Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supporting Information

Rational designing of first furoquinolinol based molecular systems for easy detection of Cu^{2+} with potential applications in the area of membrane sensing

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Analytical data

3-(4-bromophenyl)-2-((2-morpholinoethyl)amino)furo[3,2-*c*]quinolin-4-ol (FQ1).

Yellow solid (81%), mp (decomp.) = 258-259°C, IR (KBr, cm^{-1}): υ_{max} = 3369, 2963, 2864, 2821, 1655, 1602, 1498. ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 2.47 (br s, 4H), 2.61 (br s, 2H), 3.48 (br s, 2H), 3.66 (br s, 4H), 5.26 (br s, 1H), 7.21–7.29 (m, 3H)*****, 7.38 (td, 1H, *J* = 7.3 & 1.2 Hz), 7.54 (s, 4H), 7.82 (d, 1H, *J* = 7.8 Hz), 10.49 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_c = 37.2, 48.5, 52.8, 62.2, 89.9, 103.3, 106.0, 115.1, 117.7, 120.0, 123.6, 125.9, 126.6, 128.5, 130.4, 141.0, 155.0, 155.4, 160.8. HRMS (ESI) m/z calcd. for $C_{23}H_{22}BrN_3O_3$ $[M-H]^+$: 466.0760, found: 466.0765.

3-(4-chlorophenyl)-2-(pentylamino)furo[3,2-*c*]quinolin-4-ol (FQ2).

Yellow solid (78%), mp = 218-220 °C, IR (KBr, cm^{-1}): υ_{max} = 2827, 1661, 1606, 1500, 1416. 1H NMR (400 MHz, $CDCl_3$): δ_H = 0.87–0.94 (m, 3H), 1.36 (m, 4H), 1.64 (quint, 2H, *J* = 7.2 Hz), 3.39 (t, 2H, *J* = 7.1 Hz), 4.38 (br s, 1H), 7.14–7.26 (m, 2H)*****, 7.32 (m, 2H), 7.39 (d, 2H, *J* = 8.5), 7.58 (dt, 2H, *J* = 8.5 & 1.8 Hz), 7.82 (d, 1H, *J* = 7.8 Hz), 11.17 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_c = 14.0, 22.9, 29.2, 29.8, 42.6, 94.6, 107.9, 110.7, 122.4, 124.6, 128.2, 129.9, 130.4, 130.9, 131.3, 133.0, 145.7, 159.6, 160.1, 165.4. HRMS (ESI) m/z calcd. for $C_{22}H_{21}ClN_2O_2[M+H]^+$: 379.1207, found: 379.1207.

***** Solvent peak at 7.26 is overlapped with this peaks, hence higher integration is obtained.

See ^{1}H NMR spectra of both compounds at page S4 and S7 of ESI.

Figure SS1: 3-(4-bromophenyl)-2-((2-morpholinoethyl)amino)furo[3,2-*c*]quinolin-4-ol (FQ1): ^{1}H NMR

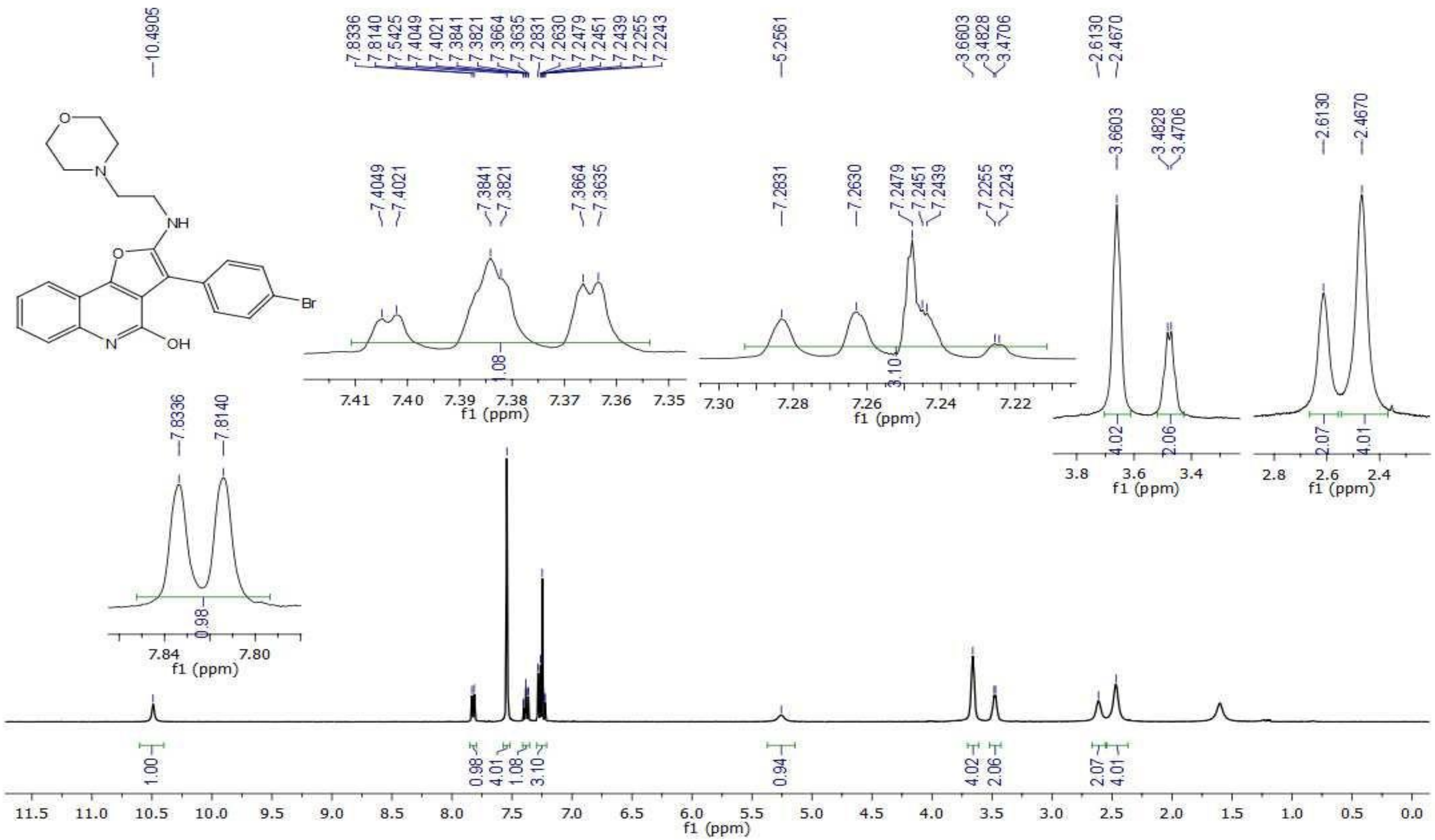


Figure SS2: 3-(4-bromophenyl)-2-((2-morpholinoethyl)amino)furo[3,2-*c*]quinolin-4-ol (FQ1): ^{13}C NMR

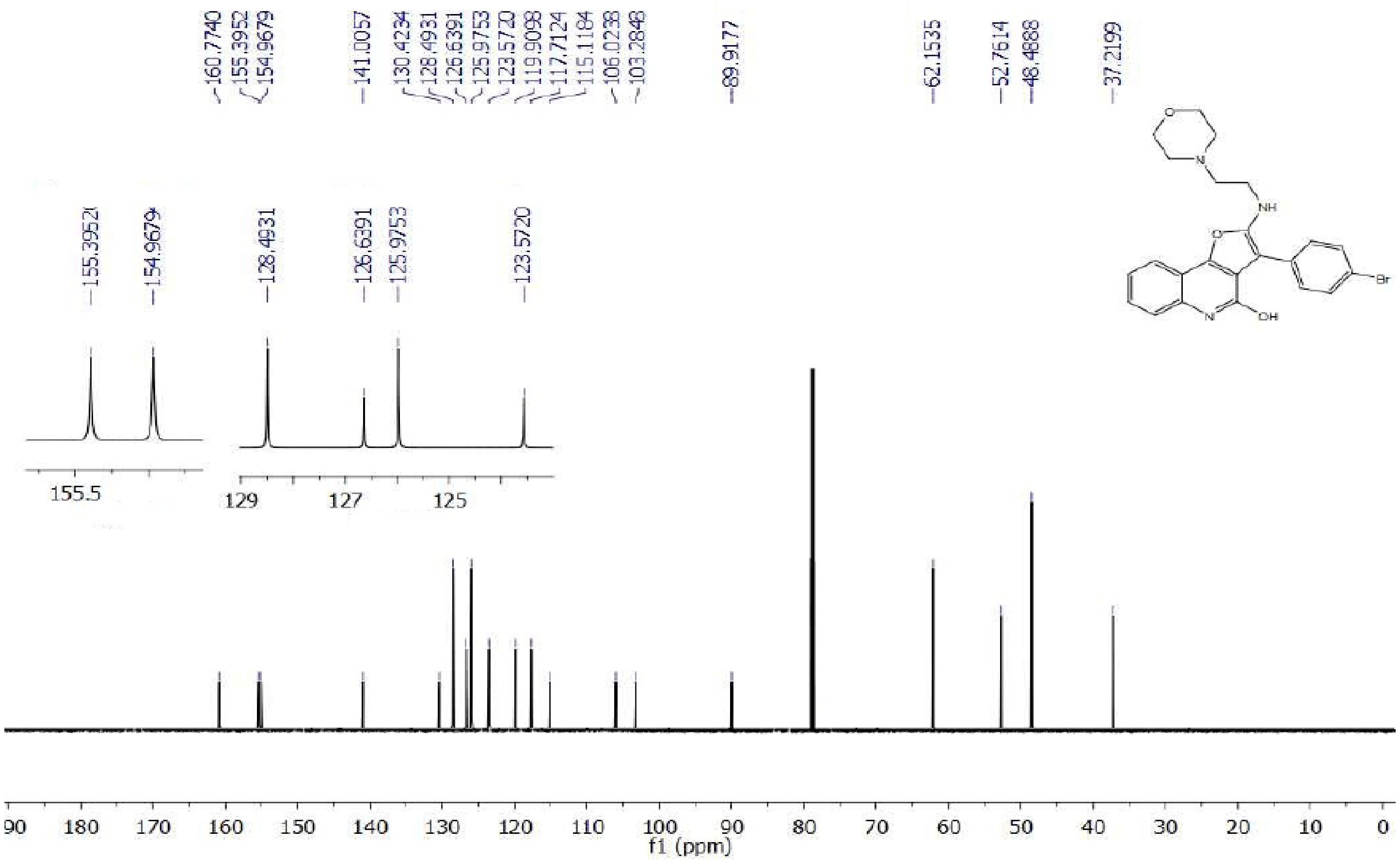


Figure SS3: 3-(4-bromophenyl)-2-((2-morpholinoethyl)amino)furo[3,2-*c*]quinolin-4-ol (FQ1): HRMS

