Supplementary Information

A novel pyrene based highly selective reversible fluorescent-colorimetric sensor for rapid detection of Cu^{2+} ion: application in bio-imaging

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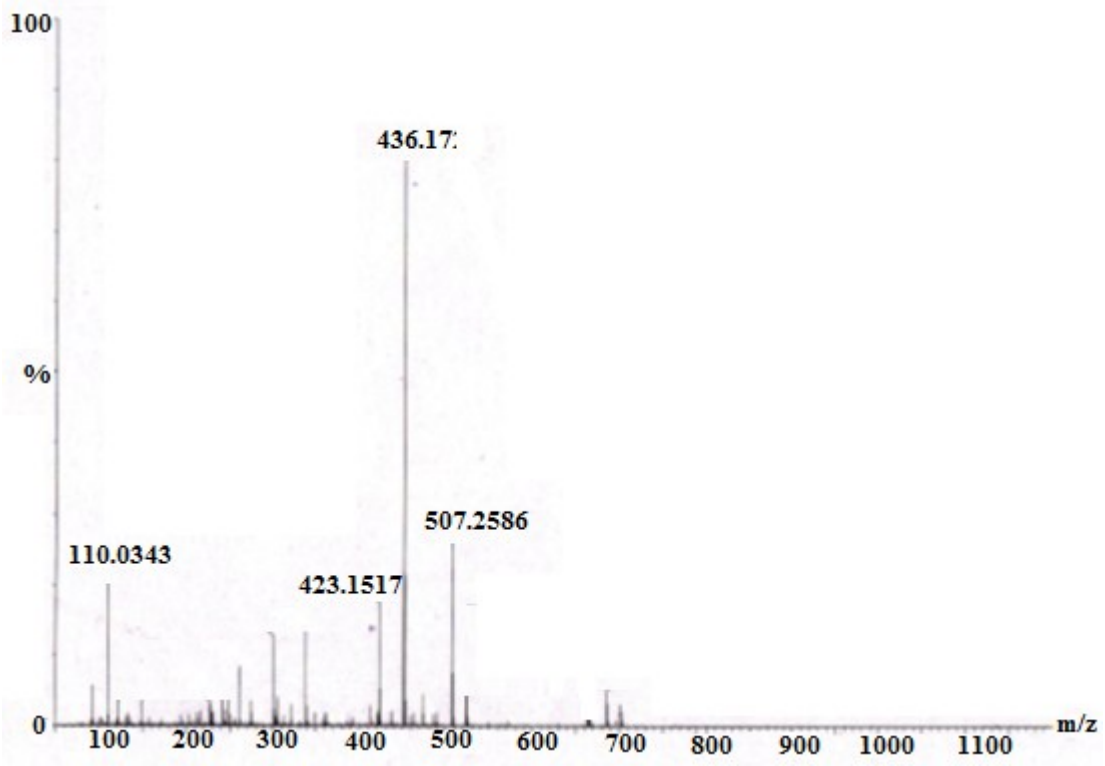

