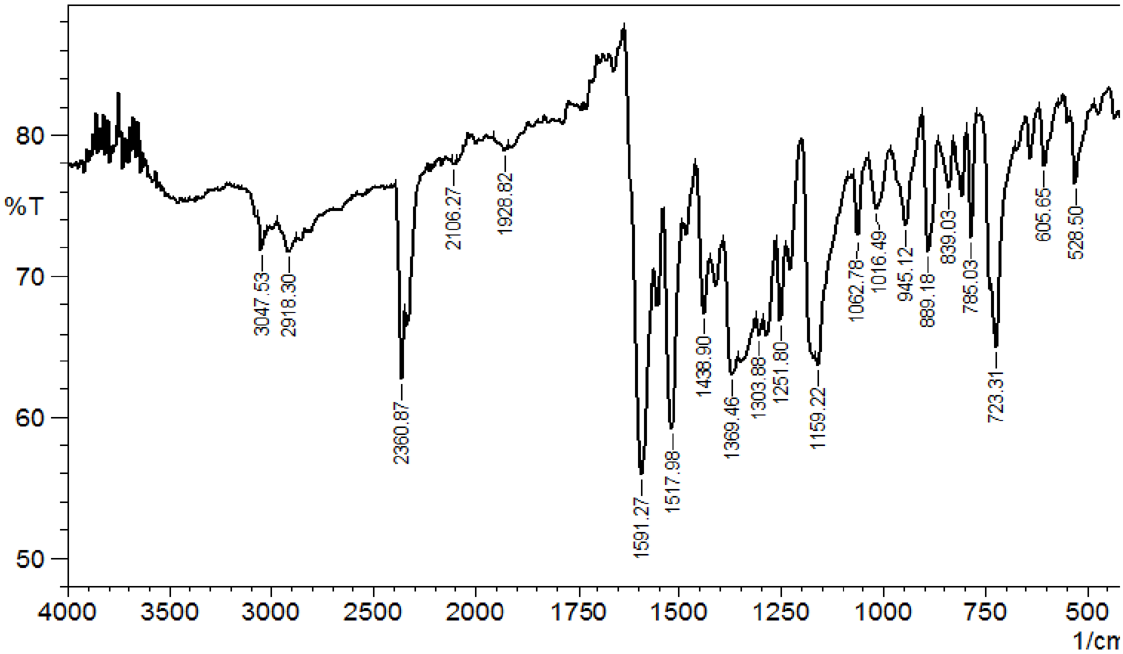

Fig.S23 FTIR spectrum of A11

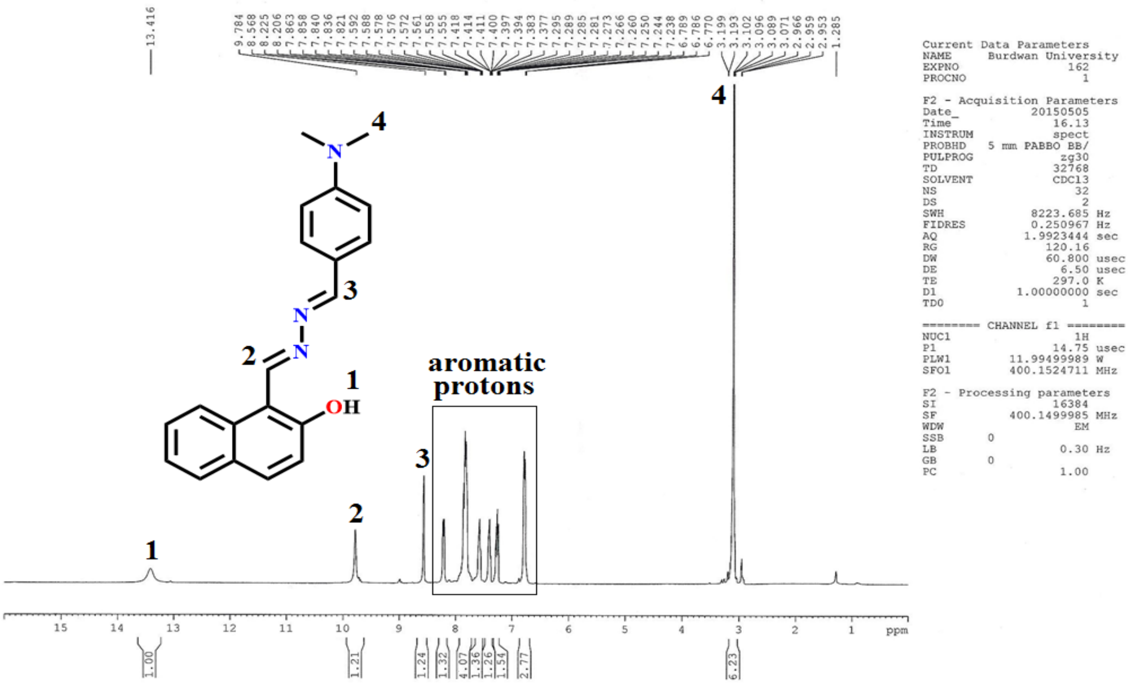

Fig.S24 ^{1}H NMR spectrum of A10a in $CDCl_3$

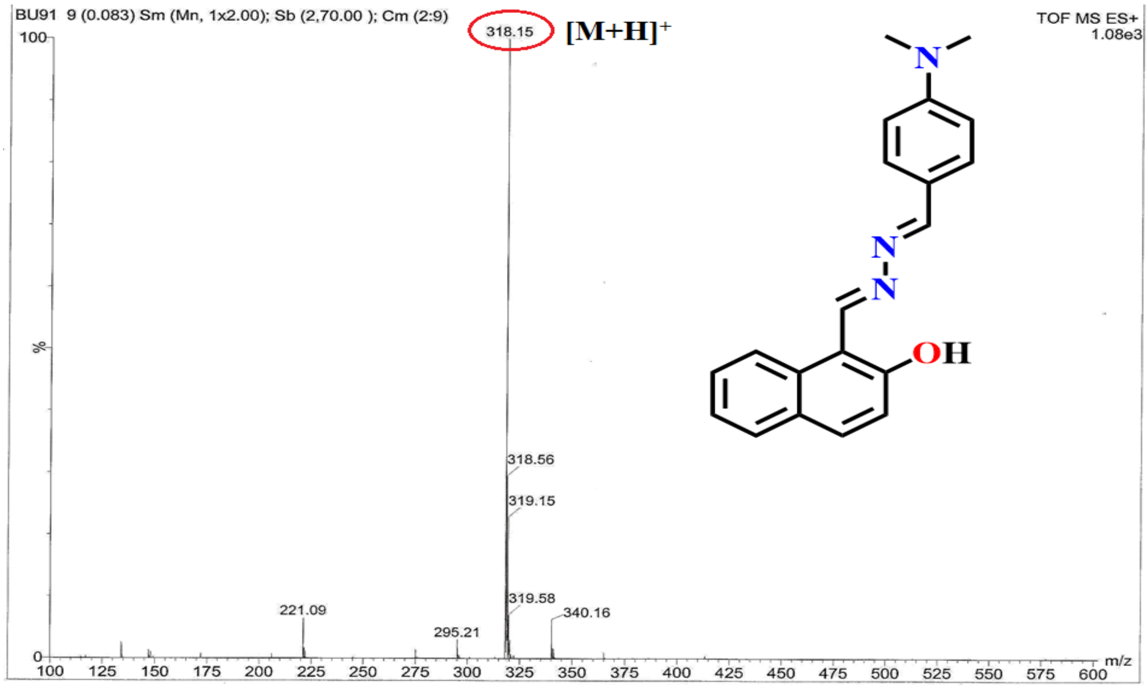

Fig.S25 Mass spectrum of A10a

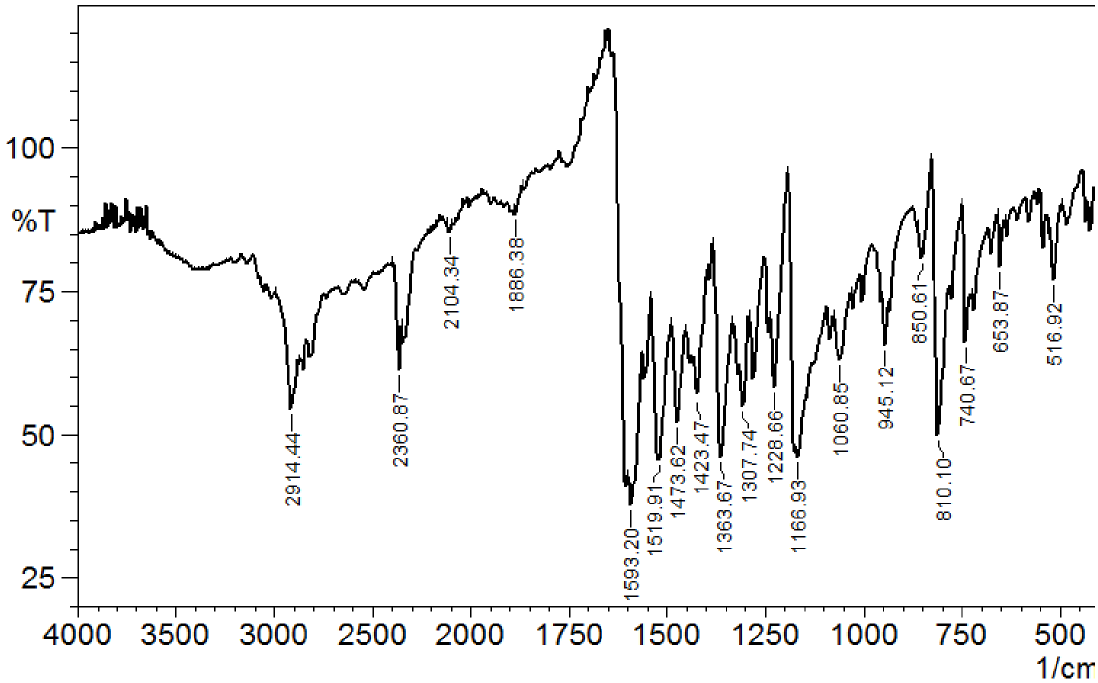

Fig.S26 FTIR spectrum of A10a

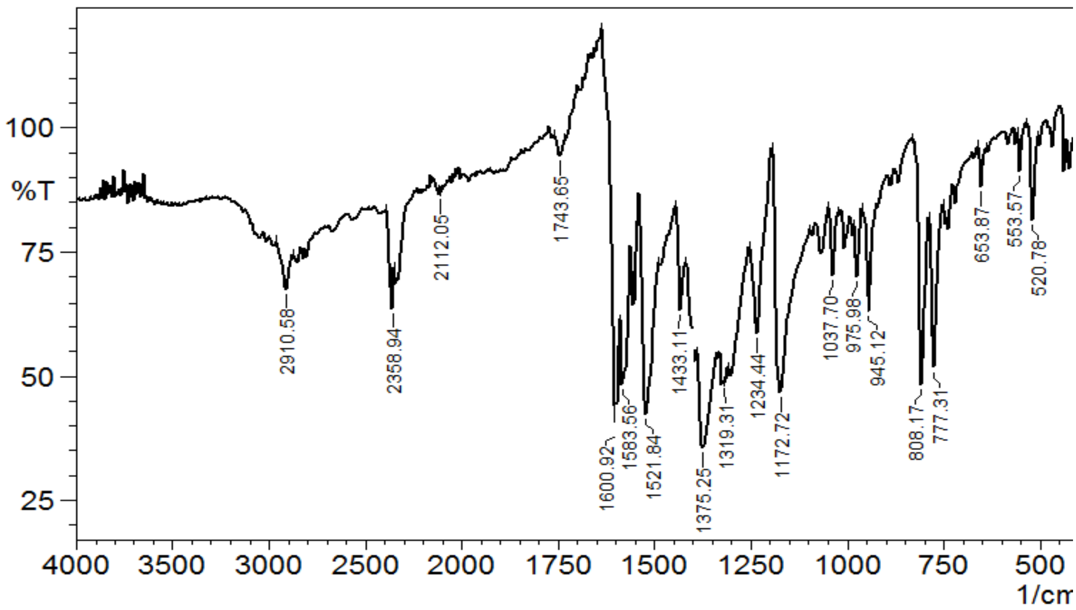

Fig.S27 FTIR spectrum of [A10- Ag^{+}] system

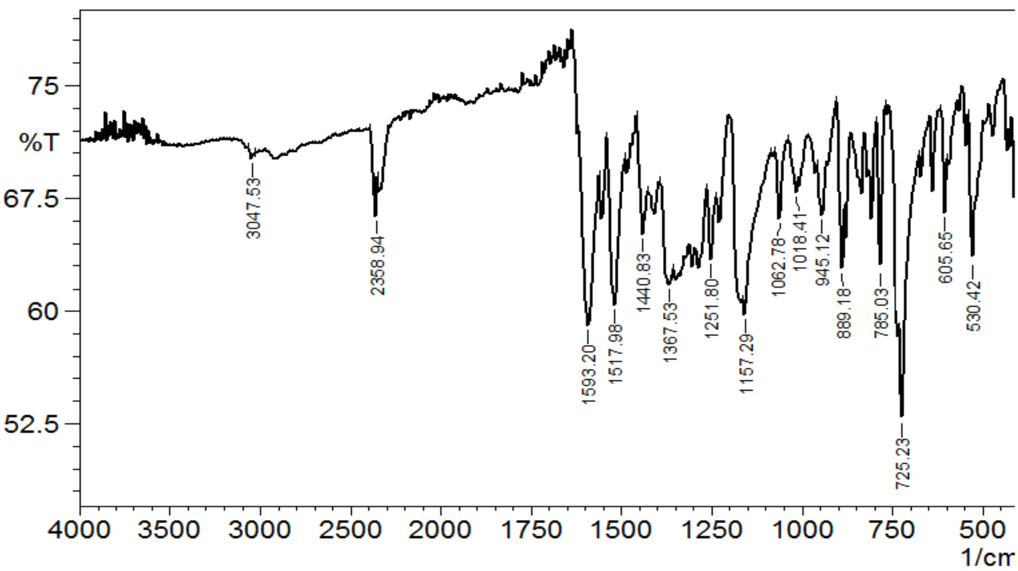

Fig.S28 FTIR spectrum of [A11- Ag^{+}] system

