

Supplementary Informations

Solvent-dependent fluorescent-colorimetric probe for dual monitoring of Al³⁺ and Cu²⁺ in aqueous solution: An application to bio-imaging

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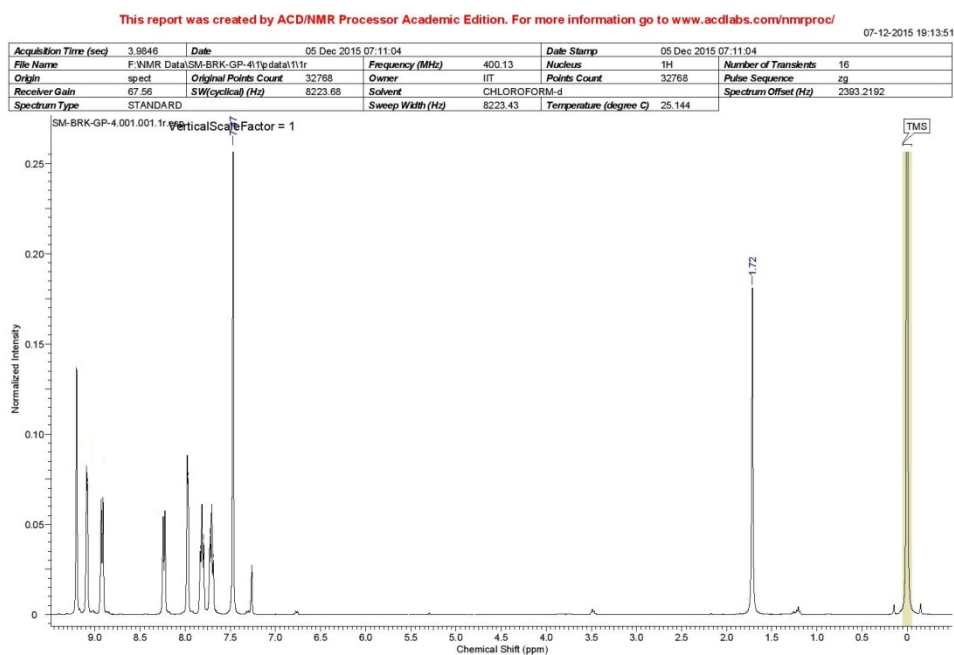


Fig. S1. ¹H NMR Spectra of **L** in CDCl₃.

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Solvent	CHLOROFORM-d	Spectrum Offset (Hz)	10061.0059	Spectrum Type	STANDARD
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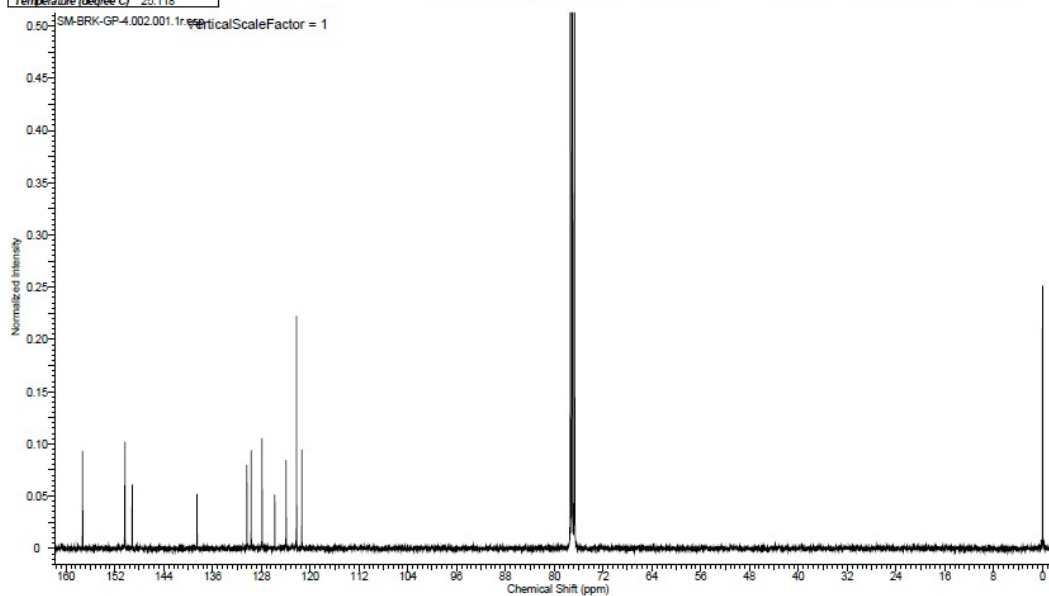


Fig. S2. ¹³C NMR Spectra of **L** in CDCl₃.

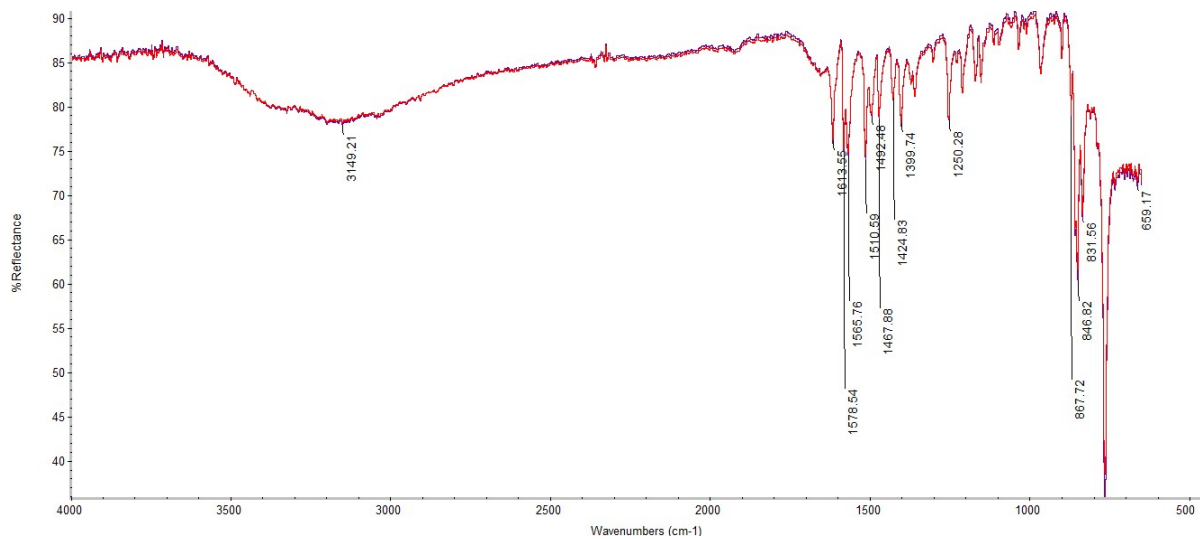


Fig. S3. IR Spectra of **L**.