Fig. S1. Mass spectra of **L**

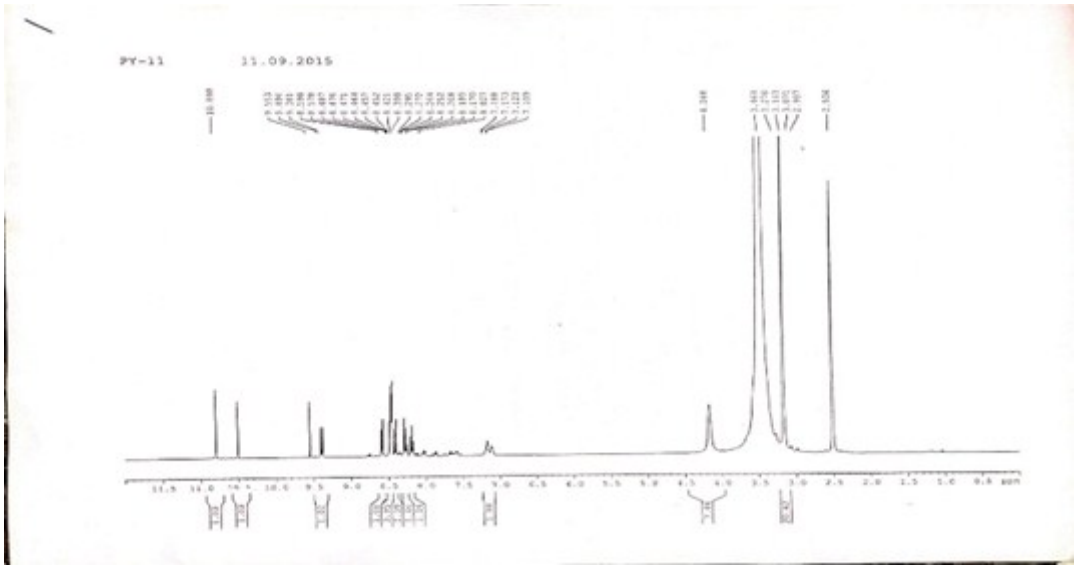

Fig. S2. ^{1}H NMR spectra of **L**

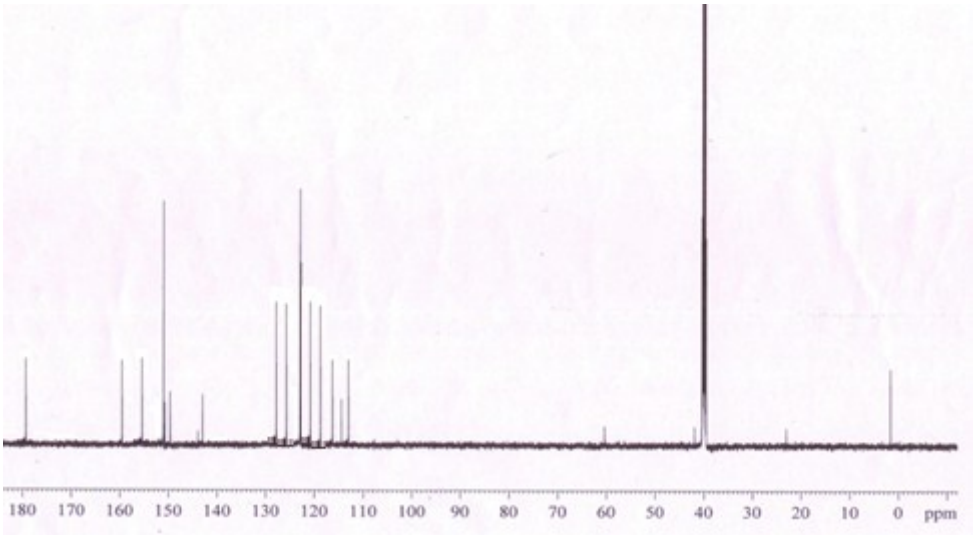

Fig. S3. ^{13}C NMR Spectra of **L**

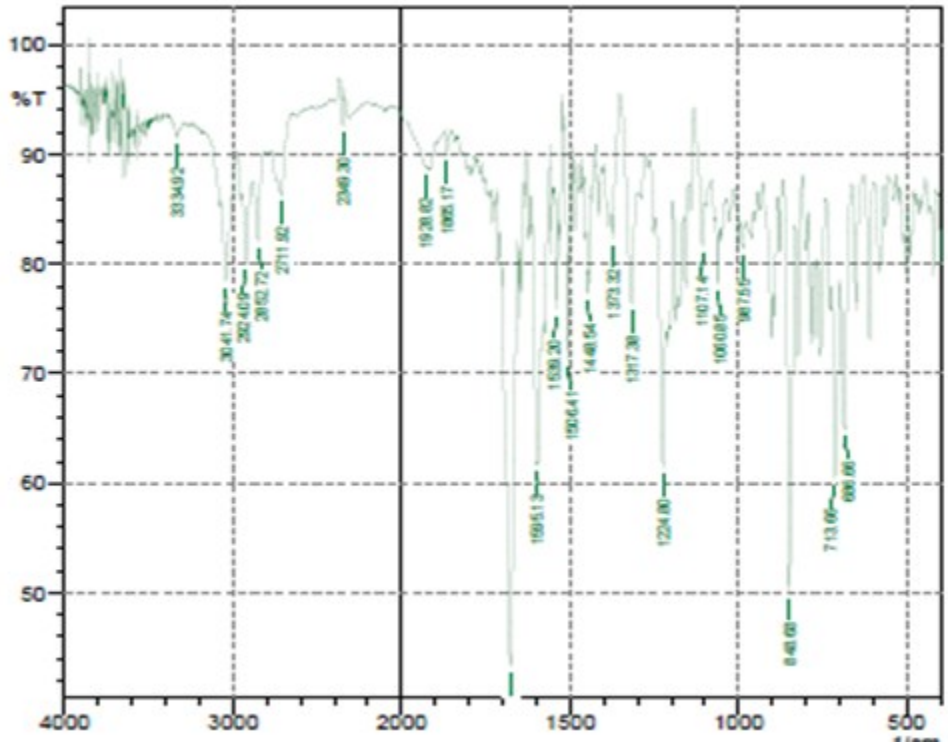

Fig. S4. FTIR spectra of **L**

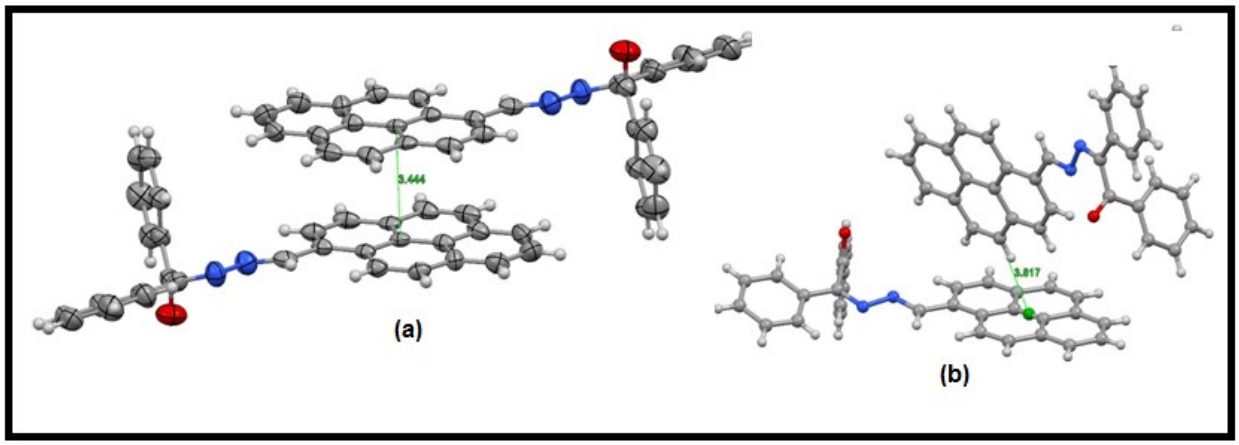

