Ag(I) induced emission with azines having donor-acceptor-donor chromophore

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Supporting Information

S1. Experimental section

S1.1 Characterization of compound **LL**, **HL**, complex **1** and **2**

S1.2. ^{1}H-NMR spectrum of compound **LL** and **HL**

S1.3 ESI-MS of **LL**, **HL** and complexes **1** and **2**

S2. UV-visible spectra

Fig S2.1 UV-visible spectrum of each ligand (8 μM) in presence Cu^{+} (40 μM) as their tetrafluoroborate salt in dry THF solvent.

Fig S2.2 UV-visible spectral changes observed for **LL** upon addition of Ag^{+} as its triflate salt in THF at 298 K. [**LL**] = 0.01 mM; [Ag^{+}] = (0 to 0.02 mM).

Fig S2.3 Job's plot of **HL** upon titration with Ag^{+}

Fig S2.4 Variation in absorbance (Δ) at 470 nm of a solution of **HL** in THF (10 μM) as a function of [Ag^{+}]. The solid blue line represents the best fit with good correlation coefficient: 0.9978

Fig S2.5 Excitation and emission spectrum of **HL** (**[HL]**= 2 μM) in presence of Ag^{+} ([Ag^{+}] = 20 μM)

Fig S2.6 Fluorescence intensity change upon addition of various metal ions; [**LL**]=2 μM, [$\mathbf{M^{n+}}$]= 40 μM

Fig S2. 7 Emission response of **HL** (2 μm) and **LL** (2 μm) in the presence of [Ag^{+}] (40 μm) in dry THF. Dark gray for **LL** and light gray for **HL**

Fig S2. 8 Emission response of **1** in THF (red line) and DMF (black line)