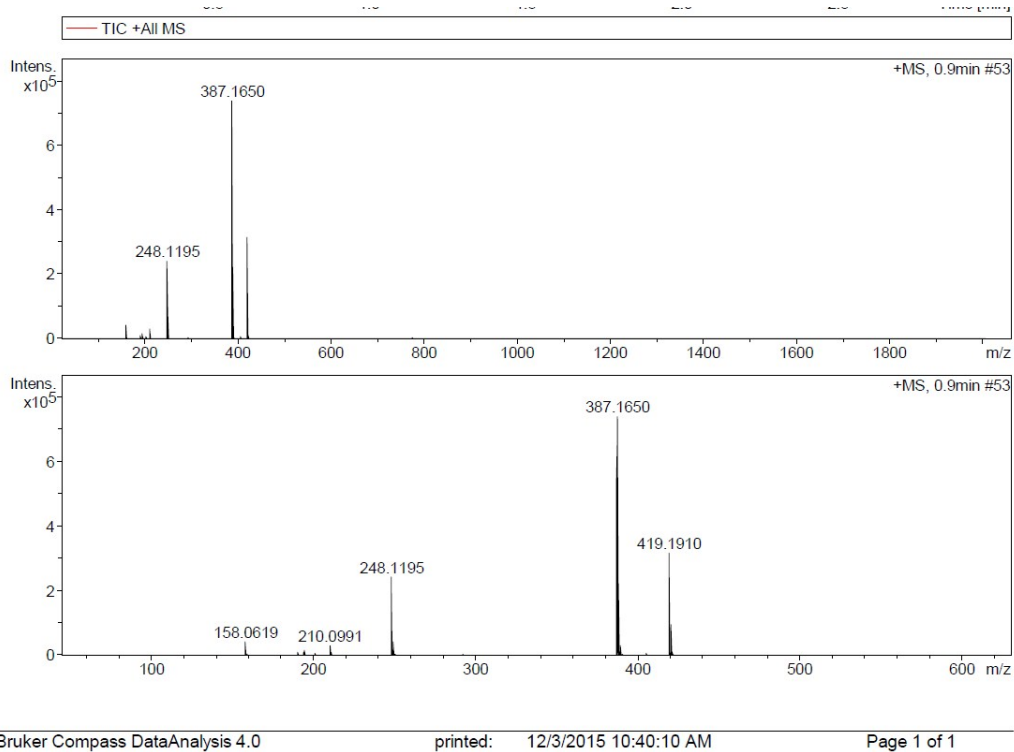


Fig. S4. Mass Spectra of L.

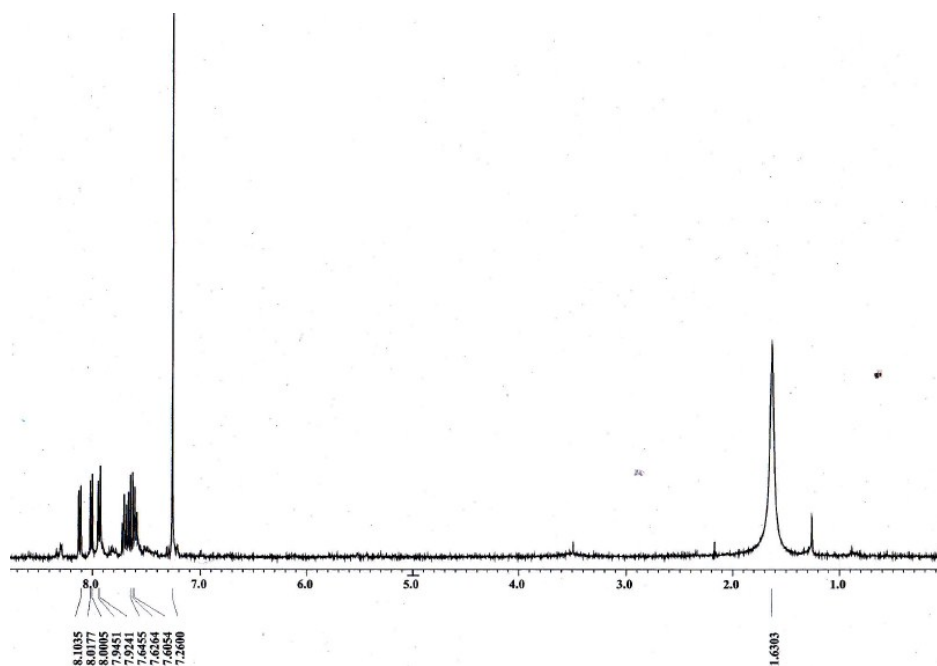


Fig. S5. ¹H NMR Spectra of L₁ in CDCl₃.

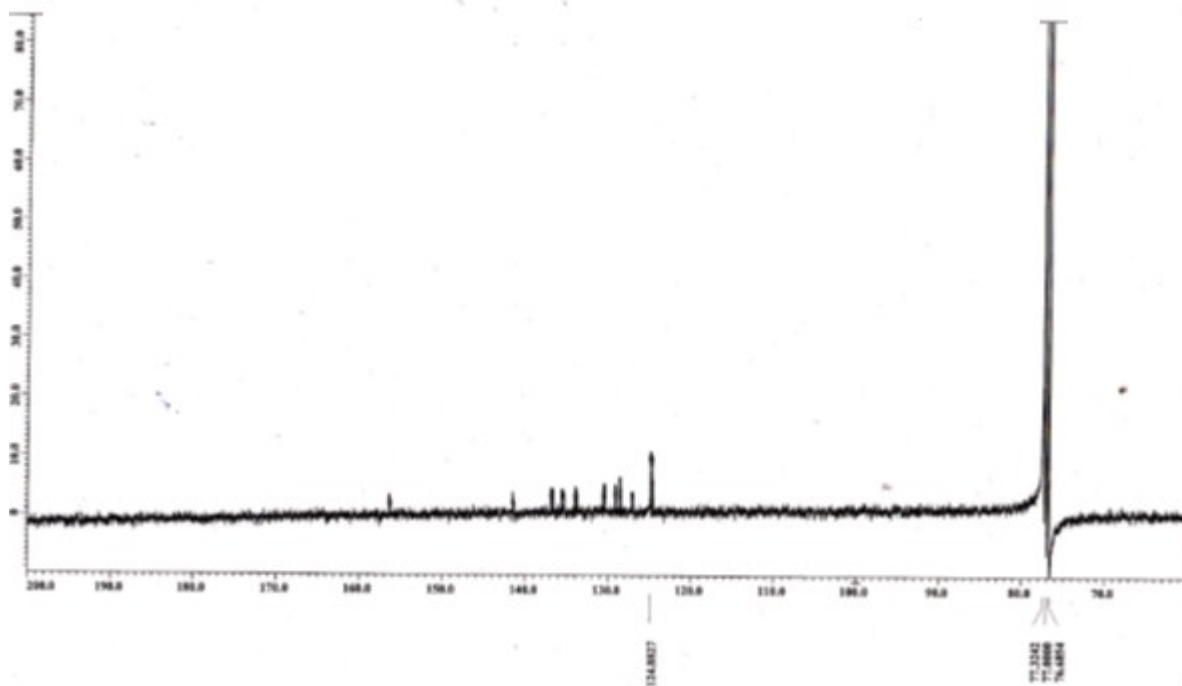


Fig. S6. ^{13}C NMR Spectra of L_1 in CDCl_3 .