Fig. S5. Packing diagram of compound **L** is (a) showing intermolecular π**...**π (top) and (b) CH-π interactions.

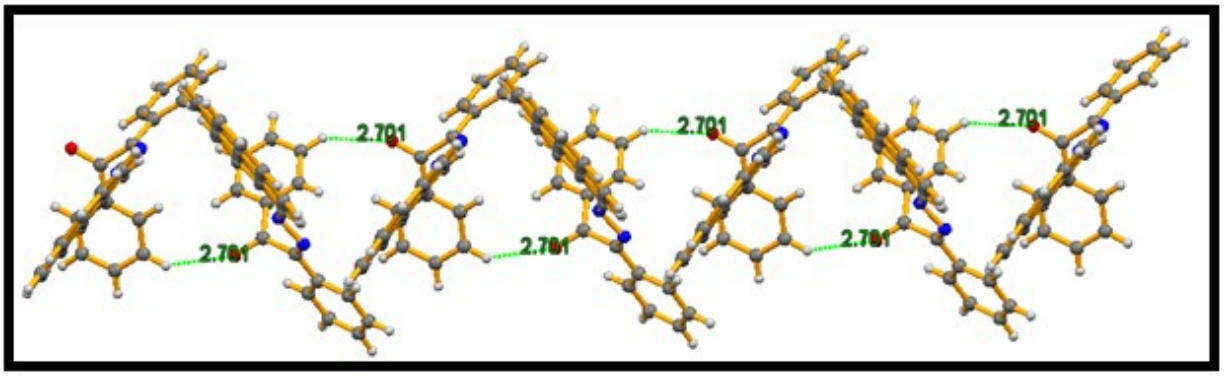

Fig. S6. Polymeric view of **L** (C: Grey, N: Blue,O: Red).

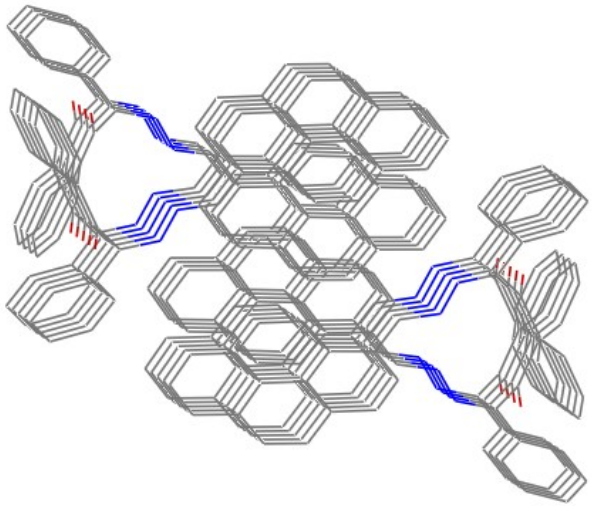

Fig. S7. 3-D supramolecular structure of **L**.