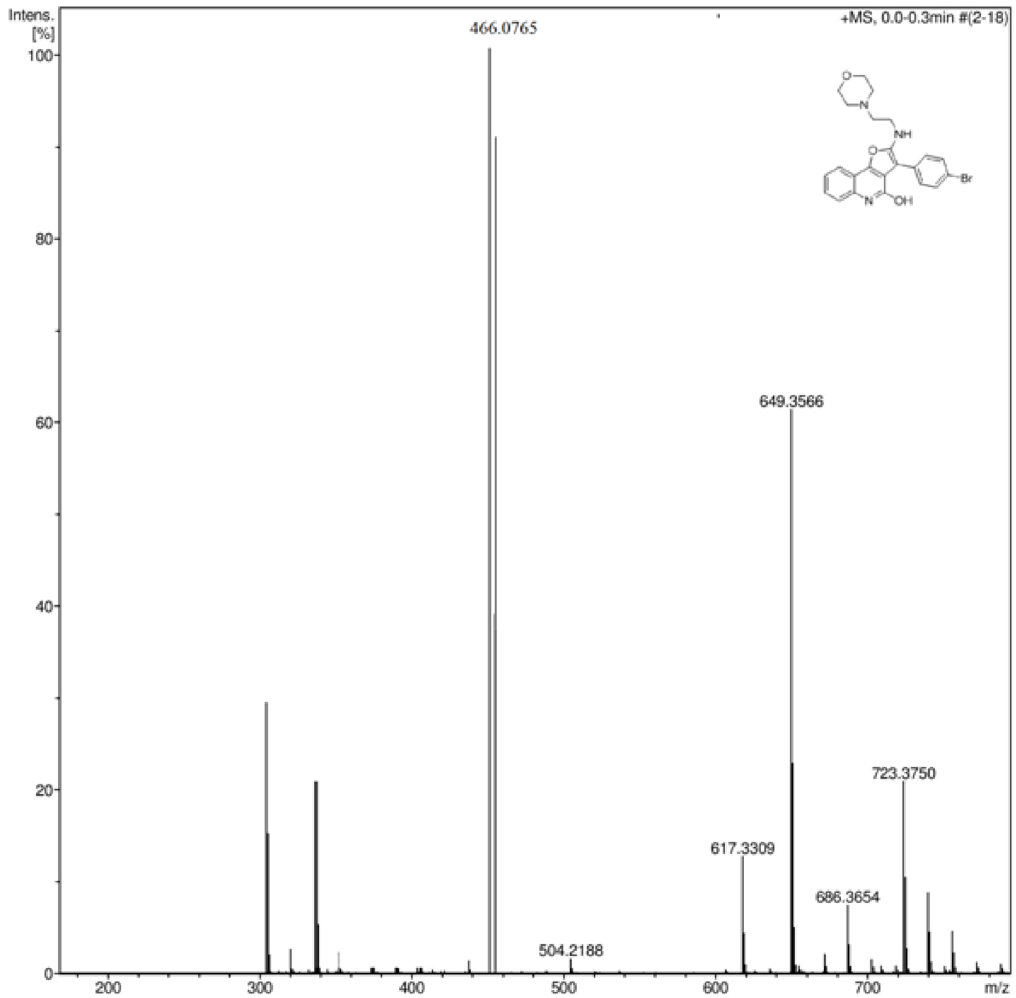


Figure SS4: 3-(4-chlorophenyl)-2-(pentylamino)furo[3,2-*c*]quinolin-4-ol (FQ2): ^{1}H NMR

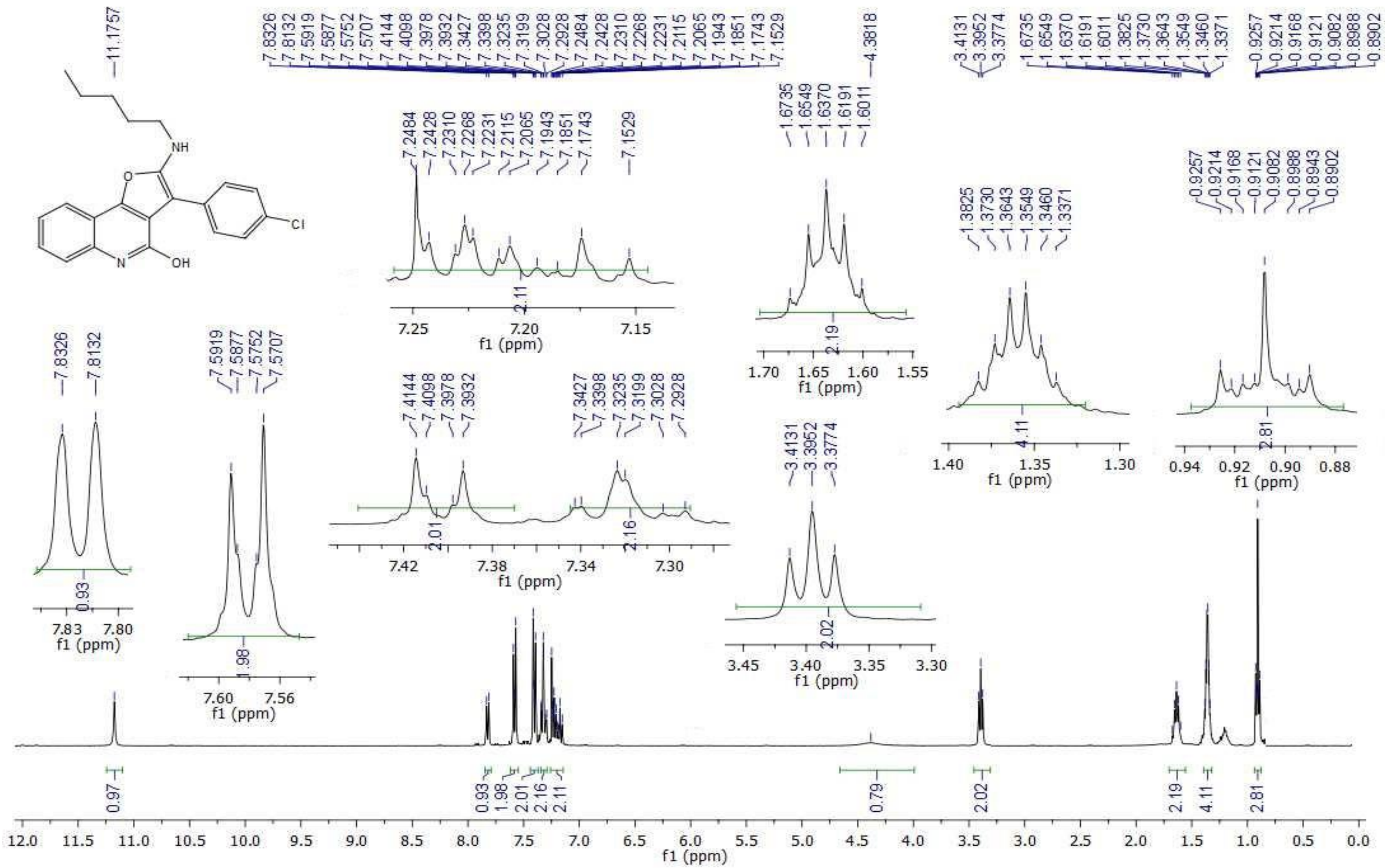


Figure SS5: 3-(4-chlorophenyl)-2-(pentylamino)furo[3,2-*c*]quinolin-4-ol (FQ2): ^{13}C NMR

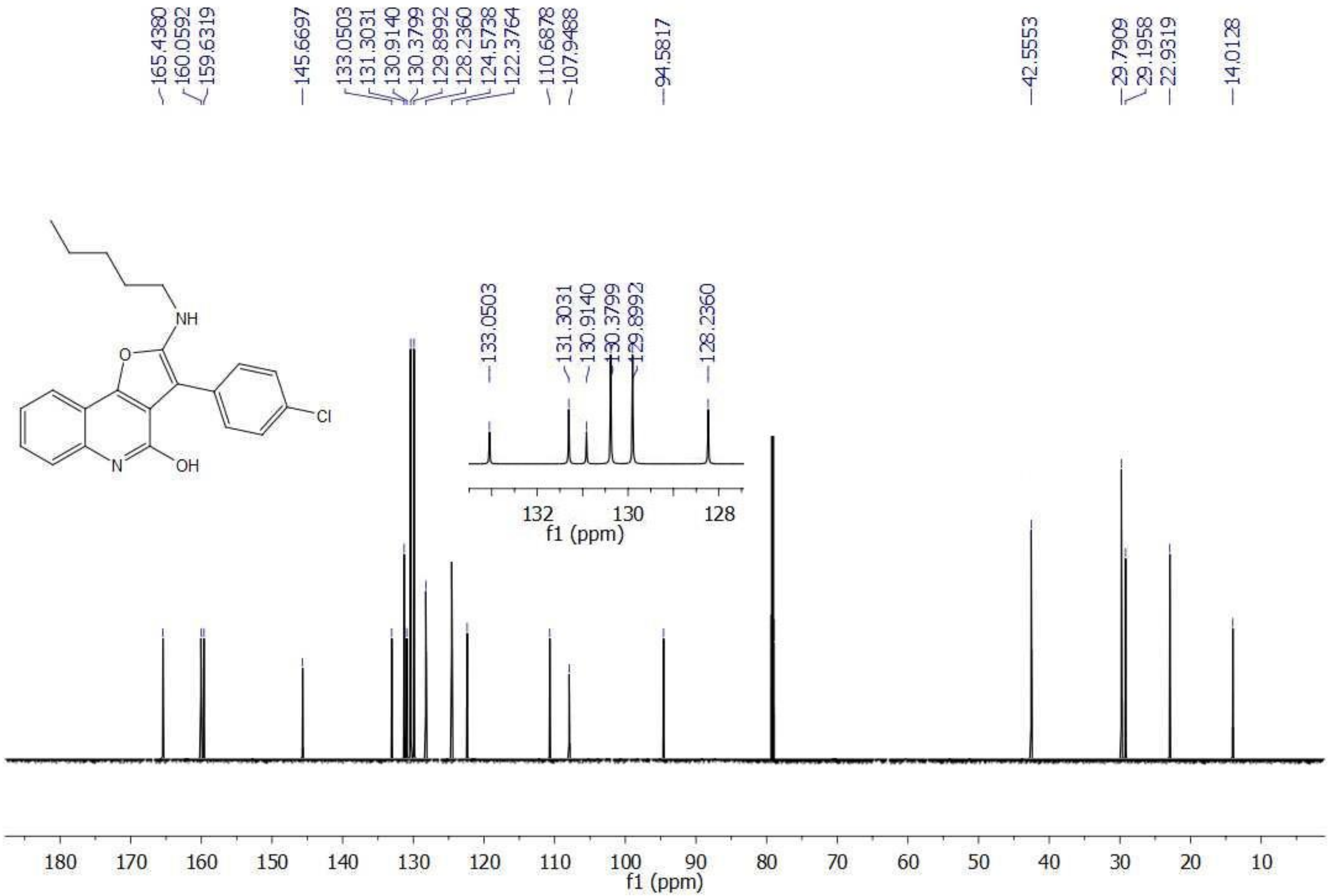


Figure SS6: 3-(4-chlorophenyl)-2-(pentylamino)furo[3,2-*c*]quinolin-4-ol (FQ2): HRMS