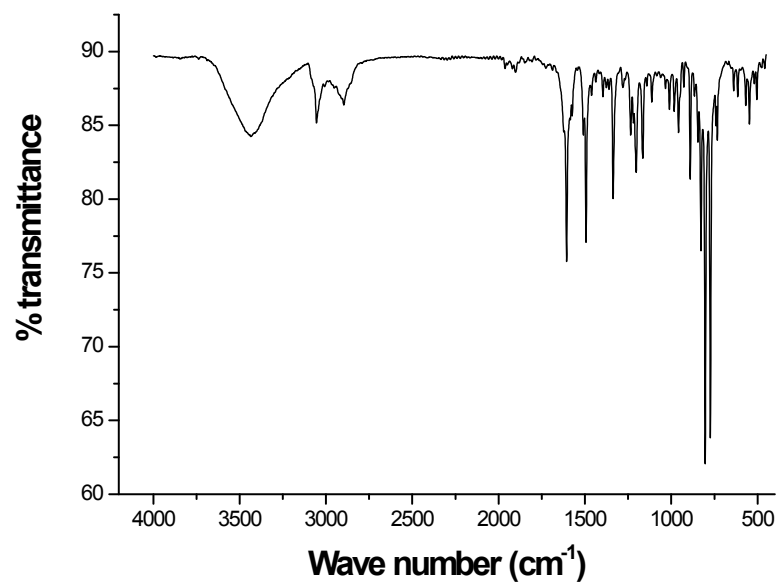


Fig. S7. IR Spectra of L_1 .

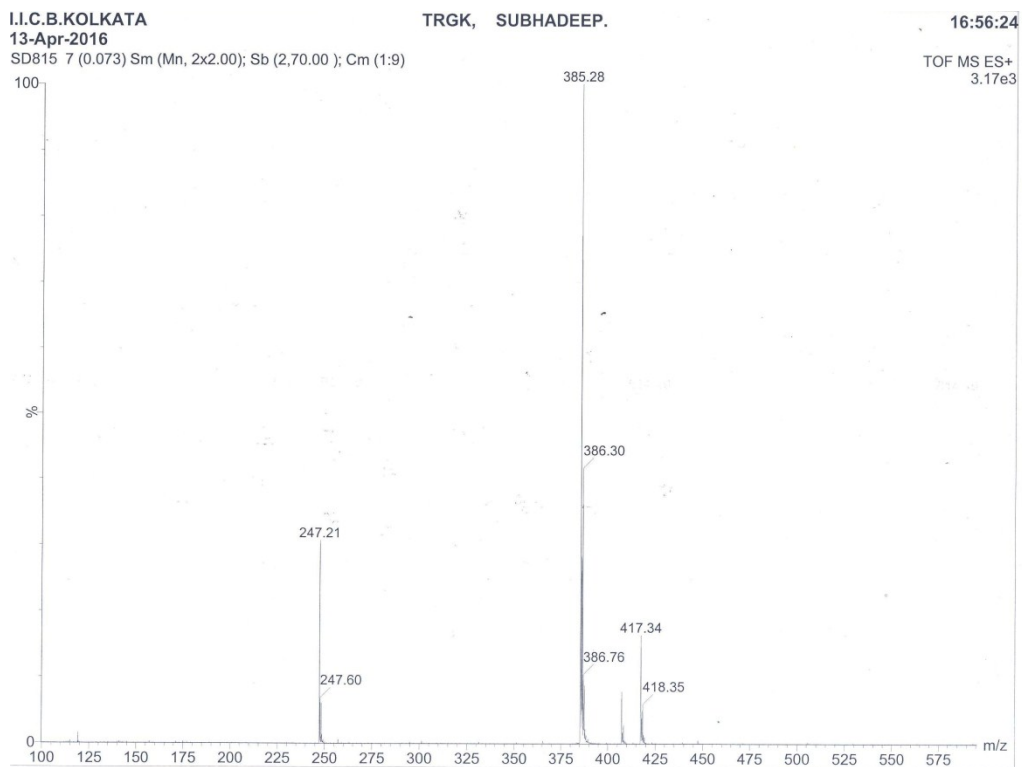


Fig. S8. Mass Spectra of L₁.

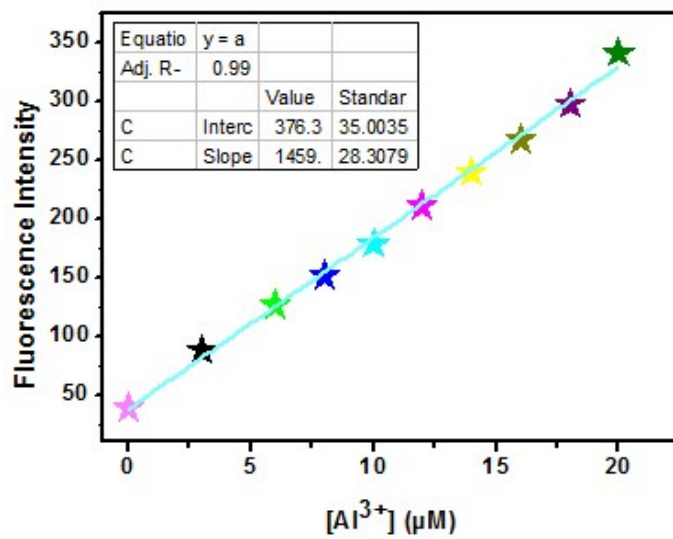


Fig. S9. Change of Fluorescence intensity on increasing amounts of Al³⁺ at pH=7.4.