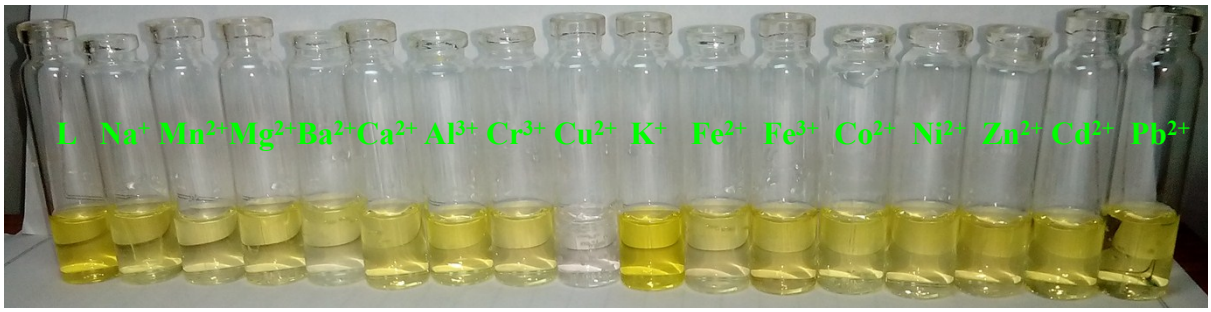

Fig. S8. The colour changes of **L** (10 μM) upon addition of various cations (10 equiv.) in MeCN-H_2O (2:1, v/v) at room temperature.

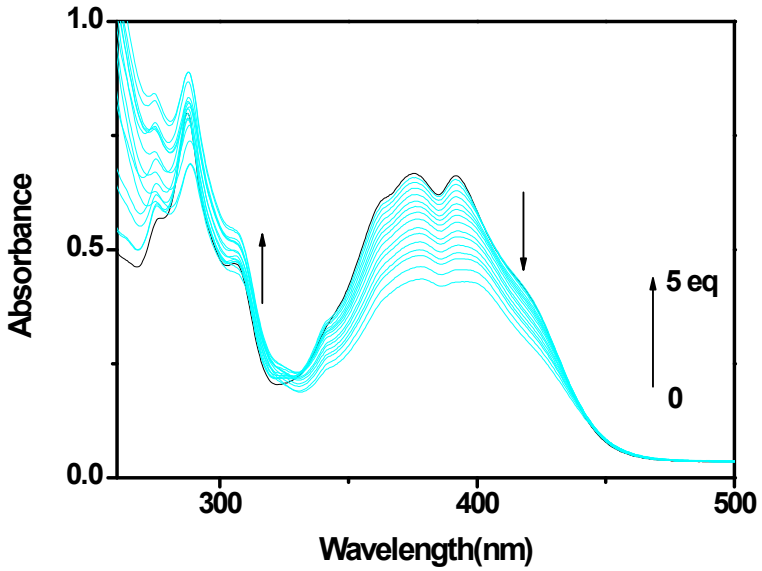

Fig. S9. Absorption spectra of **L** changes after addition of Cu^{2+} up to 5 equiv. in MeCN-H_2O (2:1, v/v) at room temperature.

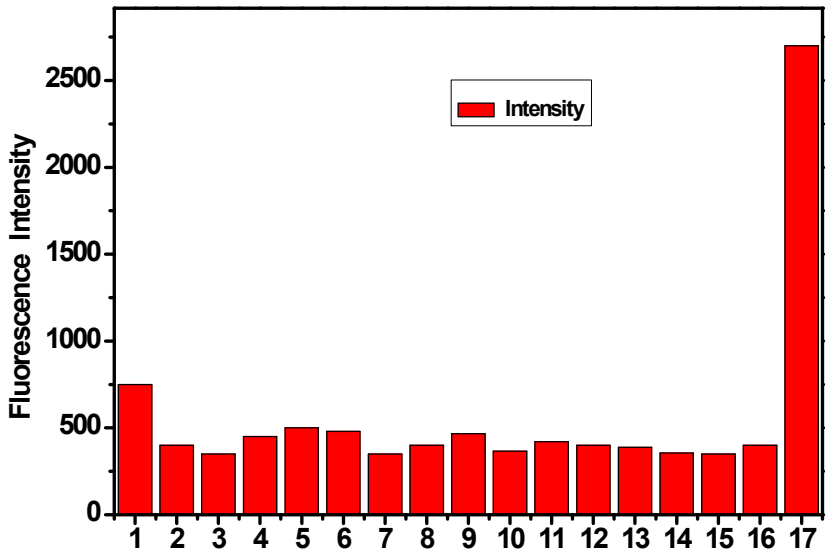

Fig. S10 (a) Fluorescence spectra of **L** (10 μM) before and after addition ofvarious metal ions (100 μM) (1.L, 2.Mn^{2+}, 3.Fe^{3+}, 4.Co^{2+}, 5.Ni^{2+}, 6.Ba^{2+}, 7.Zn^{2+}, 8.Cd^{2+},9.Fe^{2+},10.Na^{+}, 11.K^{+}, 12.Mg^{2+}, 13.Ca^{2+}, 14.Al^{3+}, 15.Pb^{2+},16.Cr^{3+} and 17.Cu^{2+}) in MeCN-H_2O (2:1, v/v) at room temperature.