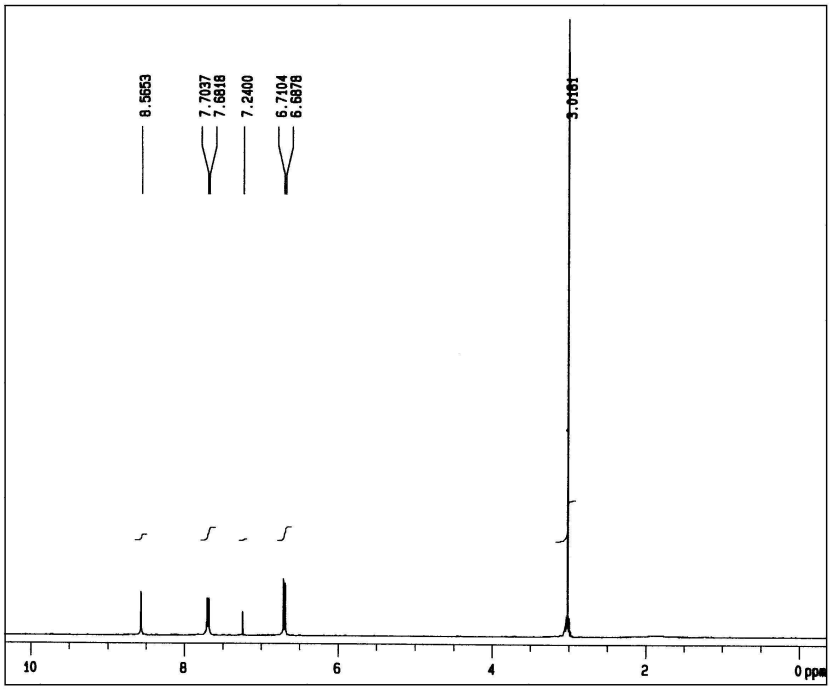

Fig S1.2.1 ^{1}H-NMR spectrum of **LL**

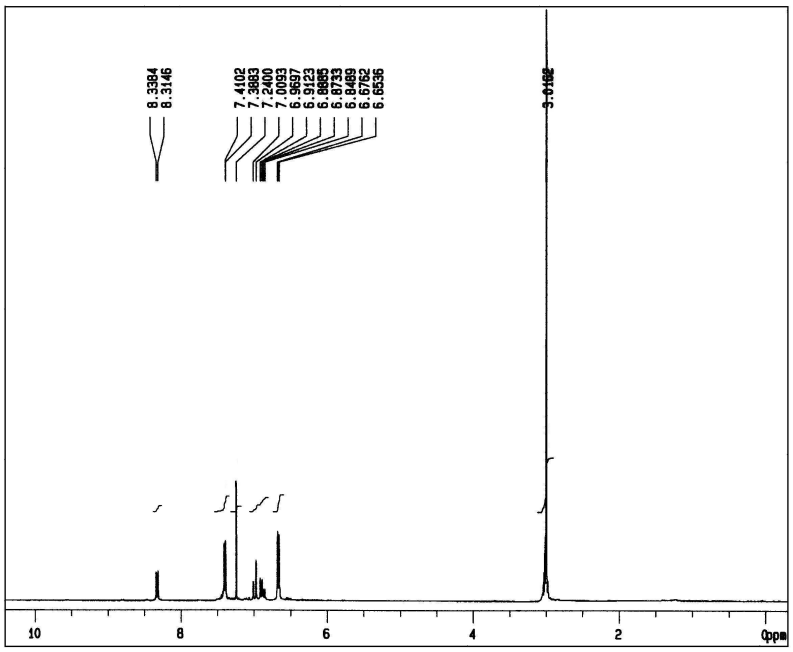

Fig S1.2. 2 ^{1}H-NMR spectrum of **HL**

S1.3 ESI-MS of **LL**, **HL** and complexes **1** and **2**

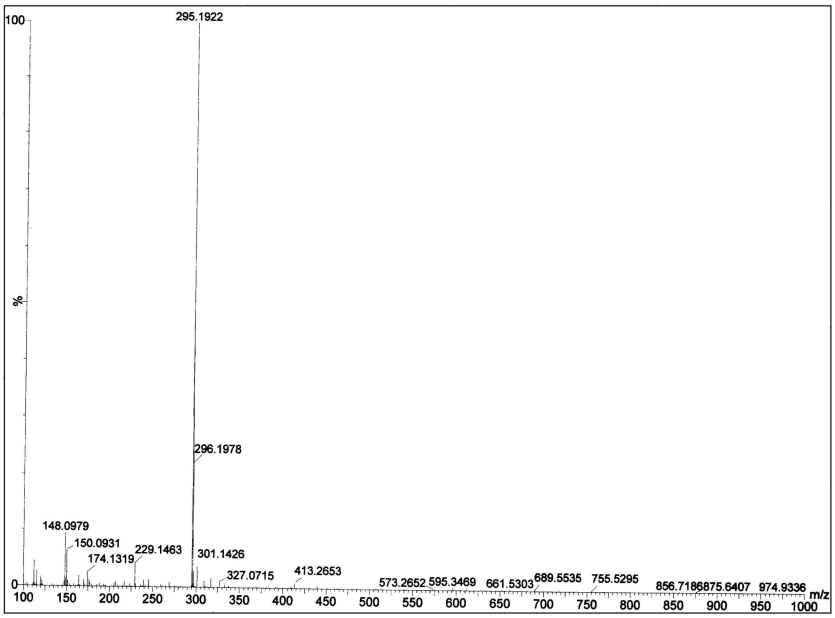

Fig S1.3.1 ESI-MS spectrum of **LL**

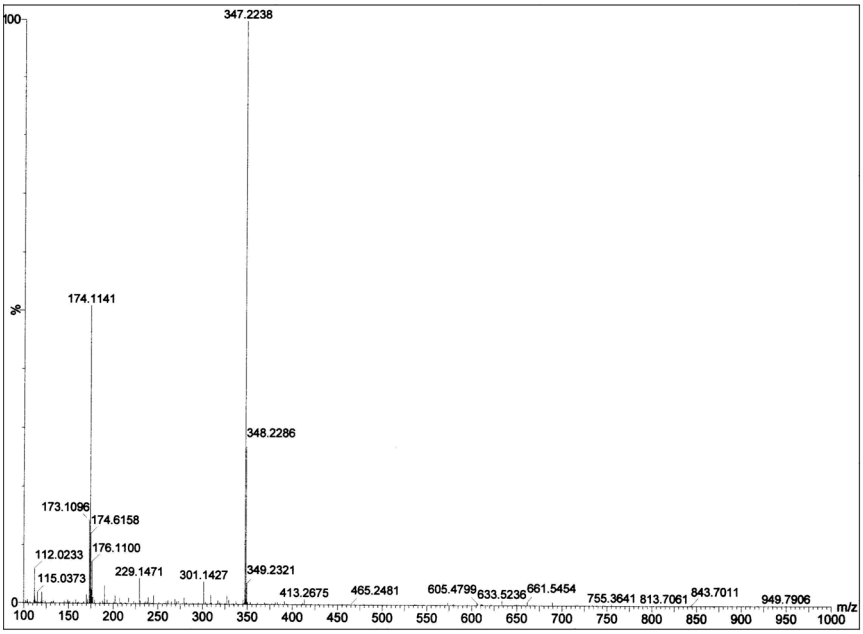

Fig S1.3.2 ESI-MS spectrum of **HL**

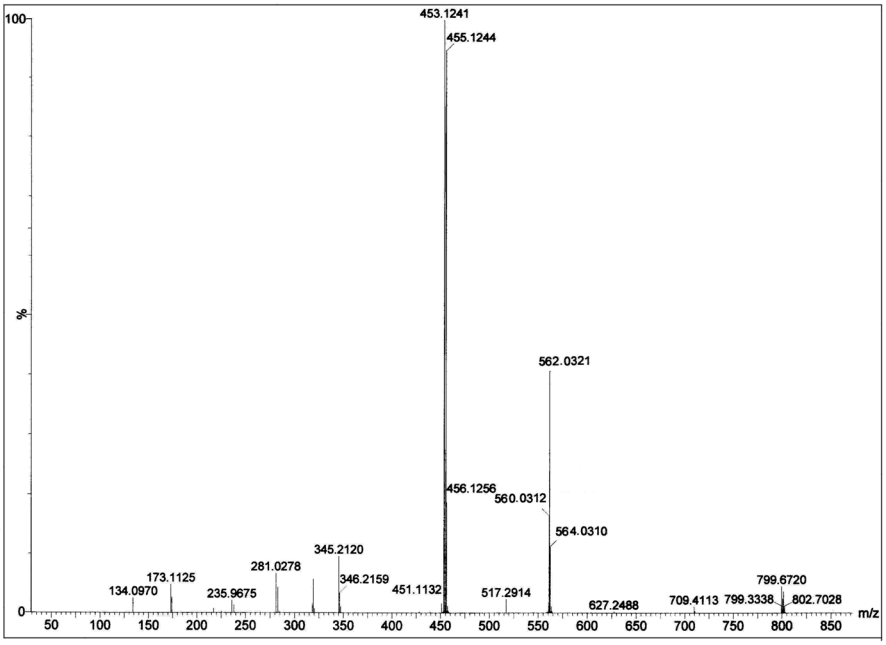

Fig S1.3.3 ESI-MS spectrum of **1**