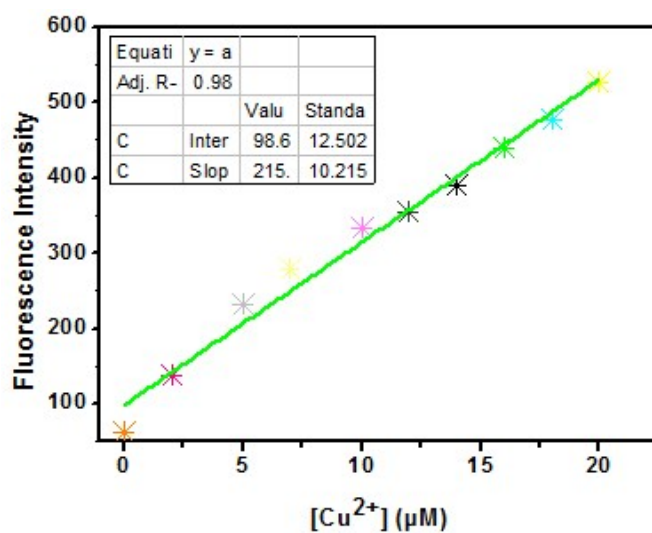
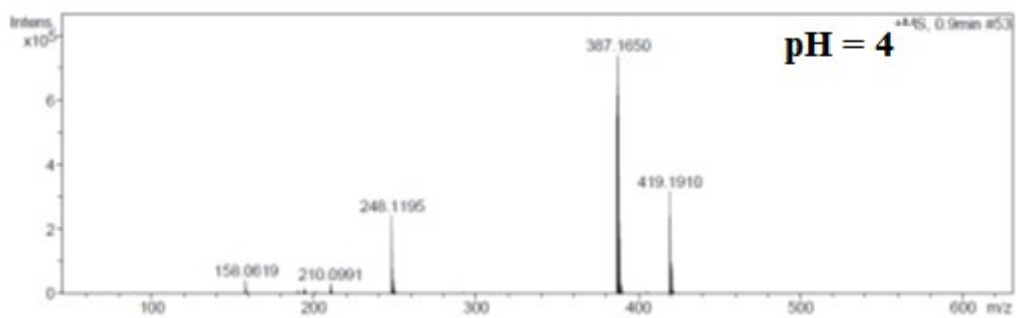
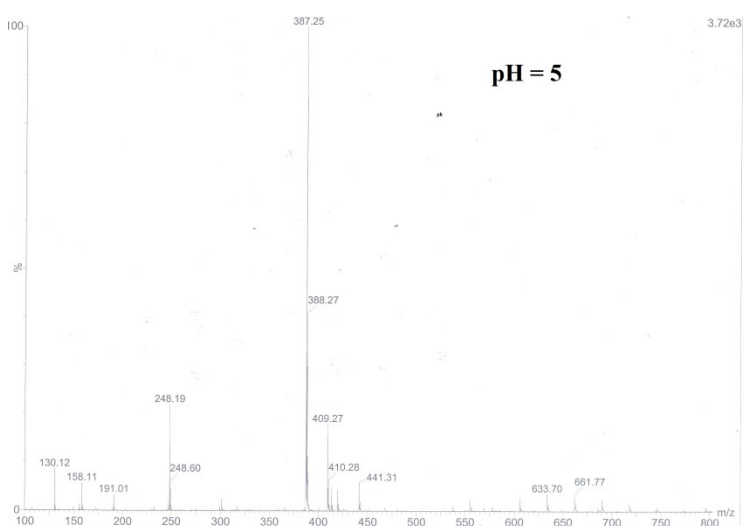


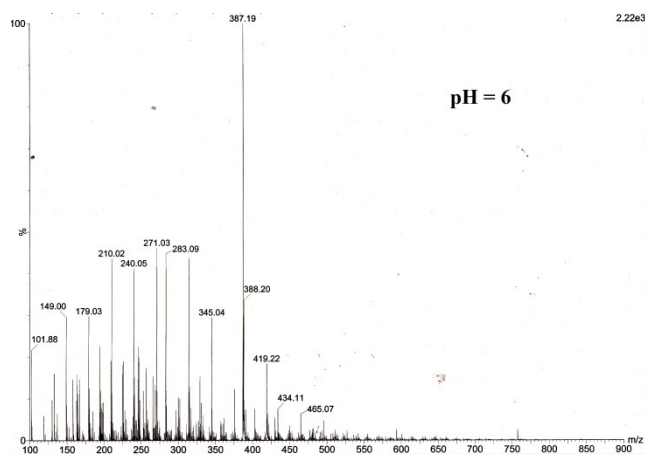
Fig. S10. Change of Fluorescence intensity on increasing amounts of Cu^{2+} at $\text{pH}=7.4$.



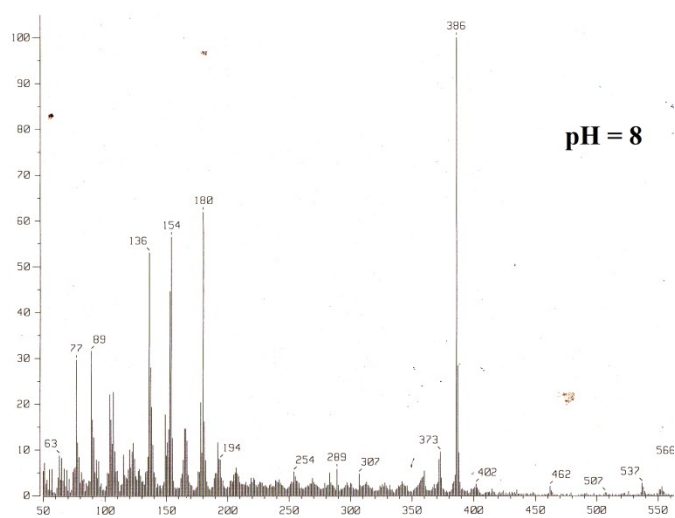
(a)



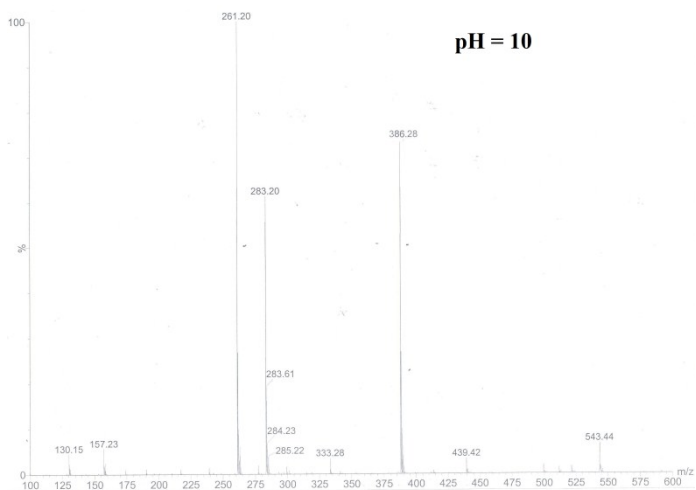
(b)



(c)



(d)



(e)