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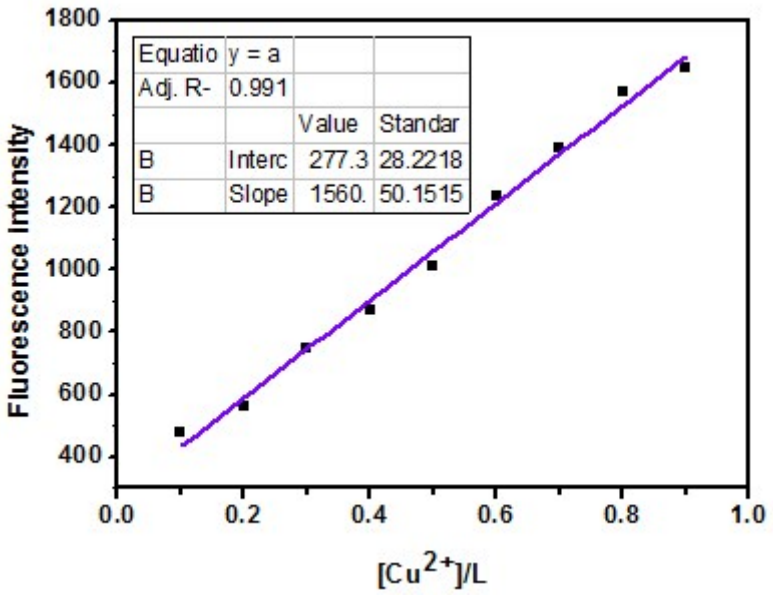

Fig. S11. Detection limit of **L**.

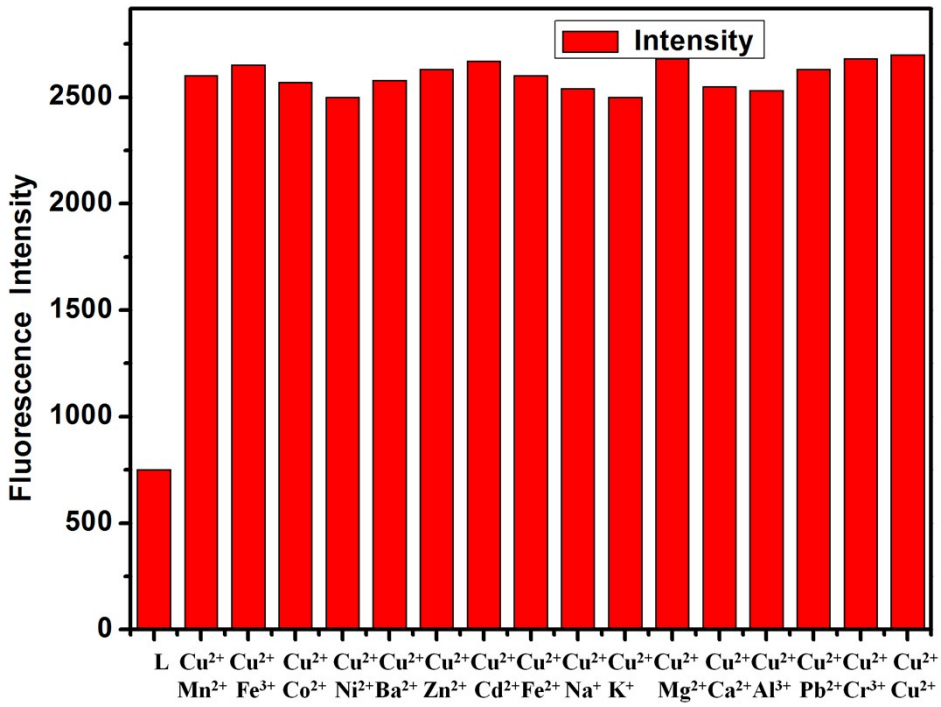

Fig. S12. Relative fluorescence of **L** and its complexation with Cu^{2+} in the presence of various metal ions (10 equiv.) λ_{ex} = 305 nm.

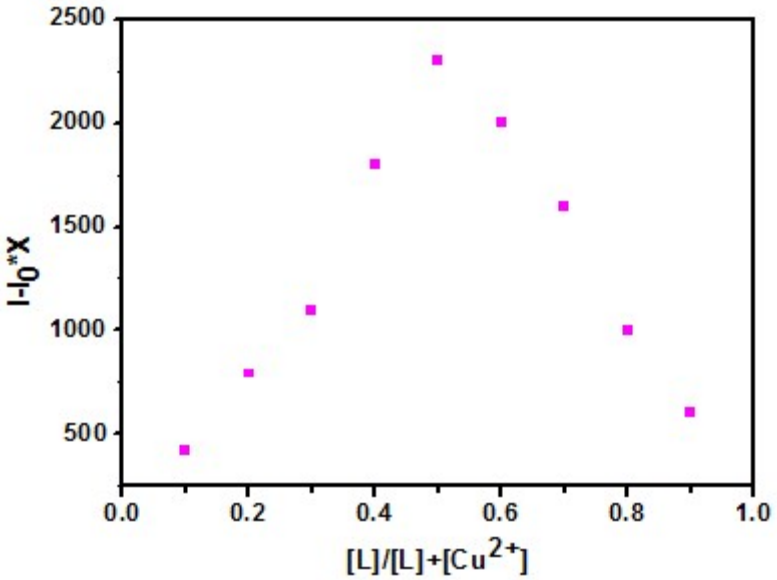

Fig. S13. Job's plot for Cu^{2+}.