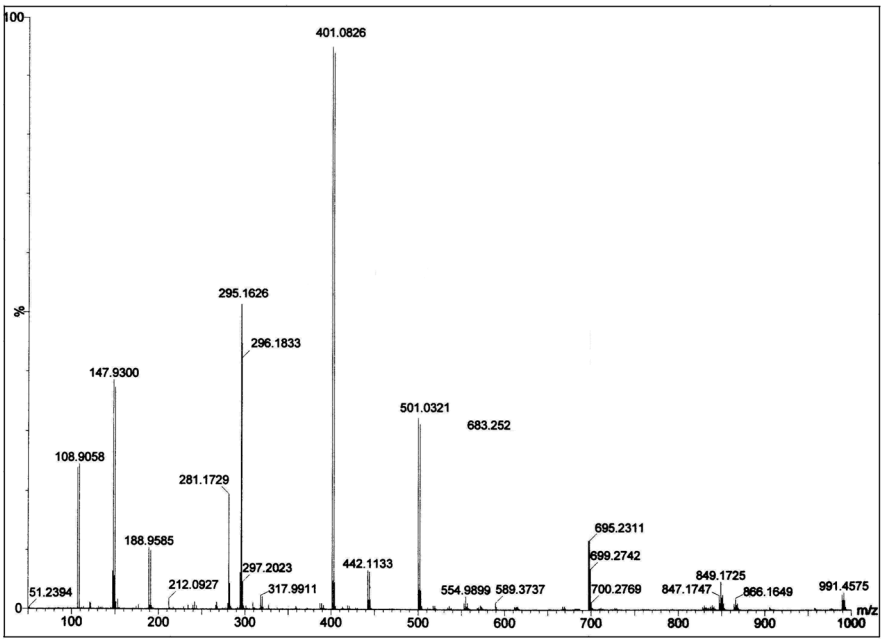

Fig S1.3.4 ESI-MS spectrum of **2**

S2. UV-visible spectra

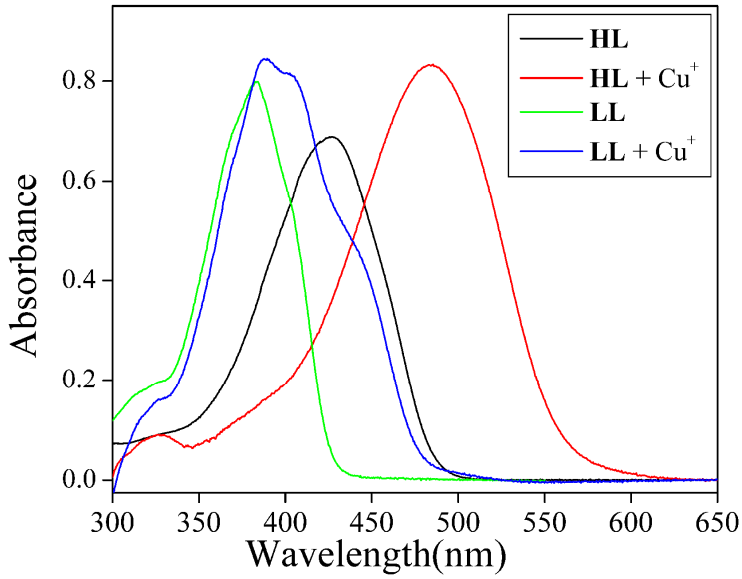

Fig S2.1 UV-visible spectrum of each ligand (8 μM) in presence Cu^{+} (40 μM) as their tetrafluoroborate salt in dry THF solvent.

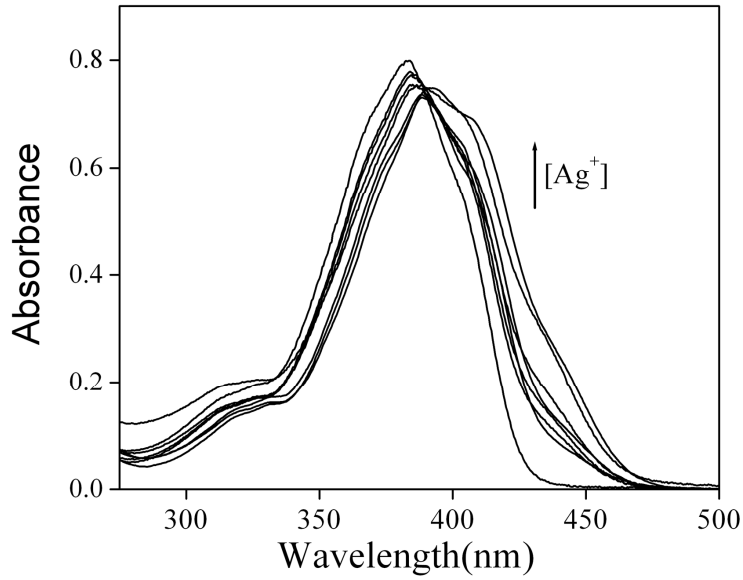

Fig S2.2 UV-visible spectral changes observed for **LL** upon addition of Ag^{+} as its triflate salt in THF at 298 K. [**LL**] = 0.01 mM; [Ag^{+}] = (0 to 0.02 mM).