Fig. S11. ESI-MS of **L** at different pH, (a) pH = 4; (b) pH = 5; (c) pH = 6; (d) pH = 8 and (e) pH = 10

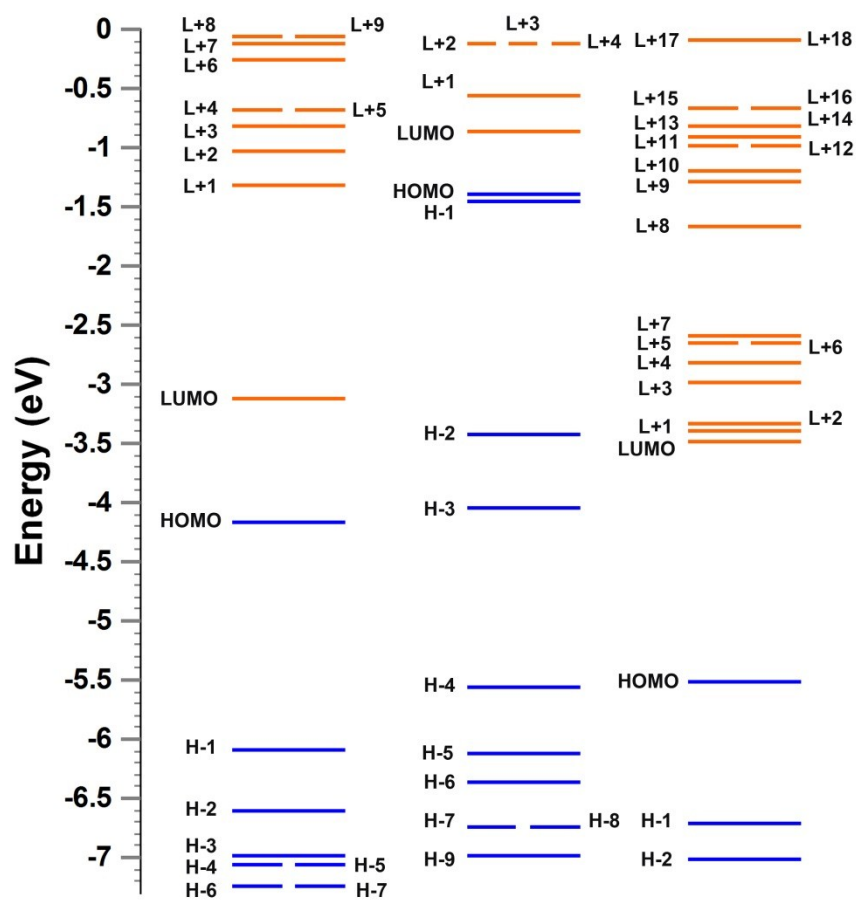


Fig. S12. The MO diagram of L (left), 1(middle) and 2 (right) are showing energy level.

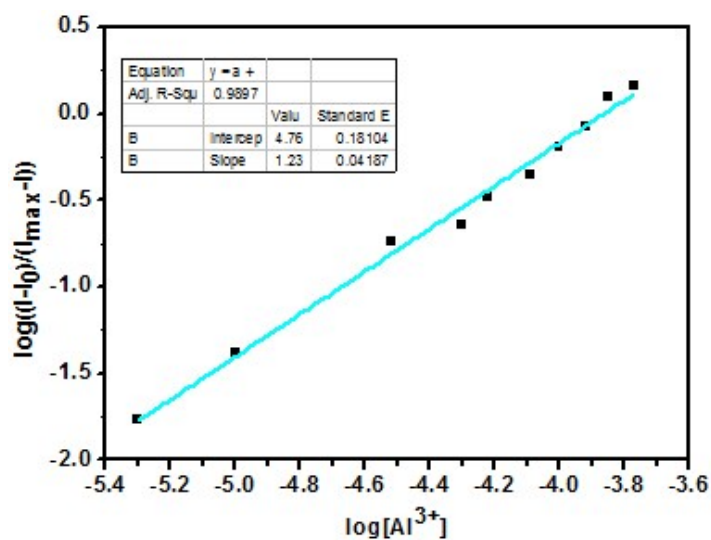


Fig. S13. Hill plot for Al^{3+} .

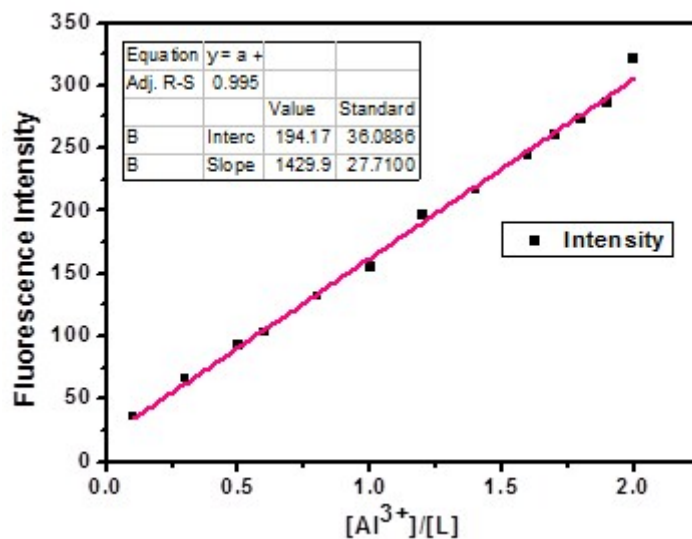


Fig. S14. Detection limit for Al³⁺.

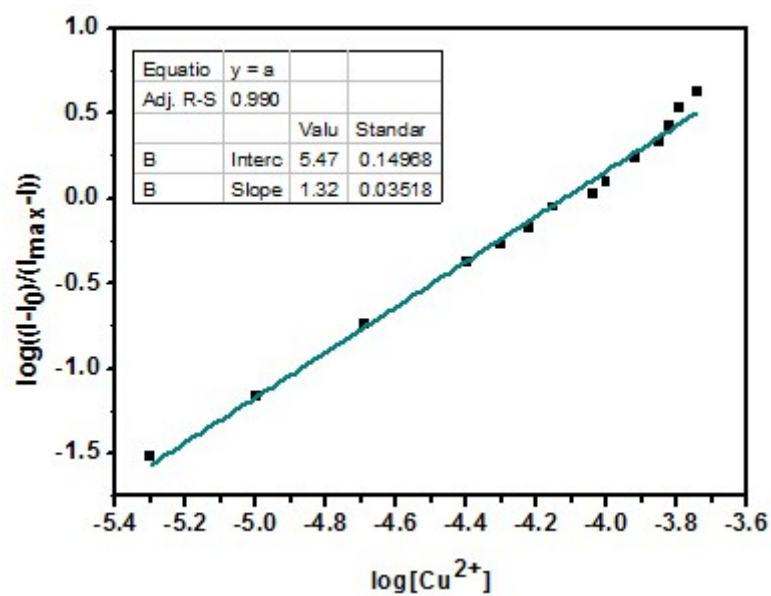


Fig. S15. Hill plot for Cu²⁺.