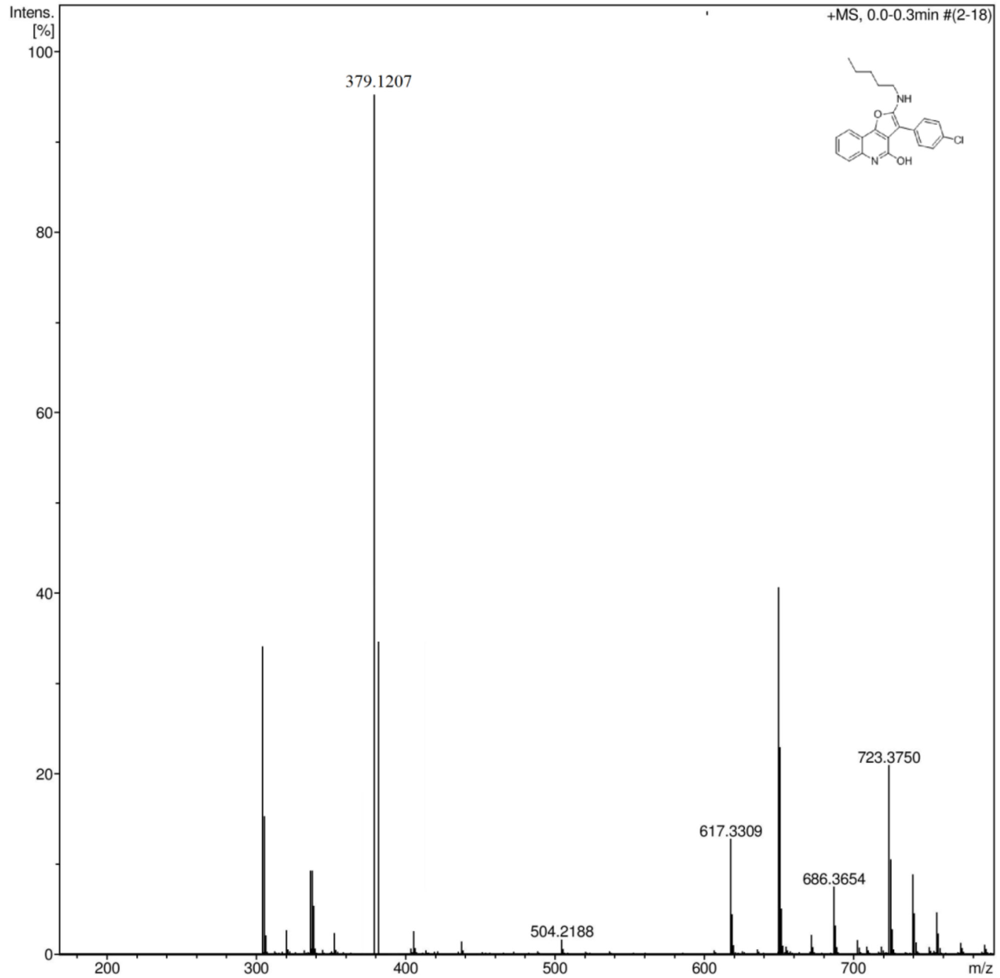


Figure SS7: UV-Vis Spectra of FQ1 (20µM in DMSO:MeOH = 1:9) in the presence of different ions (10 equiv.). The distinct behaviour of Cu^{2+} (equimolar) is apparent from figure.

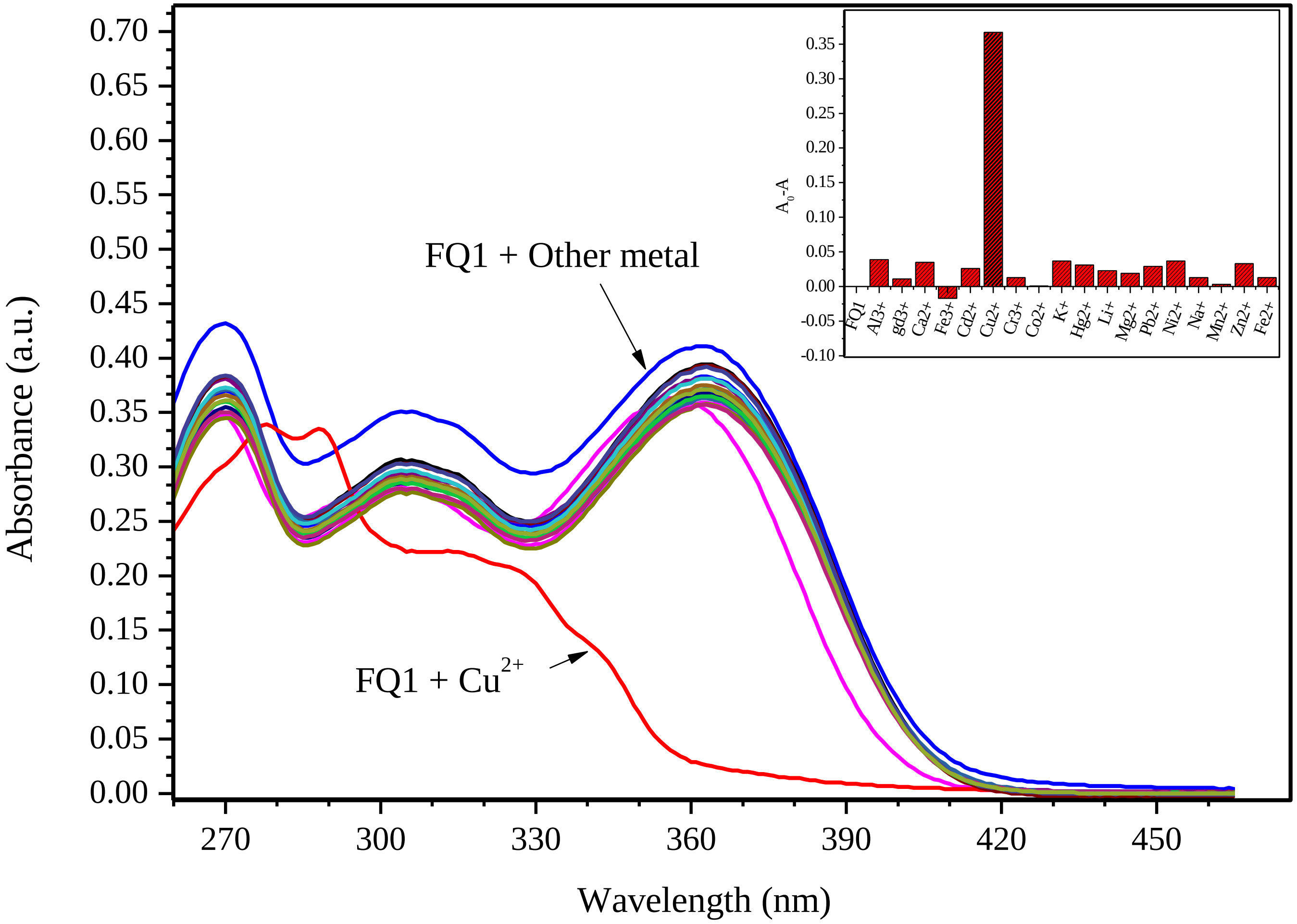


Figure SS8: UV-vis Spectra of FQ2 (20µM in DMSO:MeOH = 1: 9) in the presence of different ions (10 equiv.). The distinct behaviour of Cu^{2+} (equimolar) is apparent from figure.