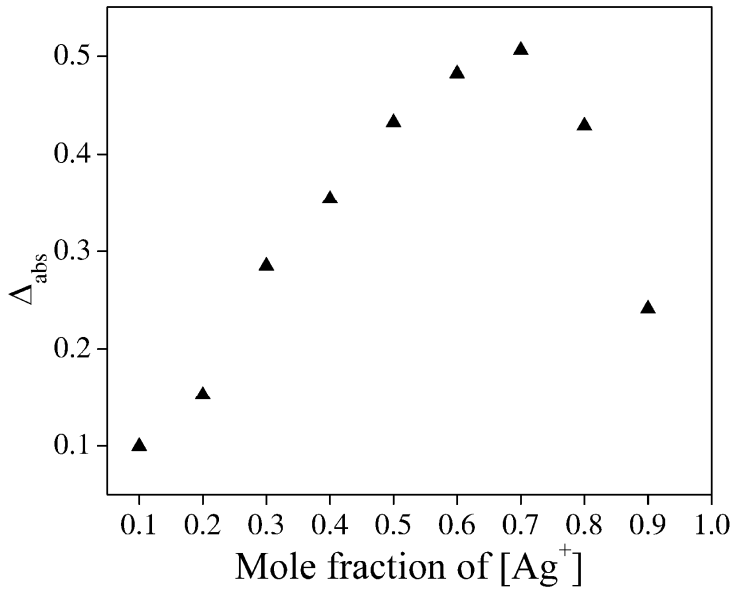

Fig S2.3 Job's plot of **HL** upon titration with Ag^+

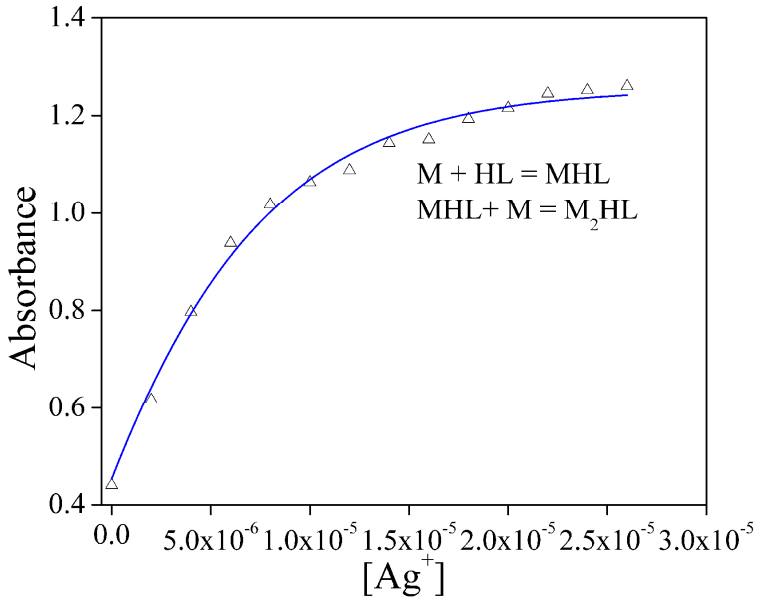

Fig S2.4 Variation in absorbance (Δ) at 470 nm of a solution of **HL** (10 μM) in THF as a function of [Ag^+]. The solid blue line represents the best fit with good correlation coefficient: 0.9978.

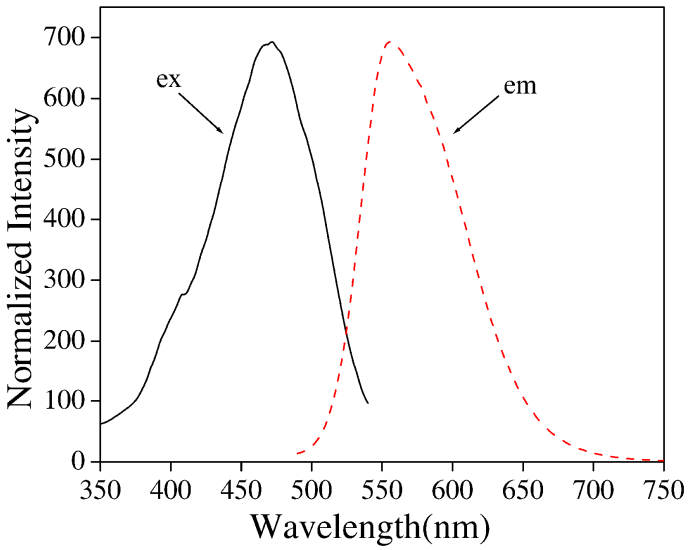

Fig S2.5 Excitation and emission spectrum of **HL** (**[HL]**= 2 μM) in presence of Ag^{+} ([Ag^{+}] = 20 μM).

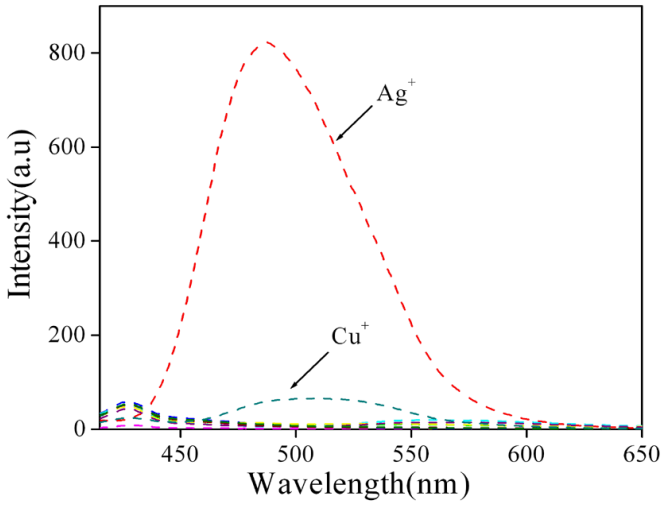

Fig S2.6 Fluorescence intensity change upon addition of various metal ions; [**LL**] = 2 μM, [M^{n+}] = 40 μM.