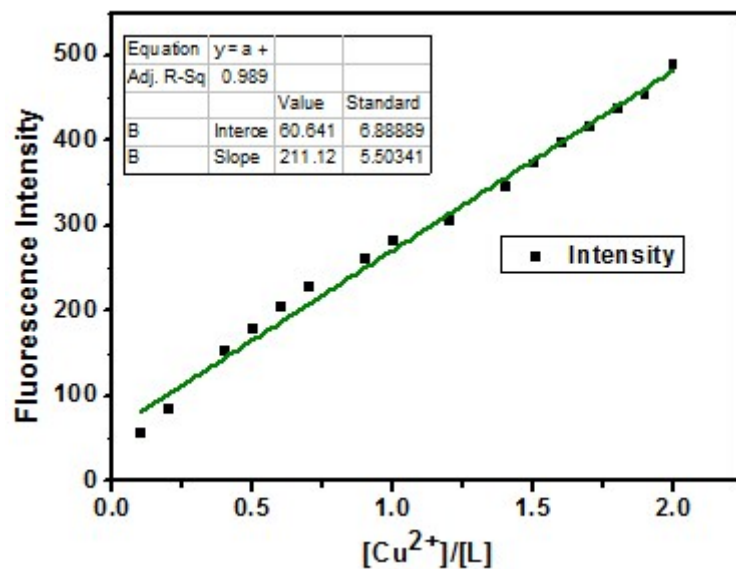


Fig. S16. Detection limit for Cu^{2+} .

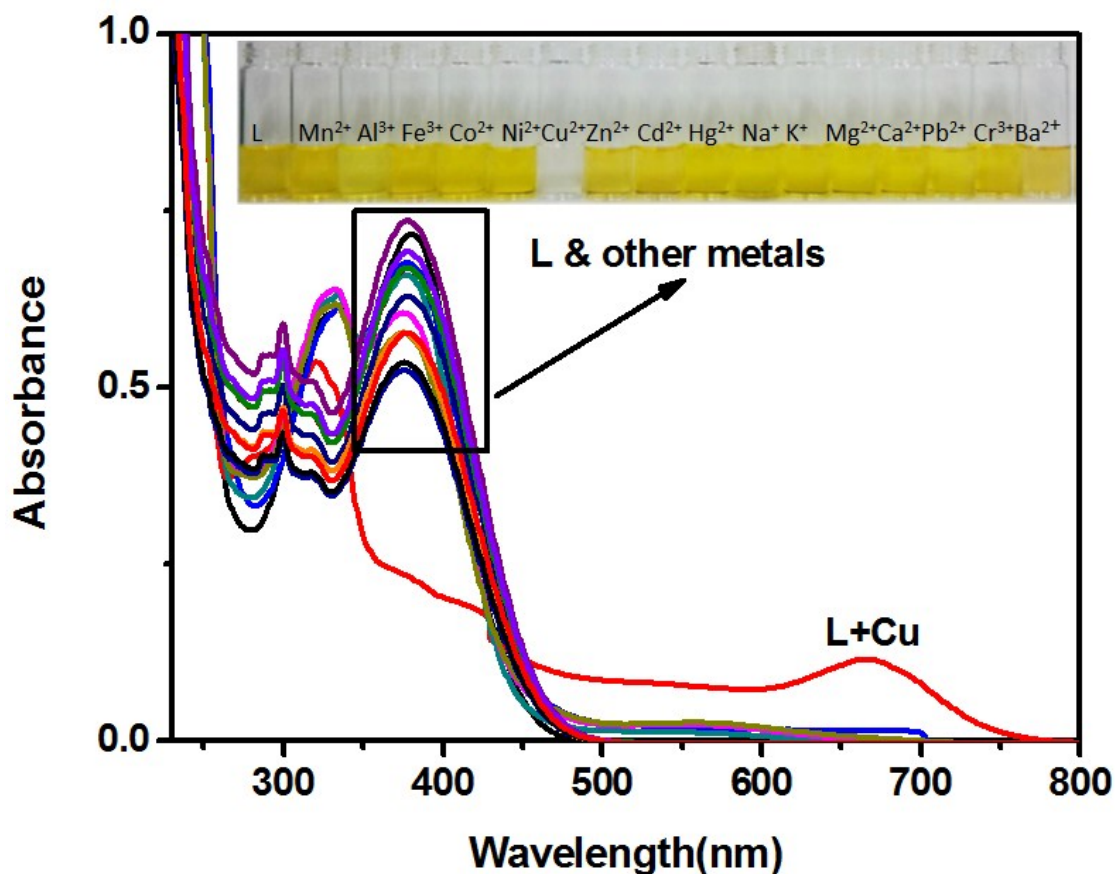
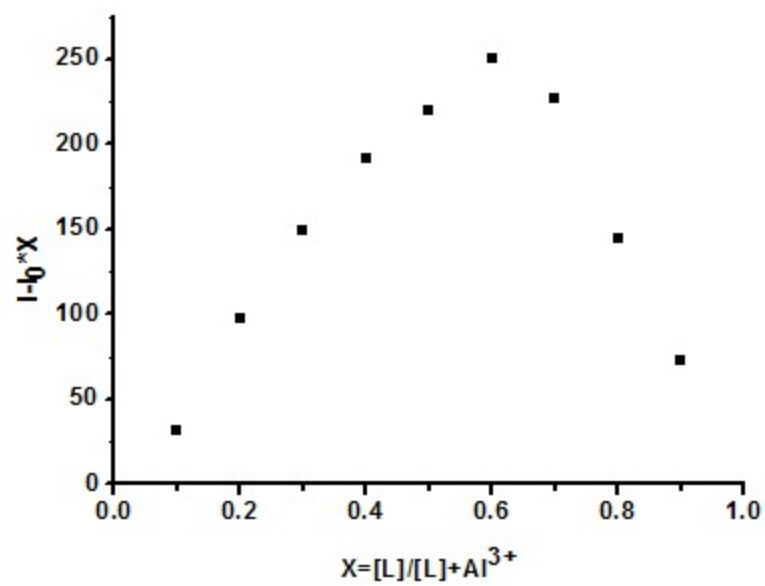
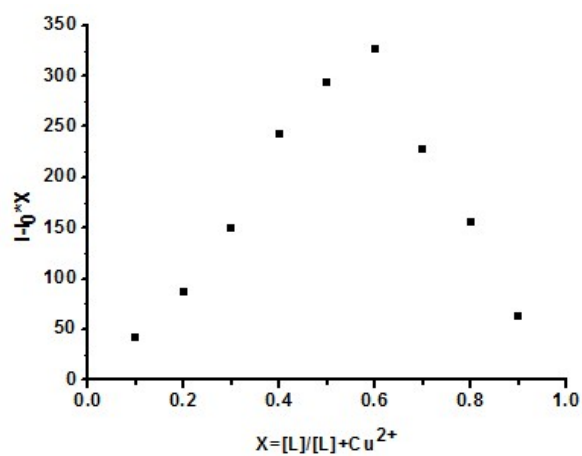


Fig. S17. Absorbance spectra of L (10 μM) before and after addition of 5 equiv. of various metal ions of Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Al^{3+} , Pb^{2+} , Cr^{3+} and Ba^{2+} in acetonitrile–water (2 : 1, v/v).