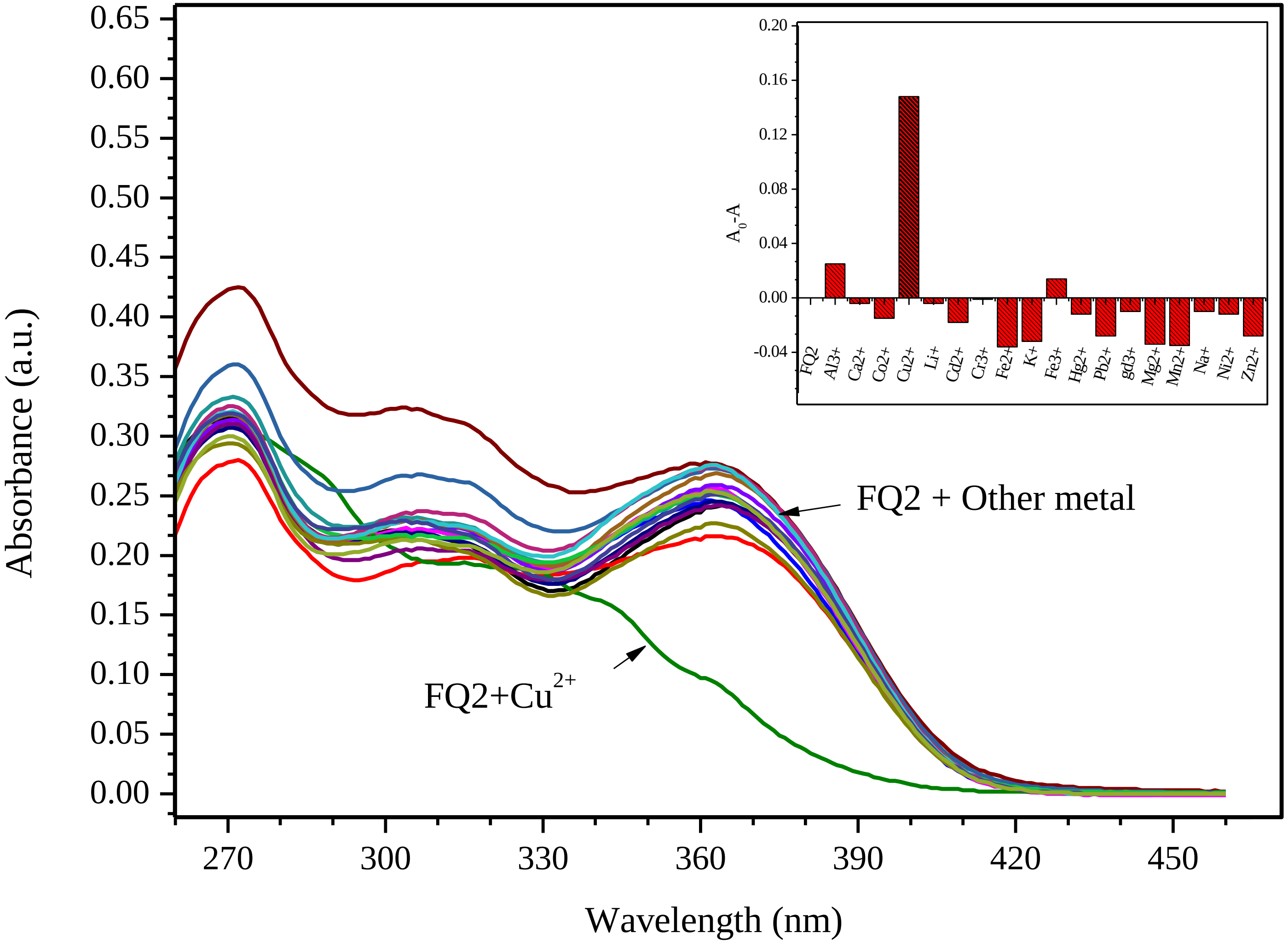


Figure SS9: Fluorescence response of FQ1 (20μM in DMSO:MeOH = 1: 9) toward 10 equiv. of different metal ions after excitation at 370 nm.

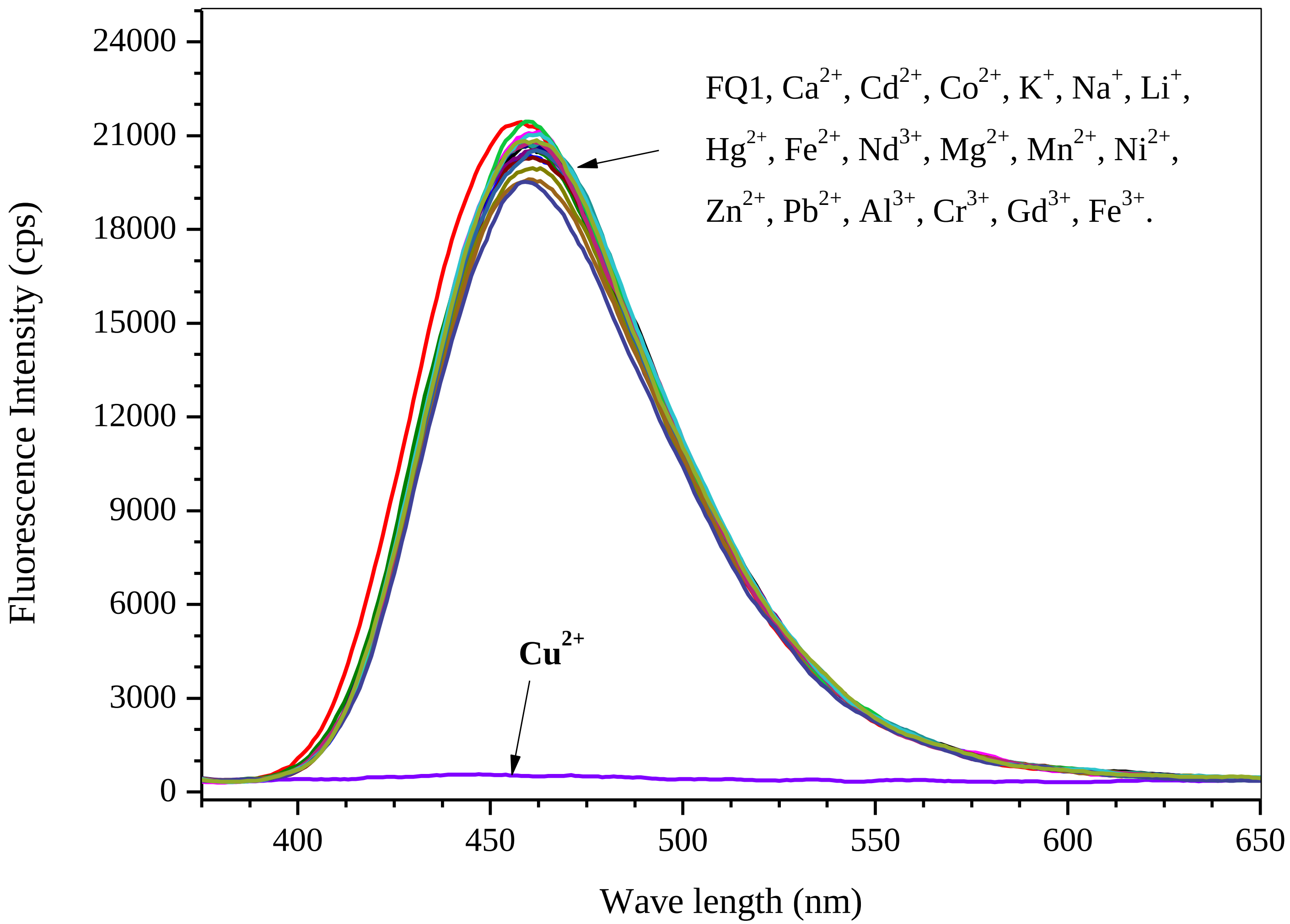


Figure SS10: Fluorescence response of FQ1 (20µM in DMSO:MeOH = 1: 9) toward 10 equiv. different metal ions after excitation at 370 nm wavelength.

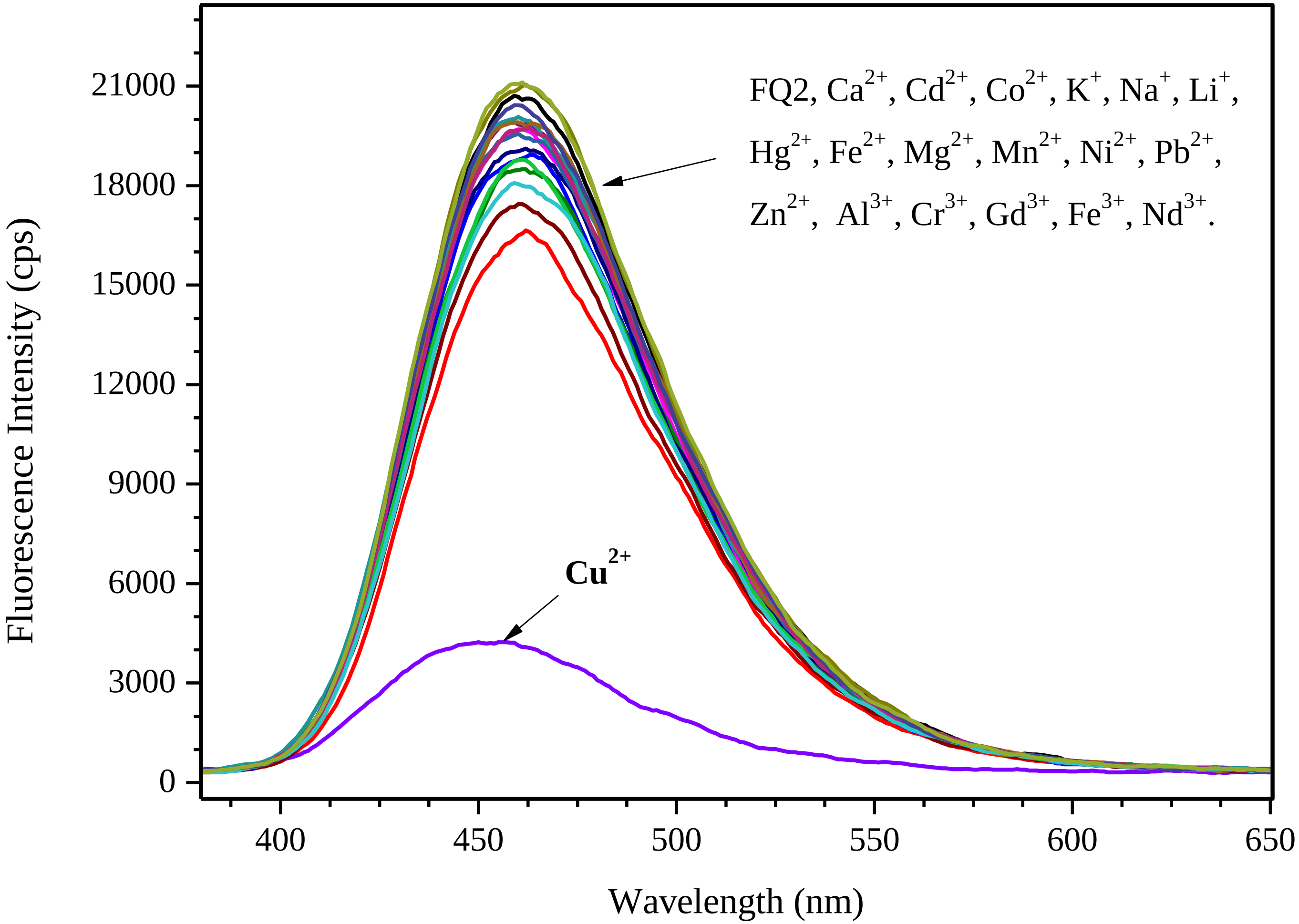


Figure SS11: Fluorescence responses of FQ1 (20μM in DMSO:MeOH = 1:9) in the presence of different metal ions.