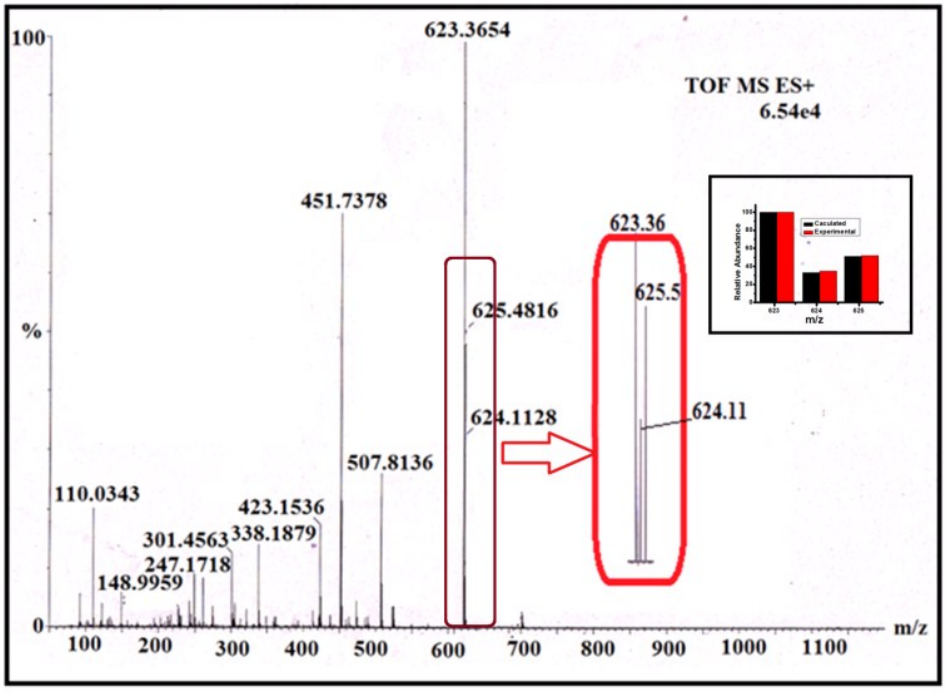

Fig. S14. ESI-MS spectra of **L**+ Cu^{2+}.