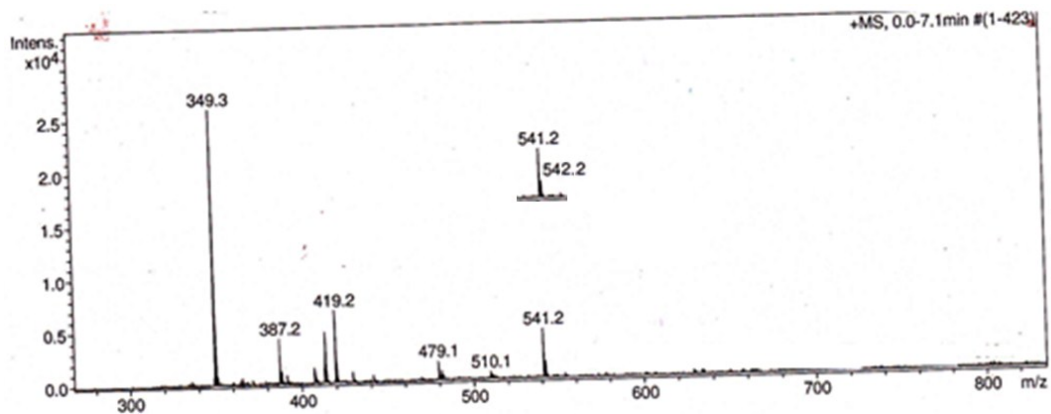


(a)

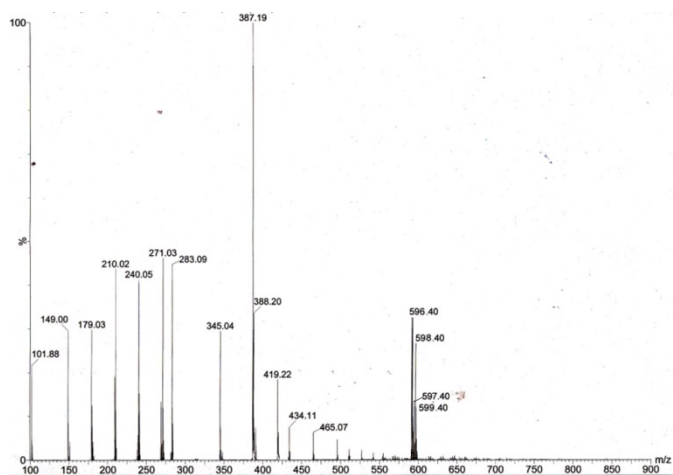


(b)

Fig. S18. Job's plot for (a) Al^{3+} and (b) Cu^{2+} .



(a)



(b)

Fig. S19. Mass spectra of (a) $L-Al^{3+}$ complex, **1** and (b) $L-Cu^{2+}$ complex, **2**.

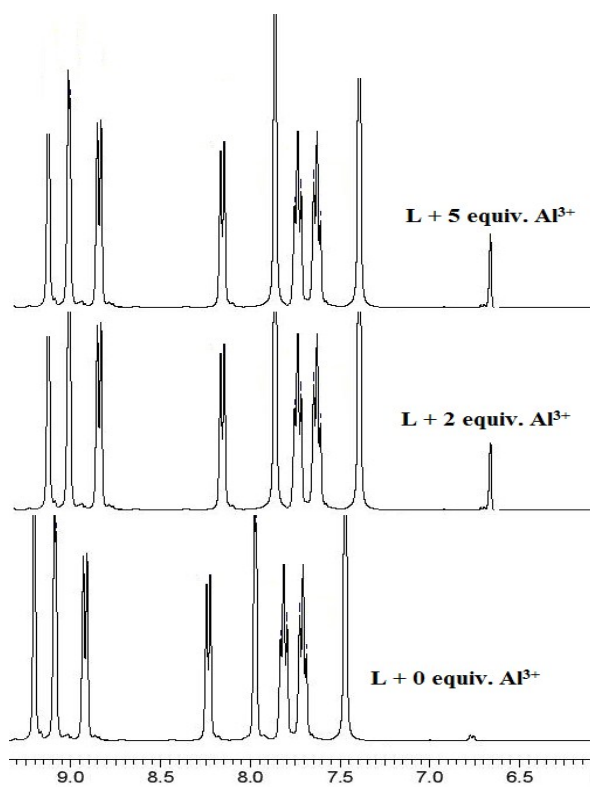


Fig. S20. 1H NMR titration of $L-Al^{3+}$ complex, **1**

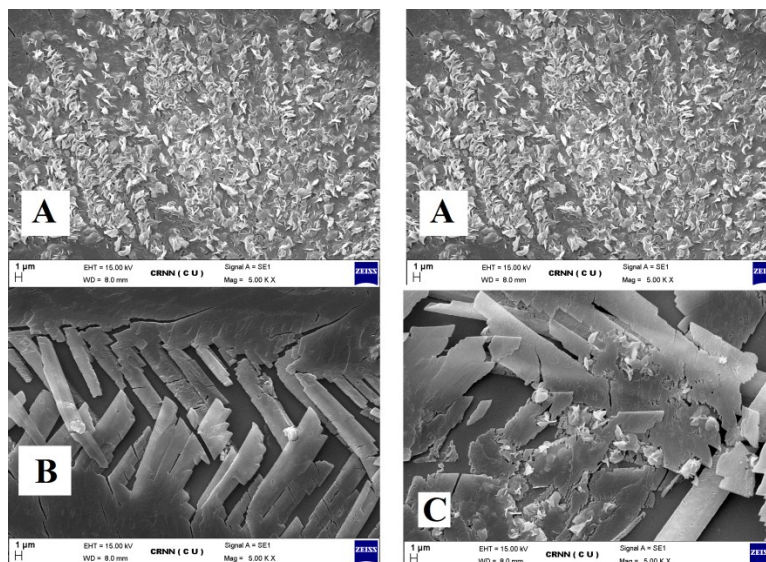


Fig. S21. SEM images of (A) L, (B) L+Al³⁺ complex, **1** and (C) L+Cu²⁺ complex, **2**.