Table S1 Crystal data and selected refinement details of ligands LL, A11 and A10a.

Compound	LL	A11	A10a
Empirical formula	$C_{18}H_{22}N_4$	$C_{24}H_{21}N_3$	$C_{20}H_{19}N_3O$
Formula weight	294.39	351.44	317.38
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$/c	$P2_1$/n	$P2_1$/c
a /Å	5.9874(4)	11.0729(5)	14.6785(9)
b /Å	7.3745(6)	6.3772(3)	6.2745(4)
c /Å	18.9986(15)	26.6135(12)	19.1494(12)
β /º	90.499(5)	98.155(3)	107.356(4)
V /Å^3	838.83(11)	1860.28(15)	1683.36(19)
Z	2	4	4
ρ_{calc} /gcm^{-3}	1.166	1.255	1.252
μ /mm^{-1}	0.071	0.075	0.079
F(000)	316.0	744.0	672.0
Crystal size /mm^3	0.18 x 0.10 x 0.04	0.20 x 0.13 x 0.06	0.17 x 0.10 x 0.04
θ range for data collection /°	3.50-28.38	3.55-26.60	1.45-24.78°
Index ranges	$-7\leq h\leq 7$, $-9\leq k\leq 9$, $-25\leq l\leq 23$	$-13\leq h\leq 13$, $-7\leq k\leq 7$, $-33\leq l\leq 32$	$-17\leq h\leq 17$, $-7\leq k\leq 7$, $-22\leq l\leq 22$
Reflections collected	14229	27818	21778
Independent reflections	2074 [R_{int} = 0.0288]	3847 [R_{int} = 0.0341]	2890 [R_{int} = 0.0666]
Data/restraints/parameters	2074/0/103	3847/0/247	2890/0 /224
Goodness-of-fit on F^2	1.040	1.035	1.005
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0475, wR_2 = 0.1406	R_1 = 0.0446, wR_2 = 0.1155	R_1 = 0.0504, wR_2 = 0.1349
Final R indexes [all data]	R_1 = 0.0761, wR_2 = 0.1665	R_1 = 0.0800, wR_2 = 0.1335	R_1 = 0.0963, wR_2 = 0.1645
Largest diff. peak/hole /eÅ^{-3}	0.17/-0.12	0.15/-0.12	0.16/-0.15

Table S2 Crystal data and selected refinement details of Ag(I) complexes.