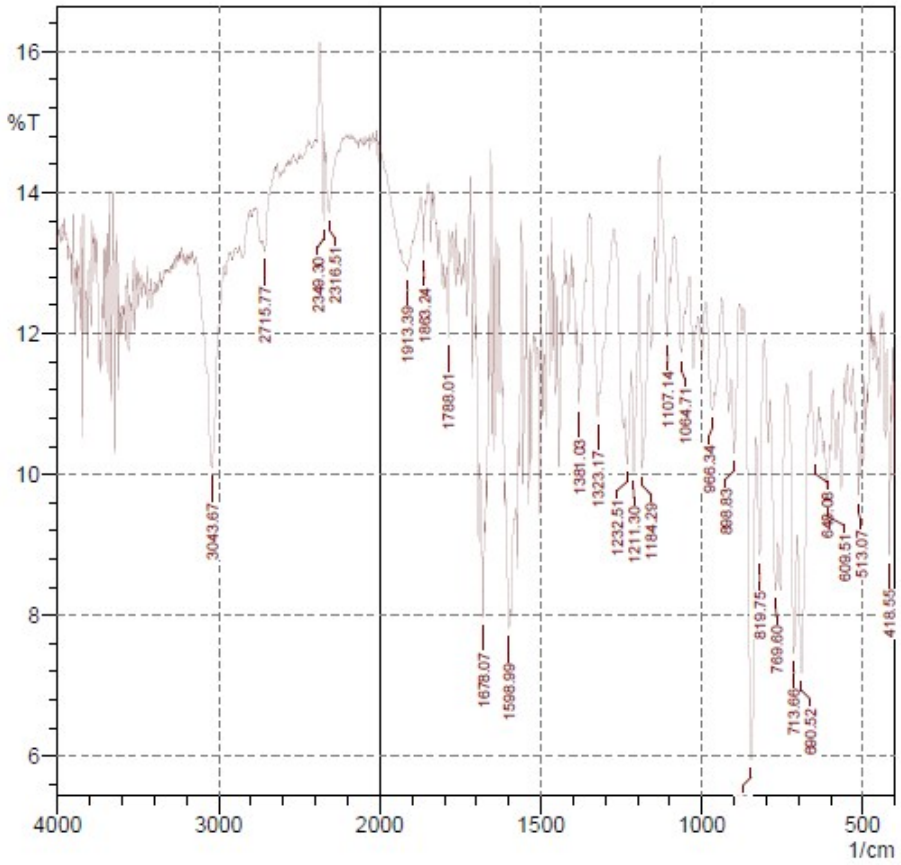

Fig. S15. FTIR spectra of **L**+ $Cu(NO_3)_2$.

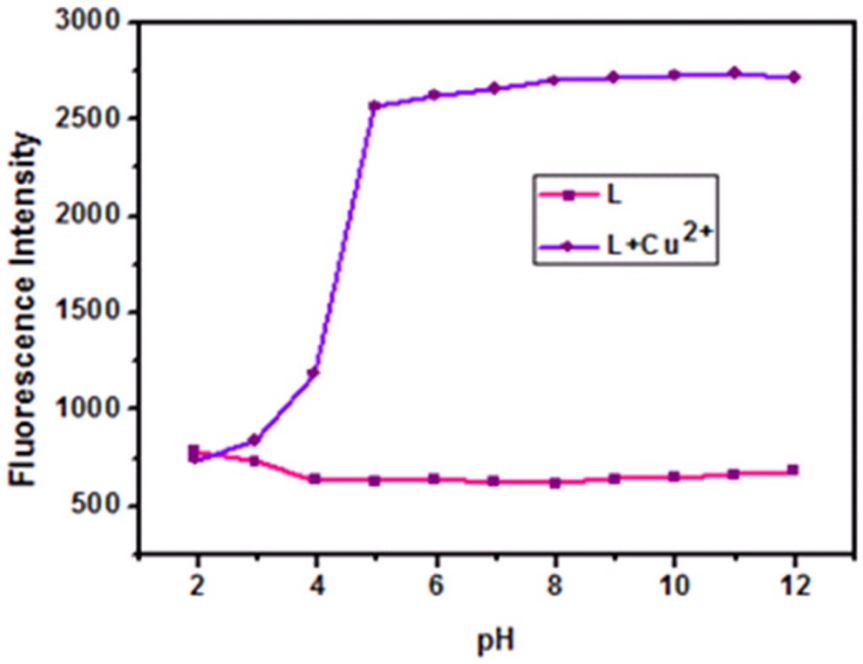

Fig. S16. Fluorescence intensity of **L** and **L**–Cu^{2+} at various ranges of pH in MeCN-H_2O (2:1, v/v) at room temperature. λ_{ex} = 305 nm. Inset: intensity at 444 nm.

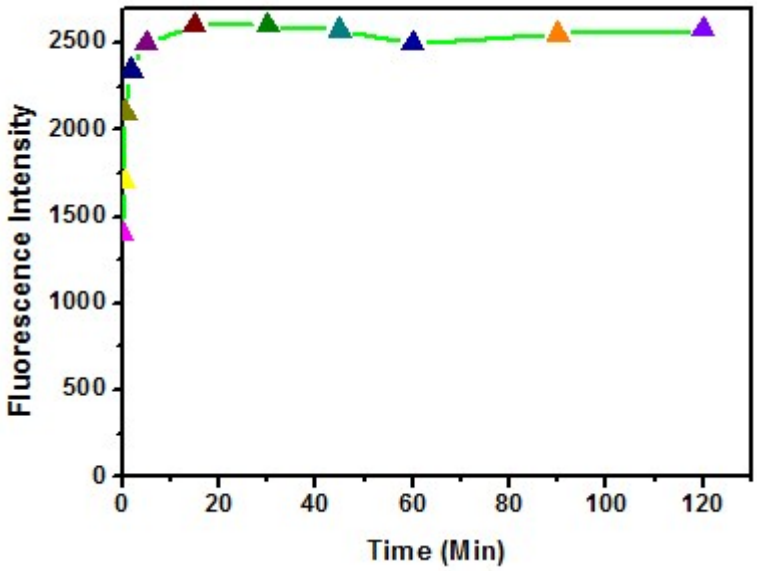

Fig. S17. Time evolution for Cu^{2+}.