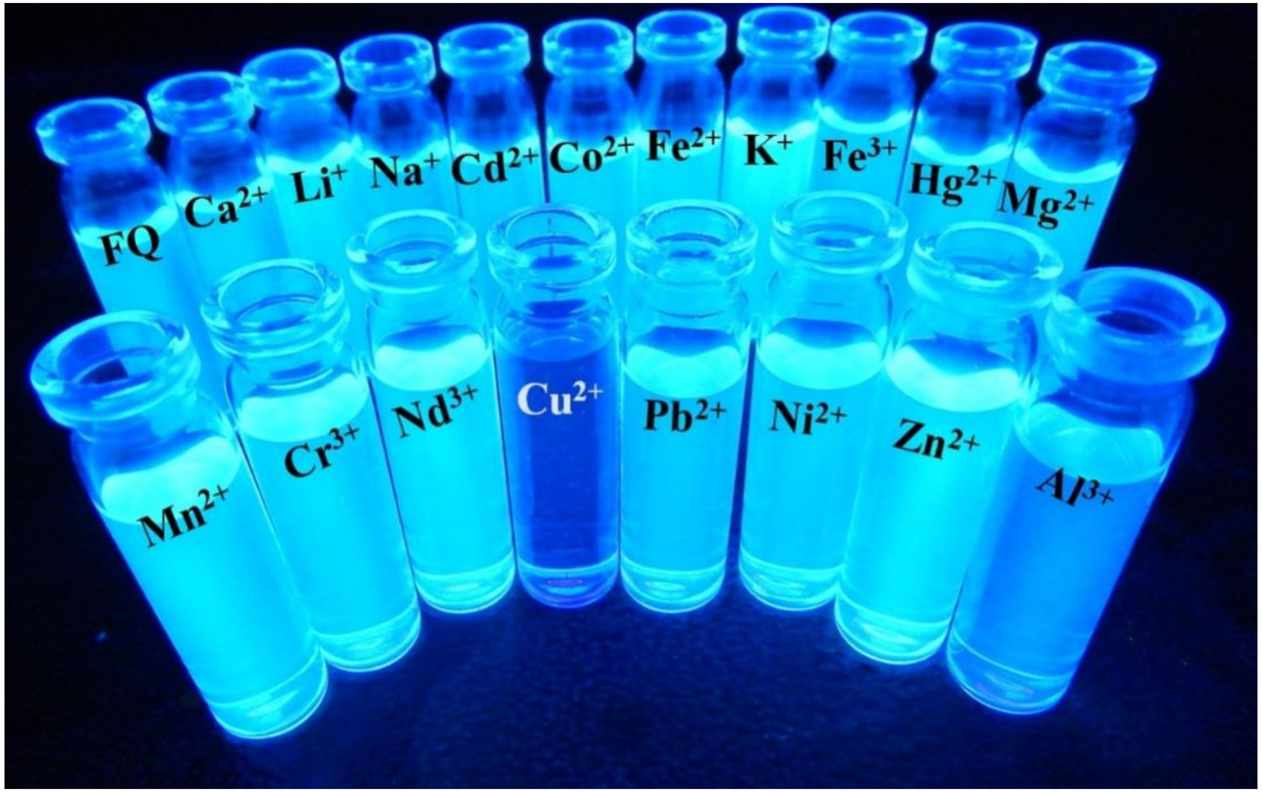


Figure SS12: Fluorescent titration of FQ1 (20 μM in DMSO:MeOH = 1:9) against Cu^{2+} (0.1 equiv. to 2.5 equiv.) after excitation at 370 nm wavelength.

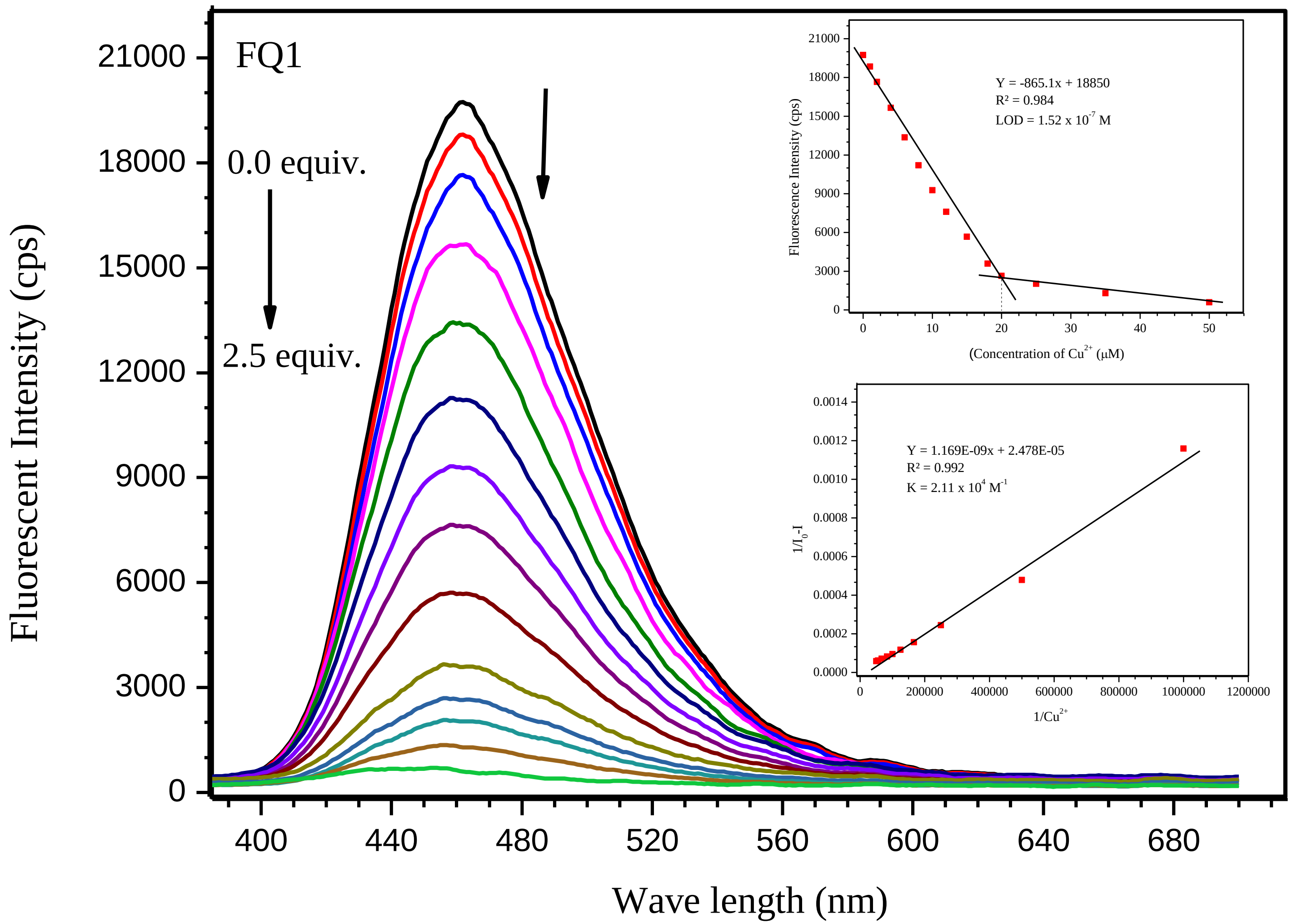


Figure SS13: Fluorescent titration of FQ2 (20 μM in DMSO:MeOH = 1:9) against Cu^{2+} (0.1 equiv. to 2.5 equiv.) after excitation at 370 nm wavelength.

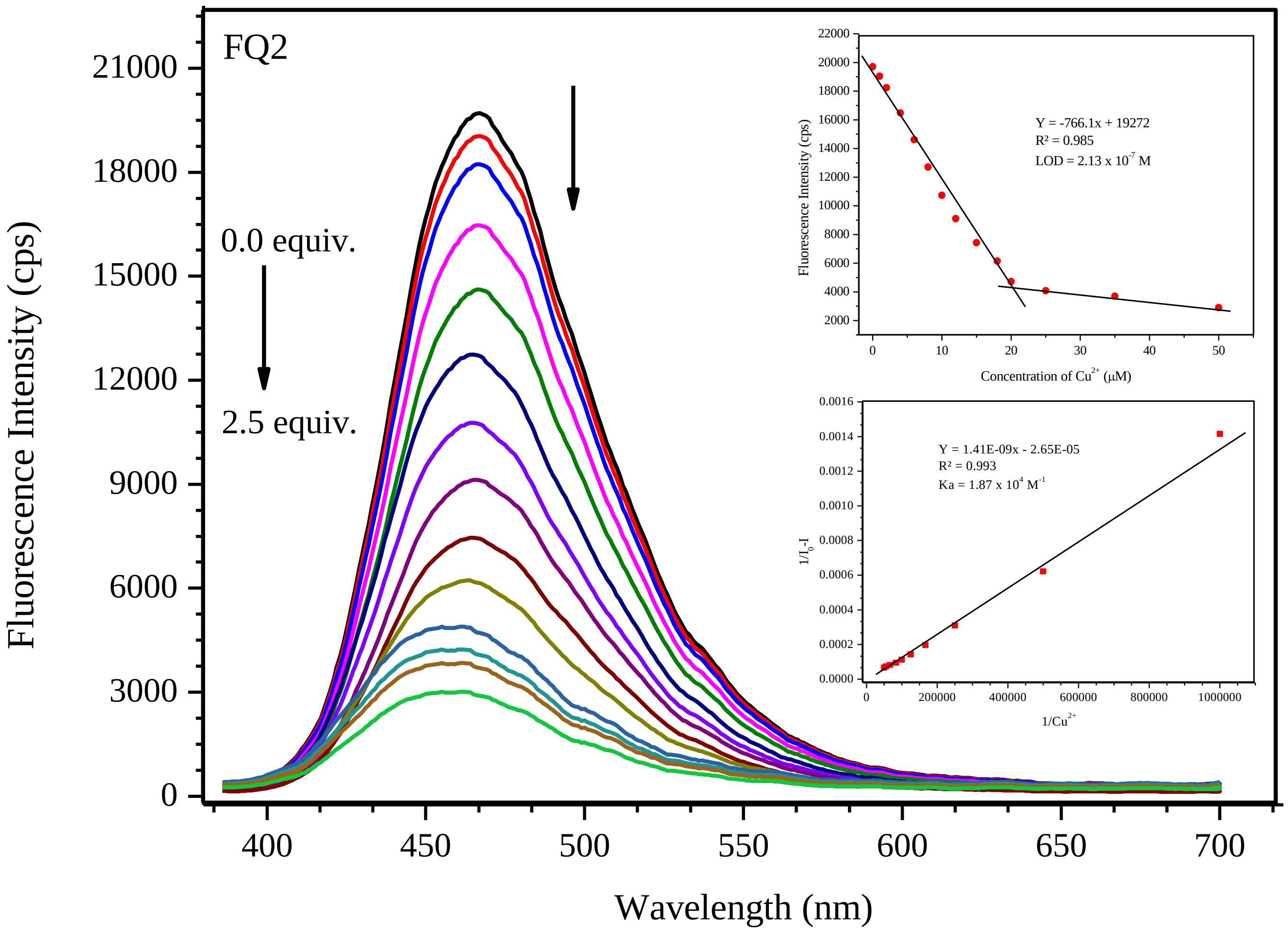


Figure SS14: Examination of selectivity of FQ1 (20 µM in DMSO:MeOH = 1:9) towards Cu^{2+} in the presence of interfering ions.