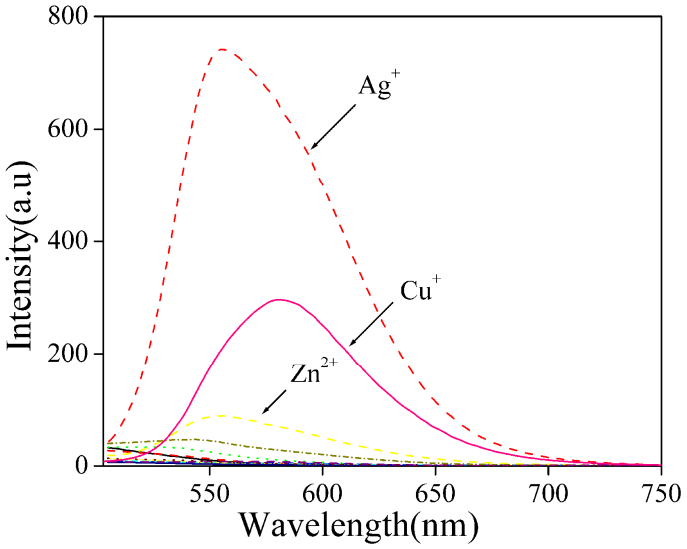

Fig S2.7 Emission response of **HL** (2 μm) in the presence of various metal ions [M^{n+}] (40 μm) in dry THF.

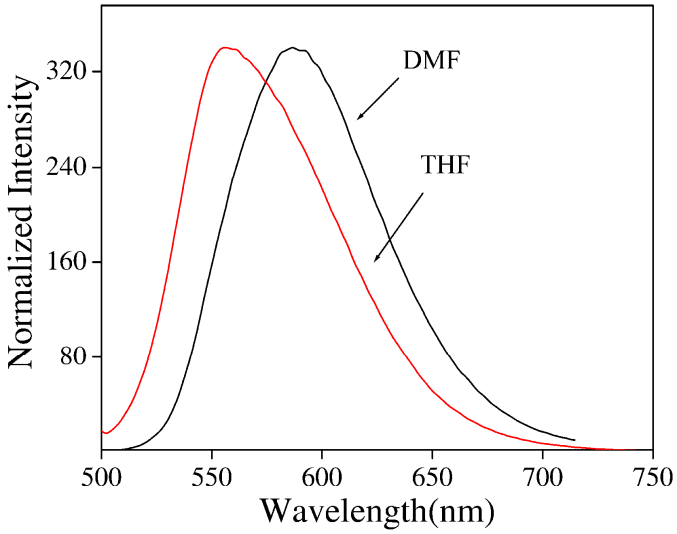

Fig S2.8 Emission response of **1** in THF (red line) and DMF (black line)

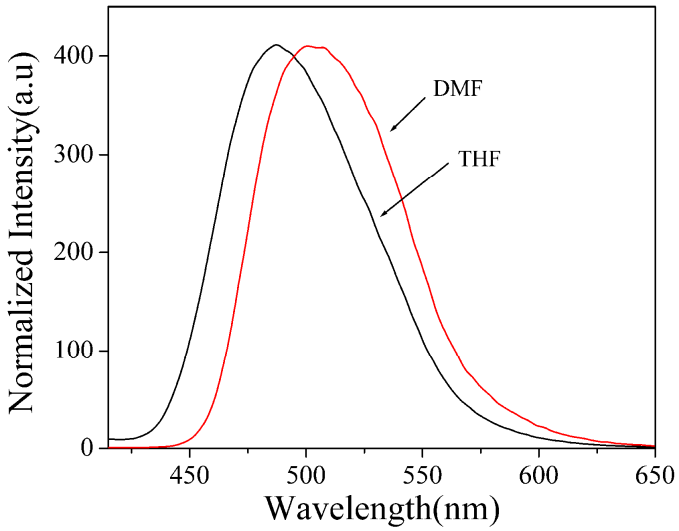

Fig S2.9 Emission response of **2** in DMF (red line) and **LL** in presence of Ag^{+}-triflate in THF

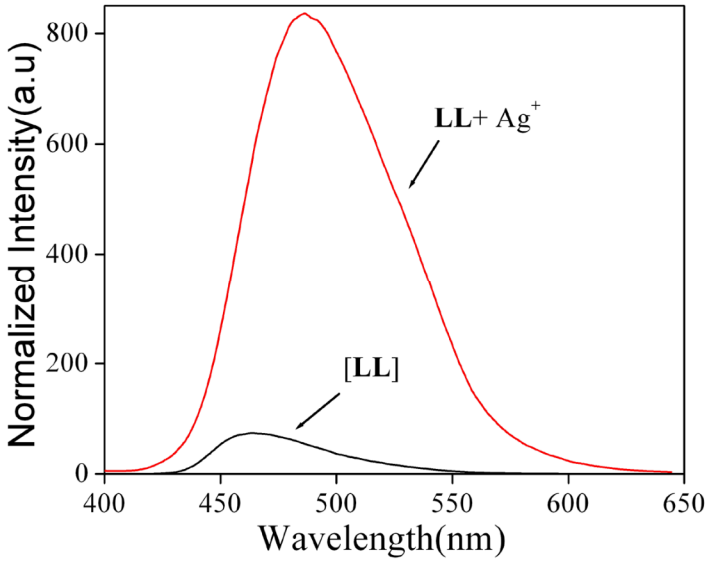

Fig S2.10 Emission response of **LL** and in presence of $AgNO_3$ in mixed solvent DCM+EtOH+DMF at 10^{-4}M concentration. Excitation wavelength was 384 nm.