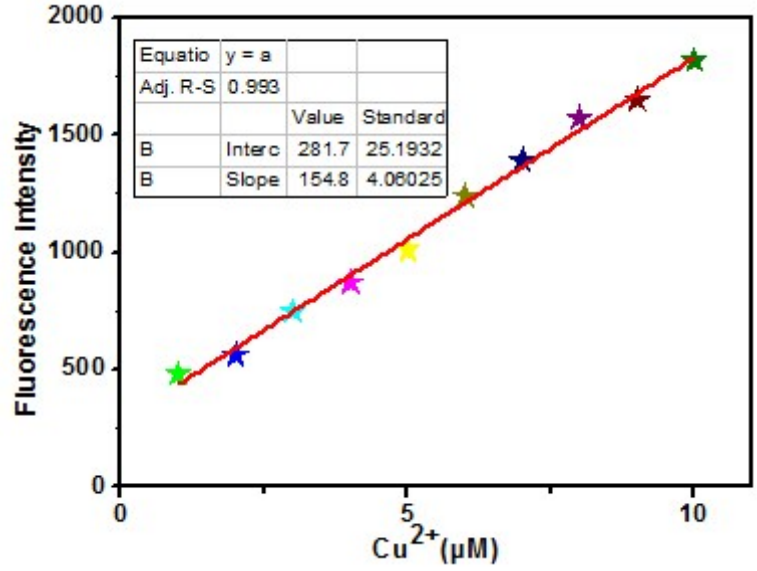

Fig. S18. Change of Fluorescence intensity on increasing amounts of Cu^{2+} at pH=7.4.

Table S1. The diagnostic experimental and calculated IR frequencies are shown for receptor **L** and **1**.

Receptor L		**1**		Assignments
Expt. (cm^{-1})	Theo. (cm^{-1})	Expt. (cm^{-1})	Theo. (cm^{-1})	
1691 (shoulder)	1699.32	1682	1682.24	ν (C=O)
1678	1678.92	1668 (shoulder)	1631.1	ν (C=N)

2852, 2924, 3041	3026.61	3041 (br), 2724, 2858	3391.33, 3248.97, 3038.04	ν (Ar-H)
		1446, 1387, 1242	1460.36, 1390.93, 1253.41	ν (NO_3^-)

Table S2. Electronic transitions of **L** calculated in CH_3OH using the TD-DFT method.

Most important orbital excitations	λ	f	Experimental λ (ε)
H→L, H→L+1	454.39	0.1374	418sh (4122)
H→L, H→L+1, H-1→L+1	430.86	0.6561	391(6596)
H-1→L+1, H-1→L+1, H-1→L+2	388.13	0.0633	375 (6744)
H→L+2, H-2→L, H-2→L+1, H-2→L+1	379.72	0.2999	306 (4677)
H-2→L+1, H→L+2	296.65	0.0672	287 (8000)
H-3→L, H→L+2, H-3→L, H-2→L+1, H→L+3	280.30	0.1068	275 (5642)
H-3→L, H-5→L, H-6→L, H-7→L, H-8→L,	277.87	0.0355	
H-4→L, H-2→L+2	268.51	0.0432	
H→L+4, H-2→L+2, H-3→L+2, H→L+7	235.01	0.0136	
H-5→L+1, H-5→L+2, H-6→L+1, H-4→L+1	228.43	0.0139	
H-5→L+1, H-8→L, H-3→L, H-2→L	214.66	0.1333	232 (12,700)

λ –wavelength (nm); ε – molar absorption coefficient ($dm^3\ mol^{-1}\ cm^{-1}$); f – oscillator strength; H – highest occupied molecular orbital; L – lowest unoccupied molecular orbital.

Table S3. Electronic transitions of **L-Cu^{2+}** calculated in CH_3OH using the TD-DFT method.

Most important orbital excitations	λ	f	Experimental λ (ε)

H→L+1, H-1→L	457.44	0.0595	428sh (2,610)
H-2→L, H-1→L, , H→L	436.06	0.0423	398 (4478)
H-3→L, H-2→L, H-2→L, H-1→L+1	394.01	0.0204	375 (4505)
H-1→L, H-2→L, H-2→L+1, H-3→L,	391.36	0.0475	
H-3→L, H-2→L, H-2→L+1, H-1→L+1	376.78	0.0847	
H-3→L, H-2→L, H-1→L+1	352.70	0.0078	
H→L+1, H-4→L, H-3→L	299.78	0.069	305 (4617)
H-5→L, H-4→L, H-3→L+1, H-3→L	287.67	0.0357	288 (7890)
H→L+2, H-4→L+1, H→L+3, H-3→L+1	265.82	0.0148	274 (6232)
H-1→L+1, H-4→L+1, H→L+2	259.77	0.0961	
H-1→L+2, H-6→L, H-5→L	240.14	0.0383	236 (38495)
H-1→L+2, H→L+3, H-3→L+1, H-6→L+1	230.58	0.1038	225 (37000)
H-2→L+2, H-7→L+1, H-8→L, H-5→L+1,	199.47	0.0734	

λ –wavelength (nm); ε – molar absorption coefficient ($dm^3\ mol^{-1}\ cm^{-1}$); f – oscillator strength; H – highest occupied molecular orbital; L – lowest unoccupied molecular orbital.