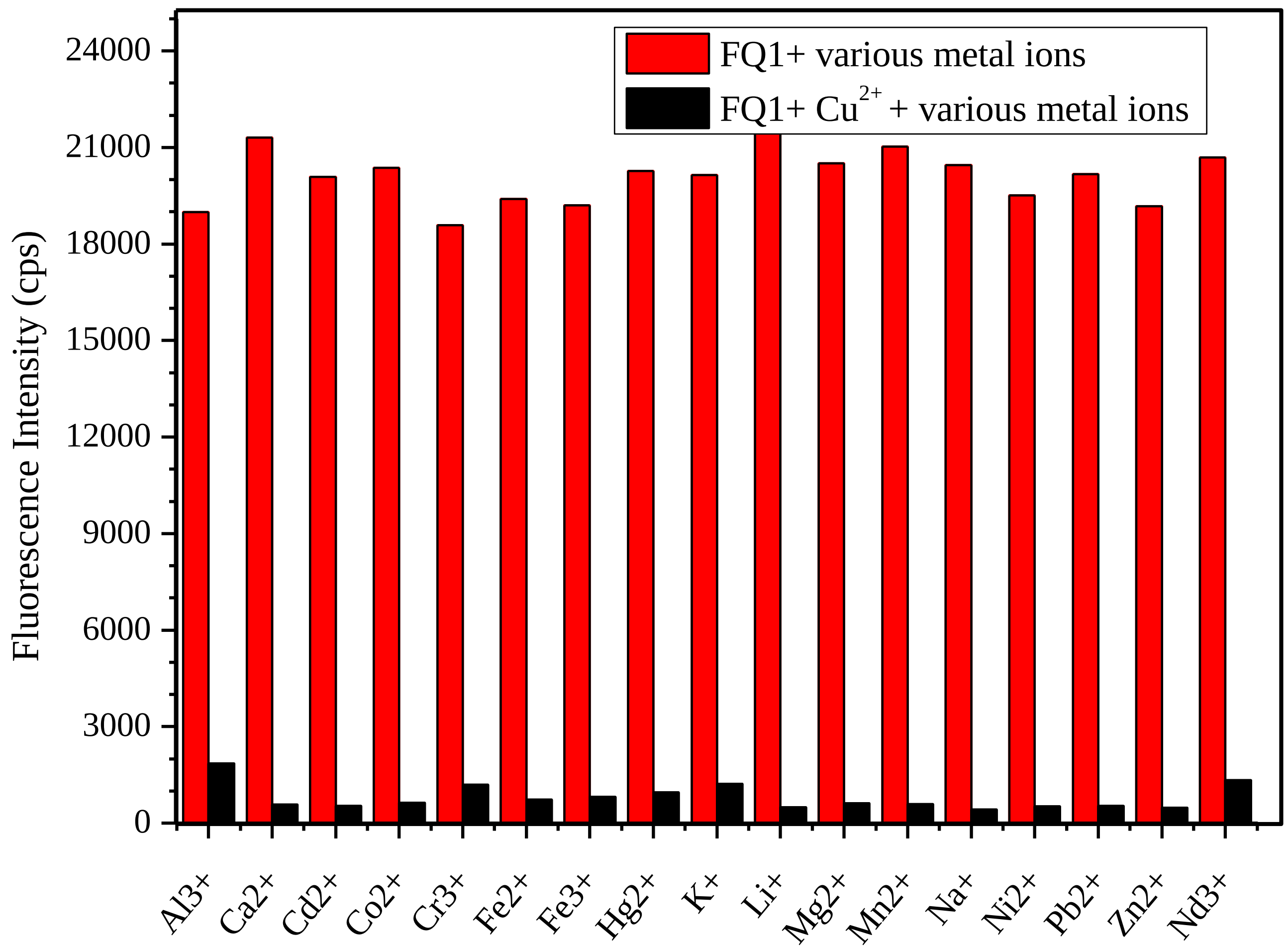


Figure SS 15: Examination of selectivity of FQ2 (20 µM in DMSO:MeOH = 1:9) towards Cu^{2+} in the presence of interfering ions.

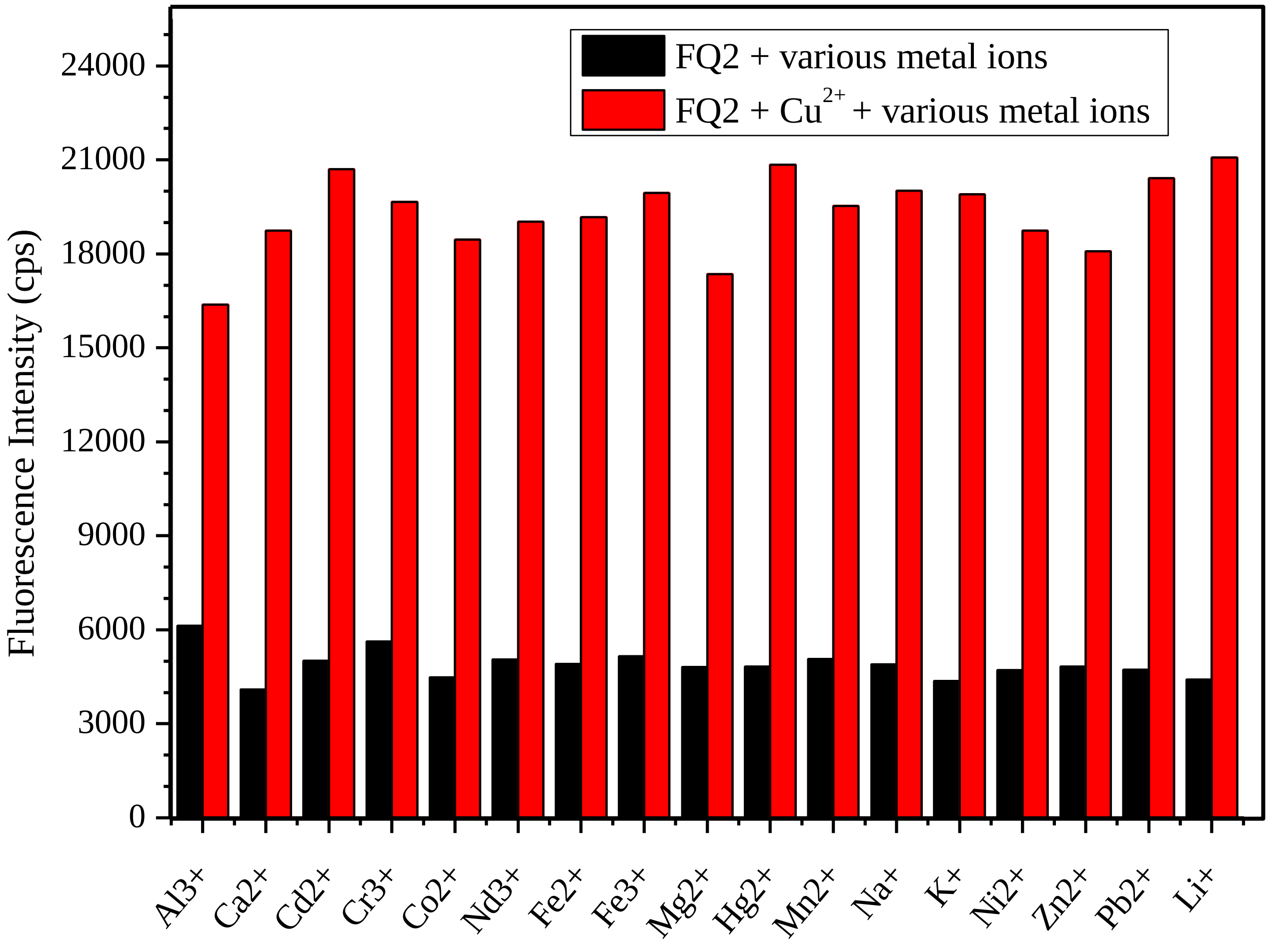


Figure SS16: Change in fluorescence response with time at 465 and 460 nm respectively for compounds FQ1and FQ2.