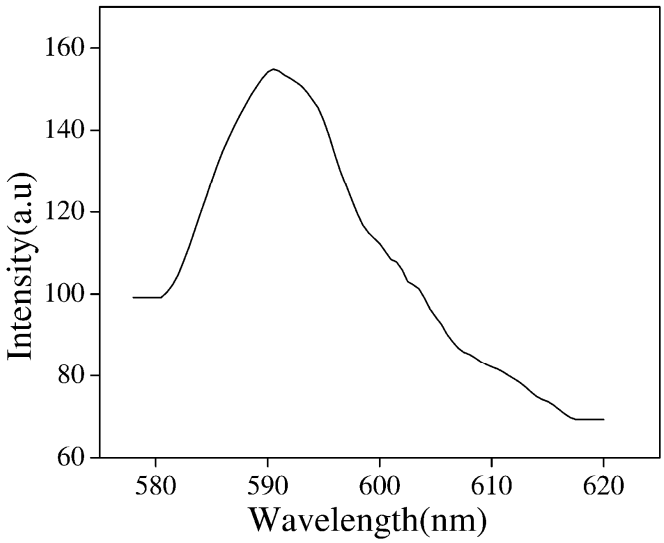

Fig S2.11 Solid-state emission of **1**

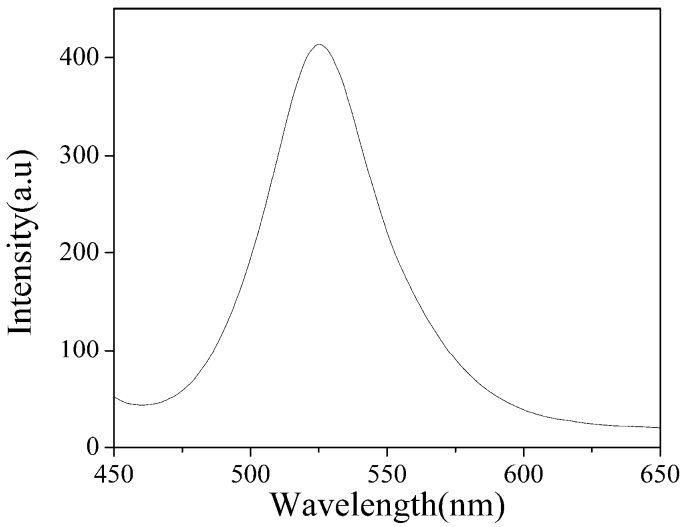

Fig S2.12 Solid-state emission of **2**

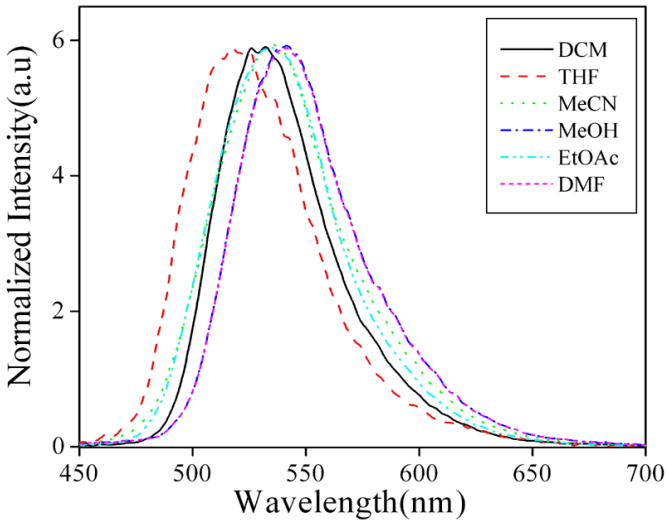

Fig S2.13 Solvent dependent study of **HL**

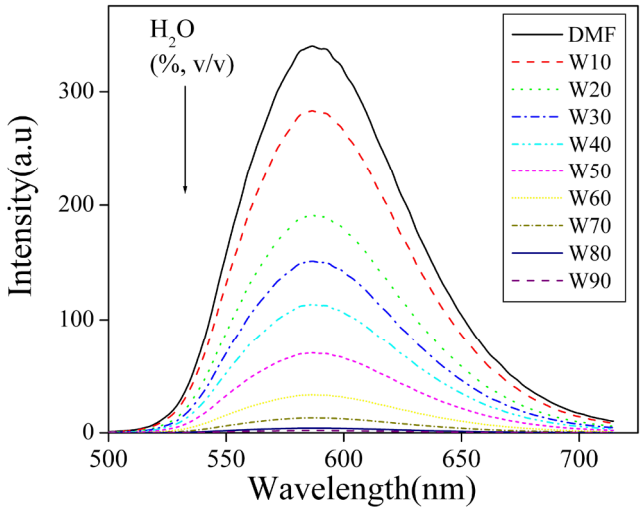

Figure S2.14 Emission response of Ag^{+}-complex of **HL** on increasing amount of water (%, v/v) in DMF. W: water.