Compound	$[Ag_2(LL)_2(NO_3)_2].CH_2Cl_2$	$[Ag_n(A11)_n (H_2O)_n(NO_3)_n]$	$[Ag(A10)(NO_3)]$
Empirical formula	$C_{55}H_{68}Ag_2Cl_2N_{14}O_6$	$C_{24}H_{21.55}AgN_4O_{3.27}$	$C_{40}H_{38}AgN_7O_3$
Formula weight	1307.87	526.23	772.64
Crystal system	Triclinic	Monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$C2/c$
a /Å	9.7677(6)	7.425(5)	18.5211(5)
b /Å	11.6665(6)	26.399(5)	14.6350(5)
c /Å	13.4972(8)	10.871(5)	13.6223(4)
α /º	71.209(2)	(90)	(90)
β /º	76.812(2)	100.611(5)	111.121(2)
γ /º	79.526(2)	(90)	(90)
V /Å^3	1407.87(14)	2094.4(18)	3444.36(19)
Z	1	4	4
ρ_{calc} /gcm^{-3}	1.543	1.669	1.490
μ /mm^{-1}	0.854	1.000	0.636
F(000)	672	1067	1592
Crystal size /mm^3	0.14x0.06x0.03	0.20x0.16x0.05	0.16x0.10x0.08
θ range for data collection /°	2.08-30.62	1.54-28.28	1.82-29.20
Index ranges	$-13\leq h\leq 13$, $-16\leq k\leq 16$, $-19\leq l\leq 19$	$-9\leq h\leq 9$, $-34\leq k\leq 35$, $-14\leq l\leq 14$	$-25\leq h\leq 25$, $-19\leq k\leq 20$, $-16\leq l\leq 18$
Reflections collected	66638	39403	22310
Independent reflections	8626 [R_{int} = 0.0313]	5190 [R_{int} = 0.0384]	4655 [R_{int} = 0.0397]
Data/restraints/parameters	8626/0/376	5190/0/319	4655/0/234
Goodness-of-fit on F^2	1.044	1.131	1.032
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0255, wR_2 = 0.0644	R_1 = 0.0414, wR_2 = 0.0875	R_1 = 0.0409, wR_2 = 0.0974
Final R indexes [all data]	R_1 = 0.0320, wR_2 = 0.0669	R_1 = 0.0549, wR_2 = 0.0919	R_1 = 0.0594, wR_2 = 0.1064
Largest diff. peak/hole /eÅ^{-3}	0.54/-0.78	1.02/-0.52	1.13/-0.79

Table S3 Select bond lengths (Å) and bond angles (°) of Ag(I) complexes

Complex [Ag(A10)(NO_3)]			
Ag(1)-O(11)	2.595(2)	Ag(1)-O(11)[a]	2.595(2)
Ag(1)-N(2)	2.210(2)	Ag(1)-N(2)[a]	2.210(2)
O(11)-Ag(1)-N(2)	102.40(7)	O(11)-Ag(1)-N(2)[a]	110.29(7)
N(2)-Ag(1)-N(2)[a]	143.97(11)	O(11)[a]-Ag(1)-N(2)	110.29(7)
O(11)[a]-Ag(1)-N(2)[a]	102.40(7)	O(11)-Ag(1)-O(11)[a]	49.57(9)
Complex [$Ag_2(LL)_3(NO_3)_2$]			
Ag(1)-O(11)	2.4820(13)	Ag(1)-O(12)	2.5996(14)
Ag(1)-N(2)	2.2311(12)	Ag(1)-N(5)	2.2600(11)
O(11)-Ag(1)-O(12)	50.310(4)	O(12)-Ag(1)-N(2)	117.46(5)
O(11)-Ag(1)-N(5)	112.48(4)	O(12)-Ag(1)-N(5)	103.59(4)
O(11)-Ag(1)-N(2)	108.91(4)	N(2)-Ag(1)-N(5)	134.36(4)
Complex [$Ag_n(A11)_n(H_2O)_n(NO_3)_n$]			
Ag(1)-O(11)	2.564(3)	Ag(1)-N(2)	2.344(2)
Ag(1)-O(12)	2.460(3)	Ag(1)-N(3)	2.292(2)
Ag(1)-N(2)[a]	2.344(2)		
O(11)-Ag(1)-O(12)	51.34(12)	O(11)-Ag(1)-N(3)	93.24(9)
O(12)-Ag(1)-N(3)	116.32(10)	O(12)-Ag(1)-N(2)[a]	106.61(10)
O(11)-Ag(1)-N(2)[a]	114.97(9)	N(2)[a]-Ag(1)-N(3)	137.07(8)

[a)] Stands for 1-*x*, *y*, 1/2-*z* in [Ag(A10)(NO_3)]; and for *x*, 5/2-*y*, -1/2+*z* in [$Ag_n(A11)_n(H_2O)_n(NO_3)_n$]