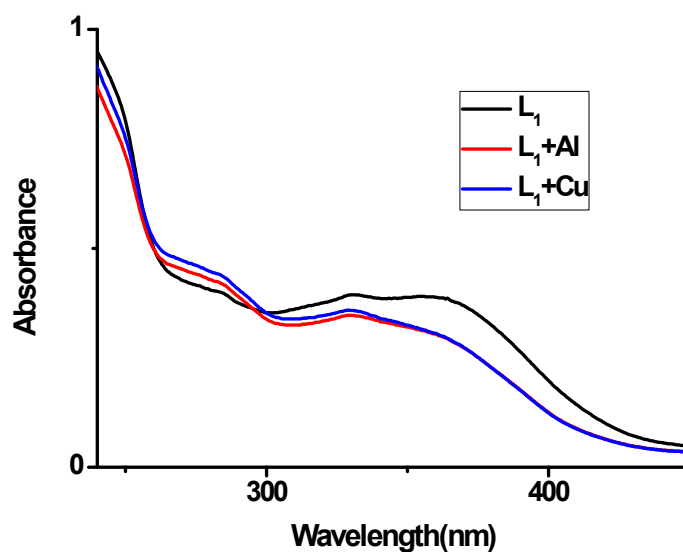


Fig. S22. Change of absorbance spectra of L₁ on addition of Al³⁺ and Cu²⁺.

Table S1. The calculated electronic transition parameters by the TD-DFT method compared with experimental results for L, **1** and **2**.

Character of Molecular Orbitals	Most important orbital excitations	λ (nm)	f	Exp. λ (nm)
L				
H (66% π nap, 21% π dab)	H \rightarrow L	489.34	0.0300	378
H-1 (46% π nap, 42% π dab)	H-2 \rightarrow L, H-3 \rightarrow L+1	452.34	0.0244	

H-2 (84% π nap, 7% π dab)	H-3 \rightarrow L, H-2 \rightarrow L+1	432.09	0.0134	315
H-3 (72% π nap, 28% π dab)	H \rightarrow L+1, H-10 \rightarrow L	384.38	0.2649	
H-4 (100% π nap)	H-8 \rightarrow L+1, H-7 \rightarrow L	362.79	0.0275	
H-5 (100 π nap)	H-4 \rightarrow L	321.85	0.1368	
L (57% π^* nap, 33% π^* dab)	H-5 \rightarrow L	315.87	0.1688	
L+1 (80% π^* nap, 17% π^* dab)	H-6 \rightarrow L, H \rightarrow L+4	296.49	0.5516	243
L+2 (92% π^* nap, 6% π^* dab)	H-5 \rightarrow L+1, H \rightarrow L+2, H-11 \rightarrow L	283.87	0.3072	
L+3 (87% π^* dab, 13% π^* nap)	H-10 \rightarrow L, H-6 \rightarrow L+1	275.19	0.1403	
L+4 (89% π^* nap, 11% π^* dap)	H-5 \rightarrow L+2, H-5 \rightarrow L+2	272.52	0.1690	
L+5 (98% π^* nap)				
1				
H (48% π W, 37% Li , 15% Al)	H \rightarrow L, H -1 \rightarrow L+1	498.97	0.1391	380 sh
H-1 (44% π W, 43% Li , 13% Al)	H-1 \rightarrow L+8, H \rightarrow L+7	457.66	0.0021	
H-2 (98% π L)	H \rightarrow L+9, H-1 \rightarrow L+10	408.07	0.1271	
H-3 (98% π L)	H-2 \rightarrow L, H-1 \rightarrow L+10	355.16	0.8223	322
H-4 (99% π L)	H-2 \rightarrow L, H-1 \rightarrow L+10, H \rightarrow L+11	344.94	0.1500	
H-5 (98% π L)	H-1 \rightarrow L+10, H \rightarrow L+11	290.20	0.0065	249
L ((22% π^* W, 70% π^* L, 8% π^* Al)	H-2 \rightarrow L+3, H-3 \rightarrow L+4, H-2 \rightarrow L+2	248.76	0.1388	
L+1 (81% π^* L, 14% π^* W, 5% π^* Al)	H-1 \rightarrow L+13, H \rightarrow L+12	241.99	0.3225	
L+2 (95% π^* L)				
L+3 (88% π^* L, 6% π^* W, 5% π^* Al)	H-2 \rightarrow L+2, H-2 \rightarrow L+8	234.85	0.0303	
L+4 (94% π^* L)				
L+5 (59% π^* L, 29% π^* W, 12% π^* Al)				
2				
H (55% d orbitals of Cu, 40% π L)	H \rightarrow L	653.04	0.0456	660
H-1 (91% π L, 8% π NO ₃ ⁻)	H-10 \rightarrow L+2, H-9 \rightarrow L	494.54	0.0606	367sh
H-2 (85% π L, 14% π NO ₃ ⁻)	H-1 \rightarrow L, H-1 \rightarrow L+1	357.14	0.3054	
H-3 (75% π L, 22% π NO ₃ ⁻)	H-1 \rightarrow L+1, H \rightarrow L+3	345.42	0.0029	
H-4 (88% π L, 10% π ACN)	H \rightarrow L+3, H-10 \rightarrow L	342.08	0.0042	323
H-5(98% π L)	H-1 \rightarrow L+2, H-4 \rightarrow L, H-5 \rightarrow L	330.99	0.0057	
H-6 (98% π L)	H-9 \rightarrow L, H-6 \rightarrow L+2, H-6 \rightarrow L+2	319.92	0.0302	
L (62% d orbitals Cu, 27% π^* L)	H-7 \rightarrow L+2, H-14 \rightarrow L	314.89	0.0508	

L+1 (43% π^* L, 56% π^* NO ₃ ⁻)	H-4 → L, H-4 → L+1	312.72	0.0355	240 sh
L+2 (67% π^* L, 31% π^* NO ₃ ⁻)	H-5 → L+1, H-8 → L+1,	304.68	0.1027	
L+3 (66% π^* L, 23% π^* ACN)	H-6 → L, H-5 → L, H-7 → L	302.43	0.0383	
L+4 (52% π^* ACN, 37% π^* L)	H-11 → L+2, H-7 → L	287.25	0.0761	
L+5 (95% L)	H-8 → L, H-7 → L+1	278.91	0.1519	
L+6 (95% L)				

H : HOMO, L : LUMO, Nap: naphthalene moiety of Ligand; dab: diaminobenzaldehyde moiety of ligand; L: ligand; ACN: acetonitrile, W: water.