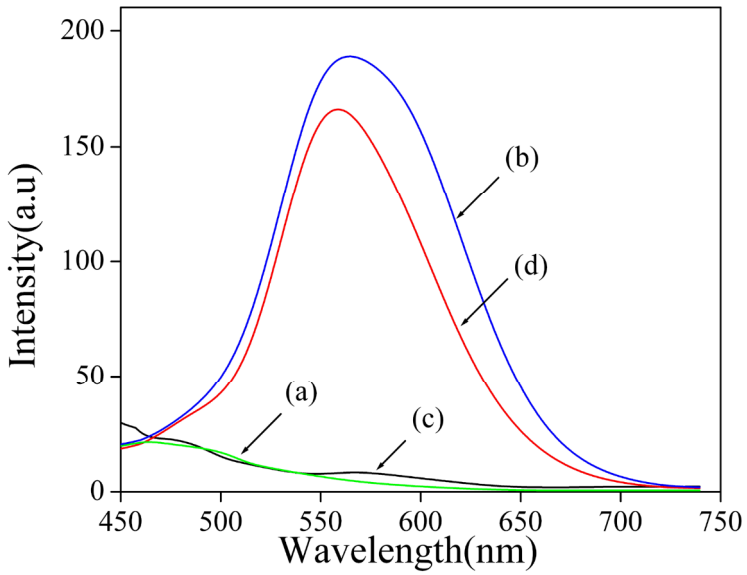

Figure S2.15 Emission response of (a) **HL** (b) complex **1** (c) complex **1** + TBNCl (d) complex **1**+ TBNCl + Ag^{+} in THF. [**1**] = 1 μM; [Ag^{+}] = 2 μM; [TBNCl] = 2 μM.

S3. Crystal structure

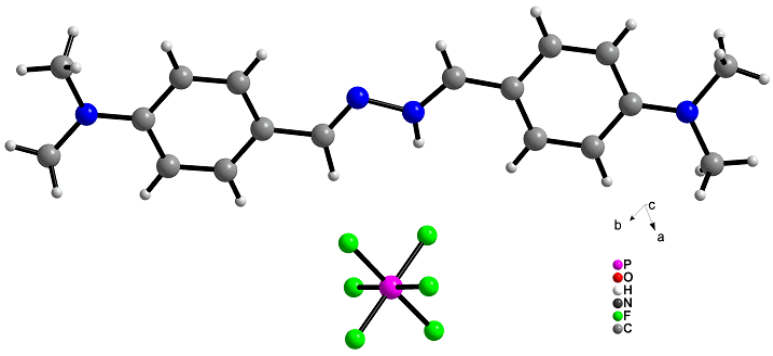

Fig S3.1 Crystal Structure of ligand **LL**.HPF_6

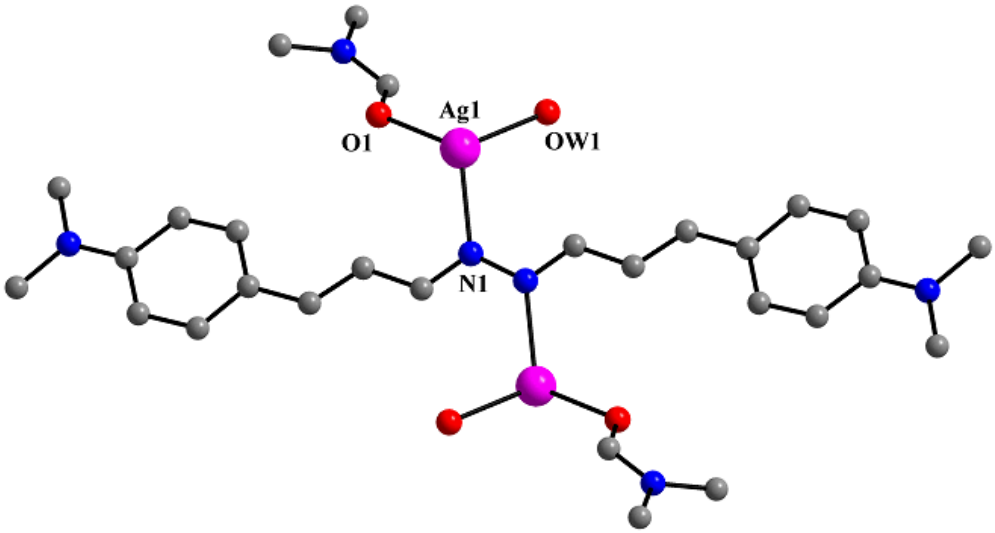

Fig S3.2 A perspective view of complex **1**: Selected bond distances (Å) and angles (°) are: Ag1–N1 2.277(7), Ag1–O1 2.326(6), Ag1–OW1 2.328(7), Ag1–C8 2.567(7), Ag1–C9 2.586(8), N1–Ag1–O1 118.5(2), N1–Ag1–OW1 109.6(3), O1–Ag1–OW1 100.8(2), N1–Ag1–C9 111.5(2), O1–Ag1–C9 87.0(2), OW1–Ag1–C9 127.4(3), C8–Ag1–C9 31.0(2).