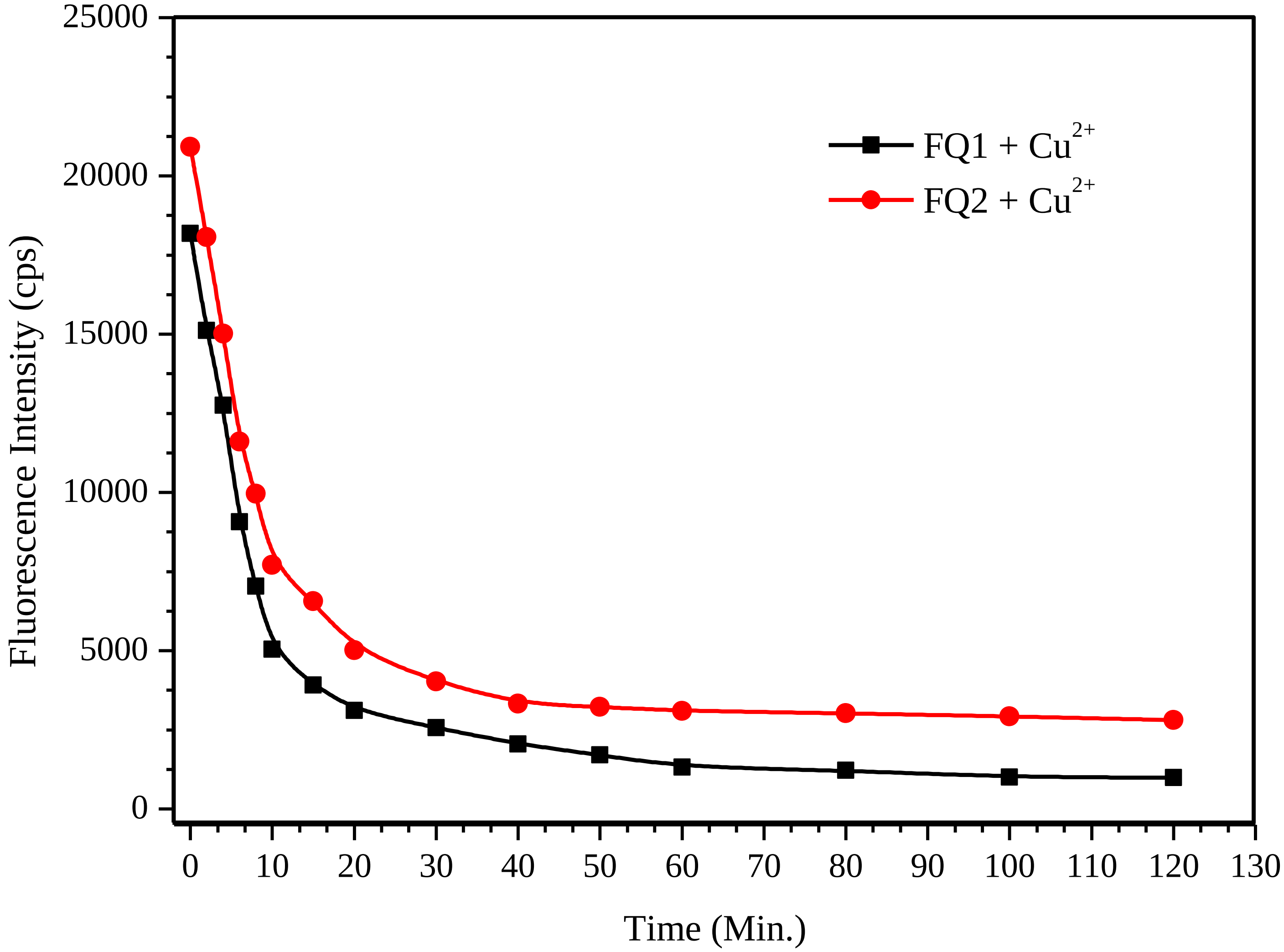


Figure SS17: Job's plot to determine binding stoichiometry of compounds FQ1 with Cu^{2+}

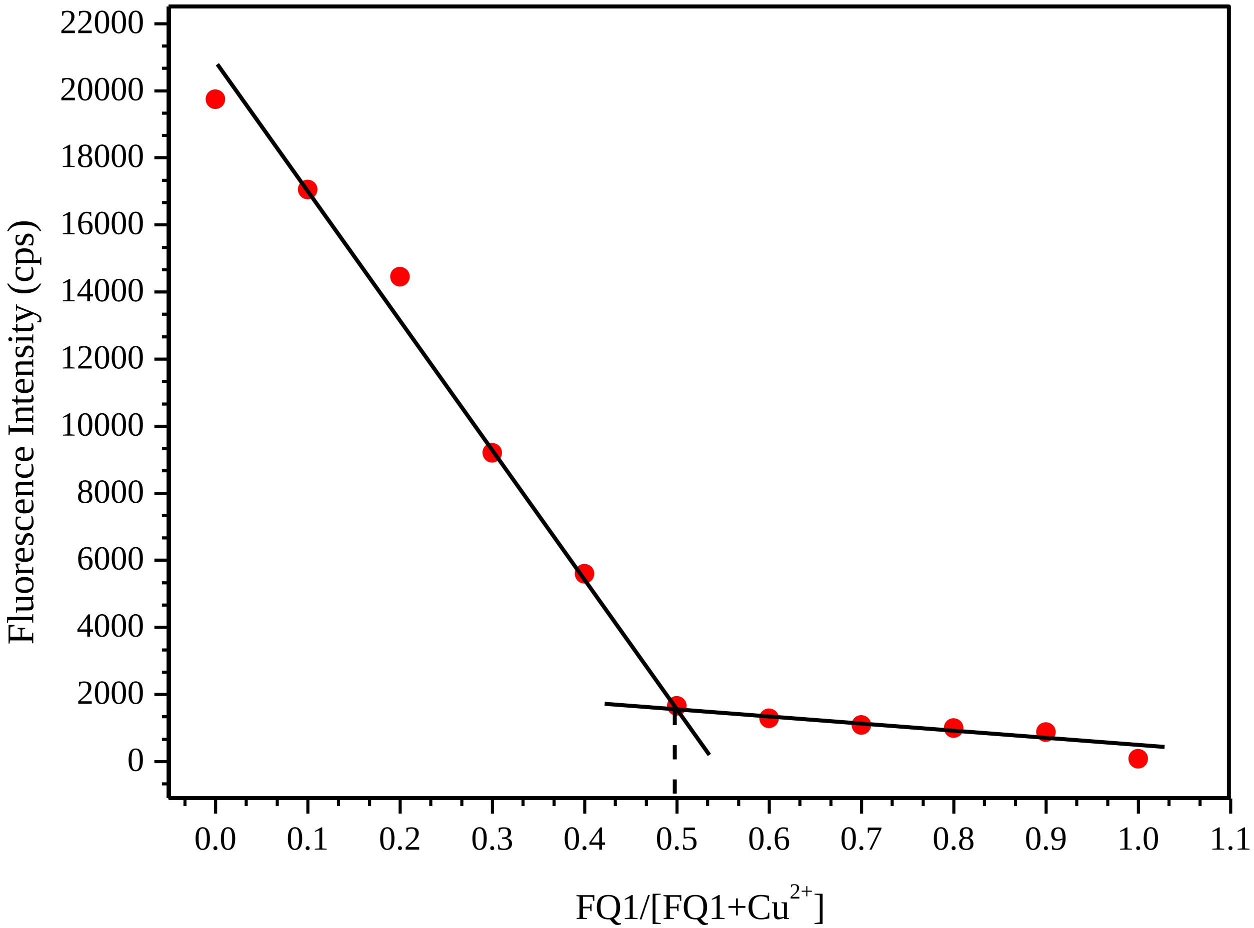


Figure SS18: Job's plot to determine binding stoichiometry of compounds FQ2 with Cu^{2+}