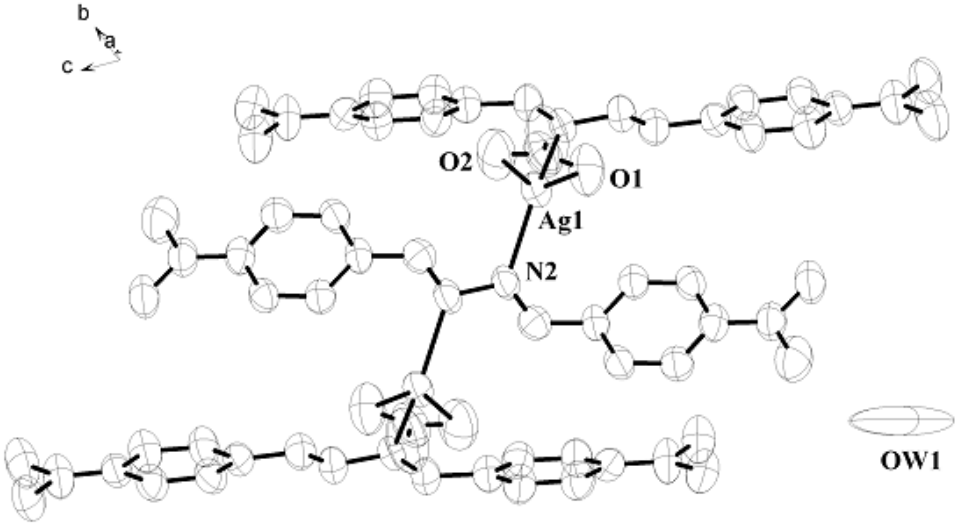

Fig S3.3 A perspective view of complex **2**: Selected bond distances (Å) and angles (°) are Ag1–N1 2.217(6), Ag1–N2 2.278(6), Ag1–O1 2.504(8), Ag1–O2 2.615(8), N1–Ag1–N2 135.4(2), N1–Ag1–O1 109.9(2), N2–Ag1–O1 109.7(2), N7–O1–Ag1 98.2(6), N3–N1–Ag1 121.3(5).

S4. Time resolved fluorescence decay analysis by femtosecond luorescence up-conversion setup

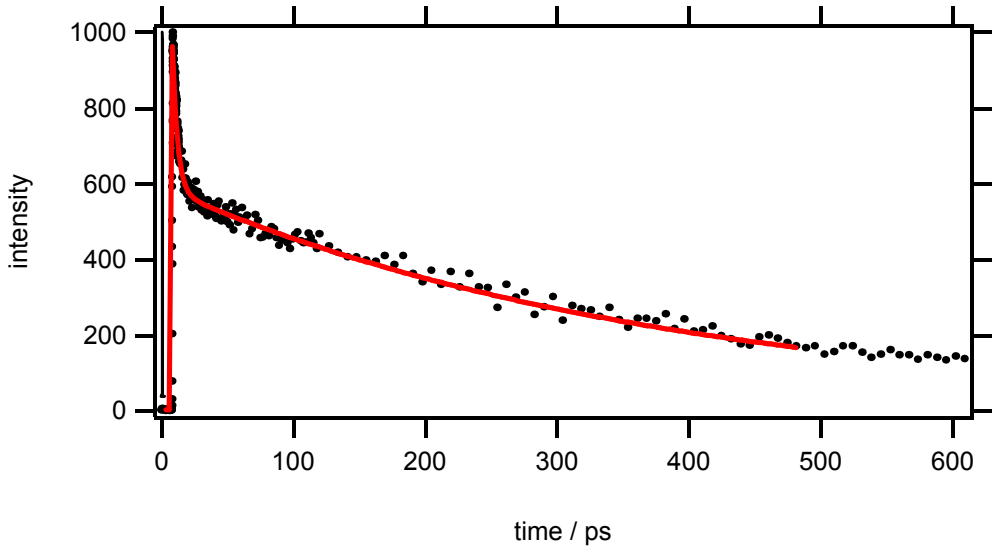

Fig S4.1 Fluorescence decay analysis of **HL** + Ag(I) complex. The decay is recorded at [**HL**] = 10^{-5} M and [Ag(I)] = 10^{-3} M

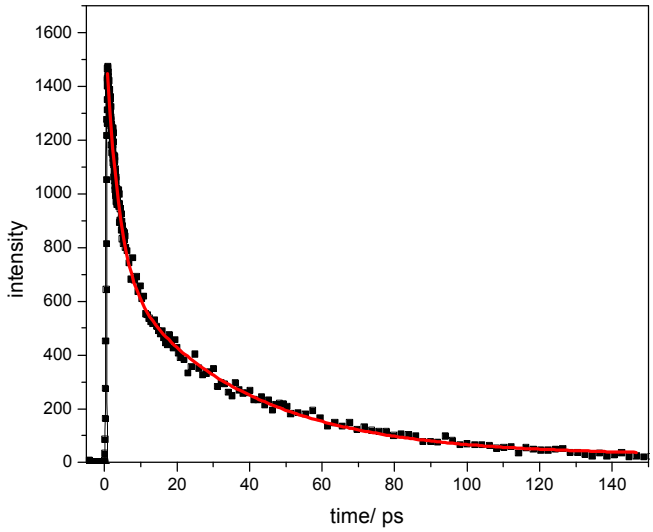

Fig S4.2 Fluorescence decay analysis of **LL** + Ag(I) complex. The decay is recorded at [**LL**] = 10^{-5} M and [Ag(I)] = 10^{-3} M

Table S4.1 The time resolved data of **HL** + Ag(I) and **LL** + Ag(I) complex

	τ1 / ps	τ2 / ps	a1	a2
HL + Ag(I)	3.9	401	.43	.57
LL + Ag(I)	3.36	34.74	.54	.46