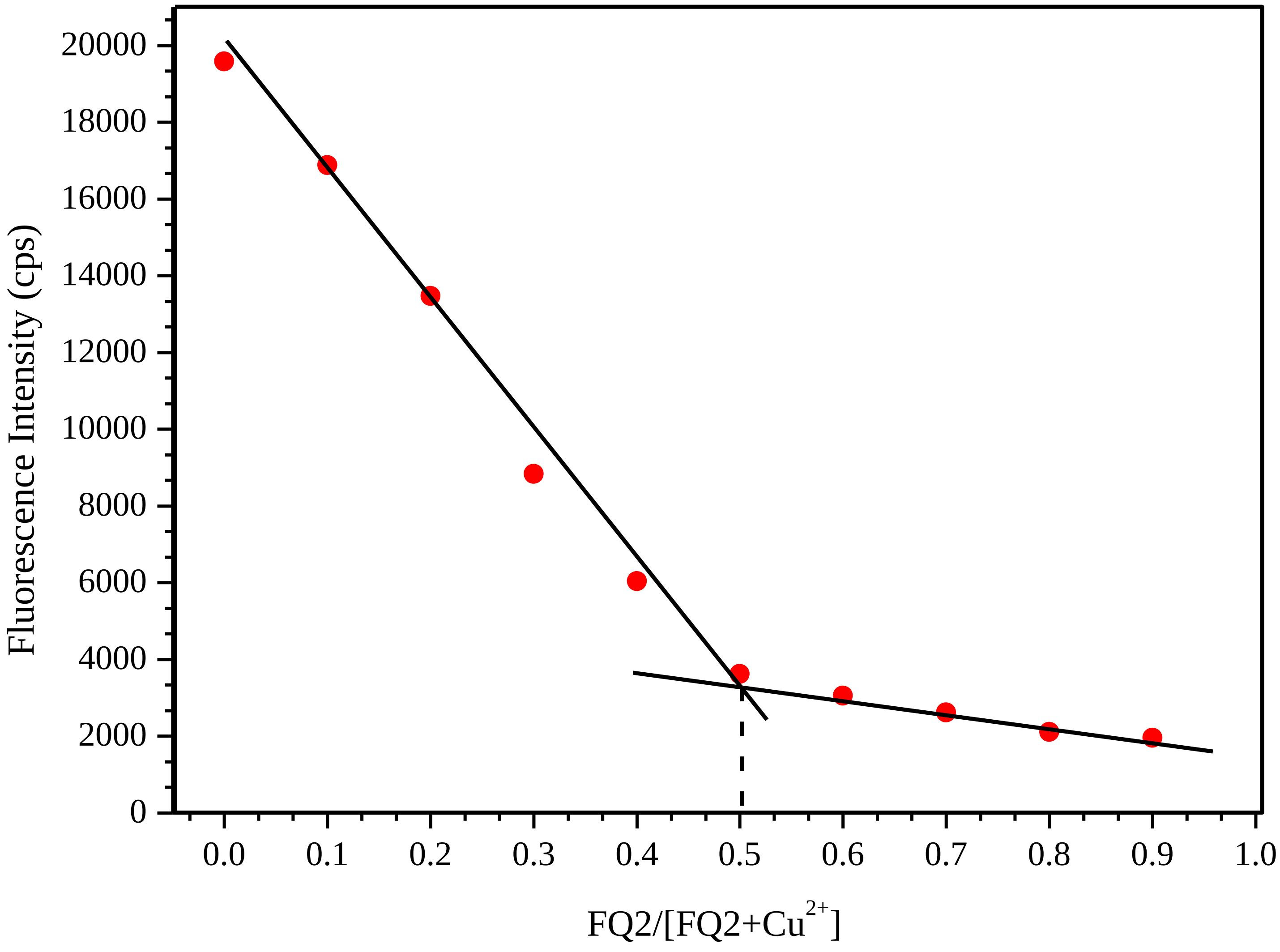


Figure SS19: HRMS of possible complex of compound FQ1 with Cu^{2+}

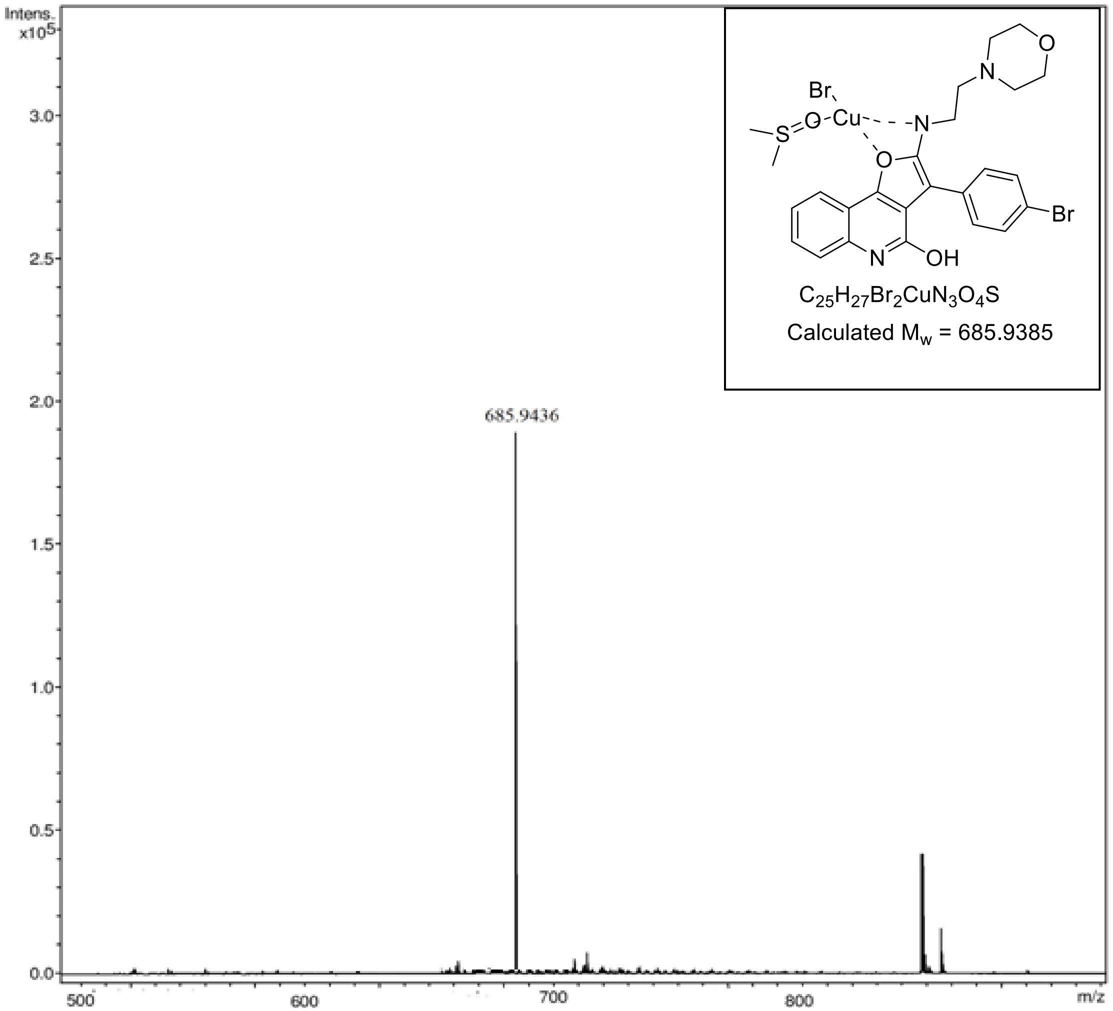


Figure SS20: HRMS of possible complex of compound FQ2 with Cu^{2+}

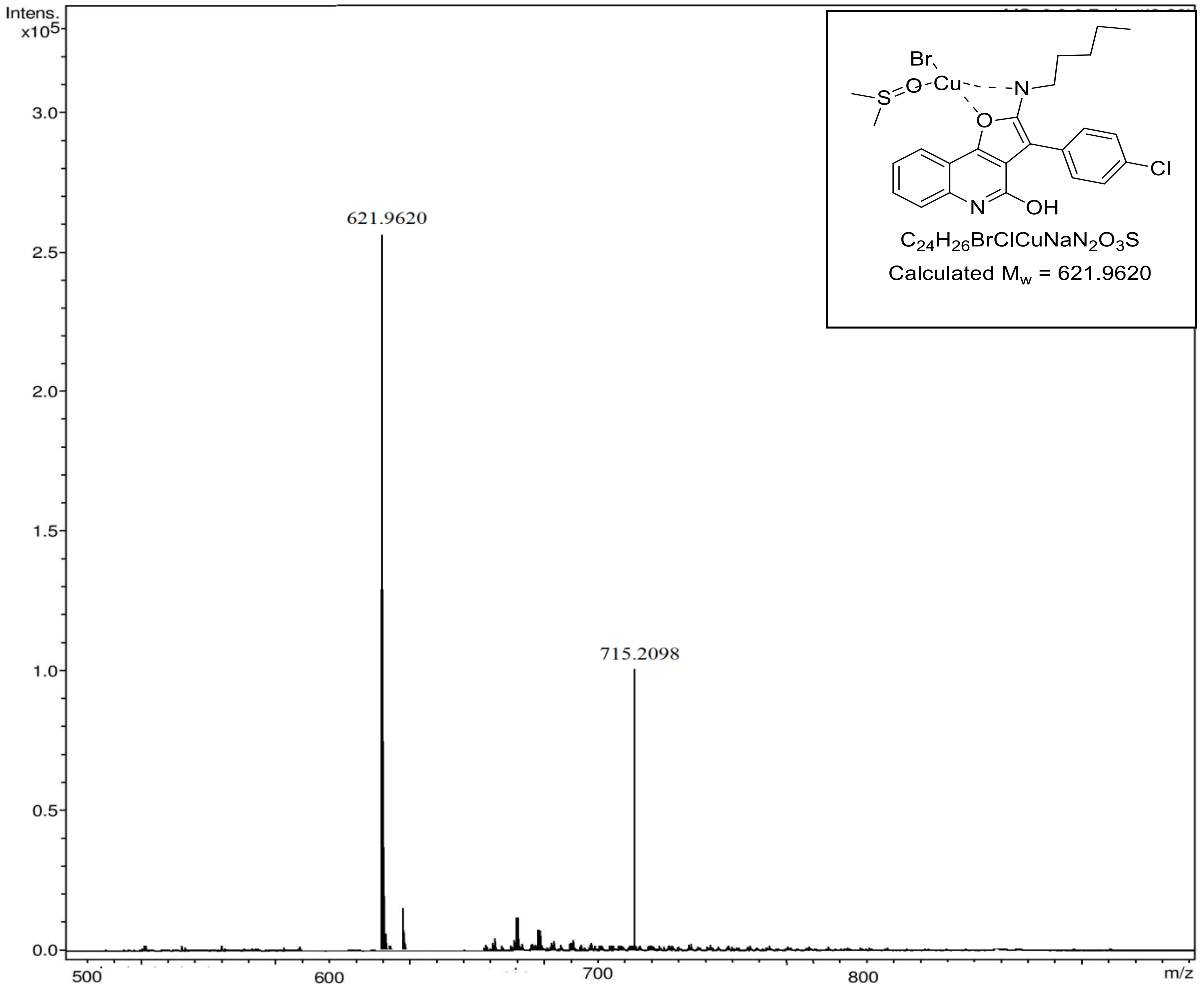


Figure SS21: Reversibility Studies

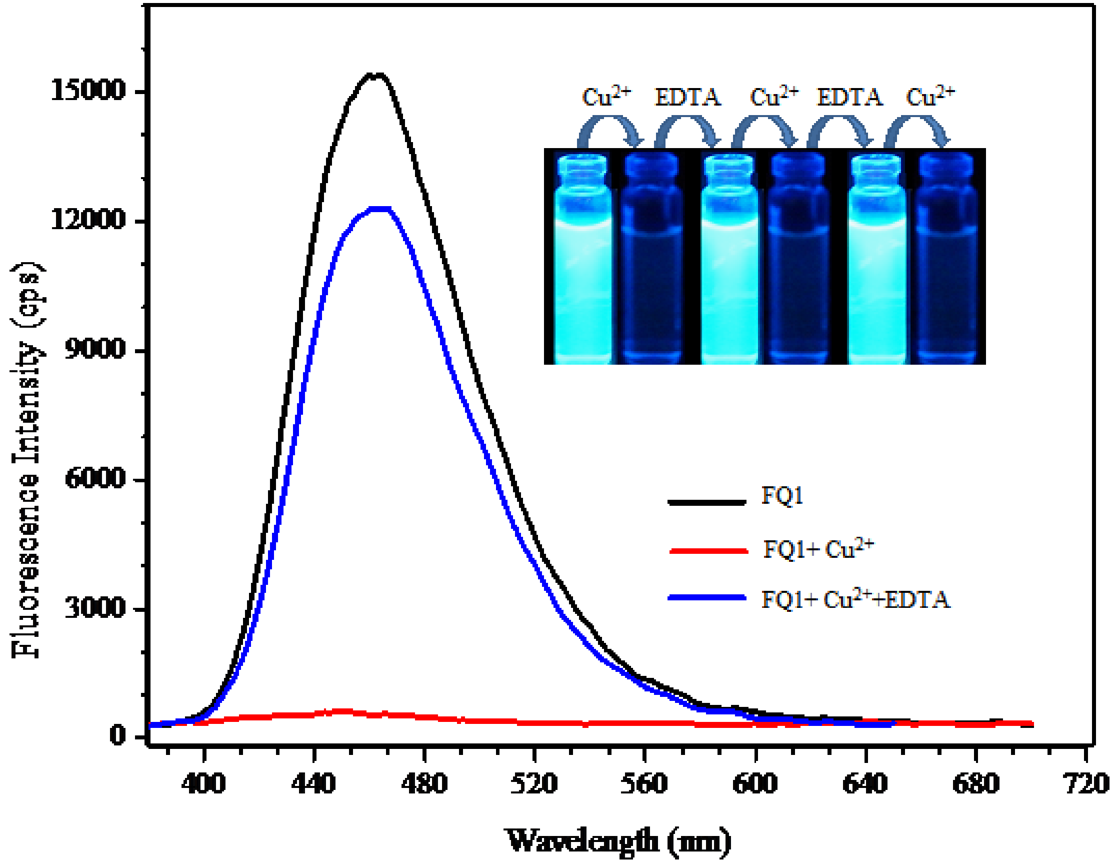


Figure SS22: NMR Titration (FQ1) in the presence of different conc. of Cu^{2+} (DMSO-d_6 was used as NMR solvent and TMS as internal standard).

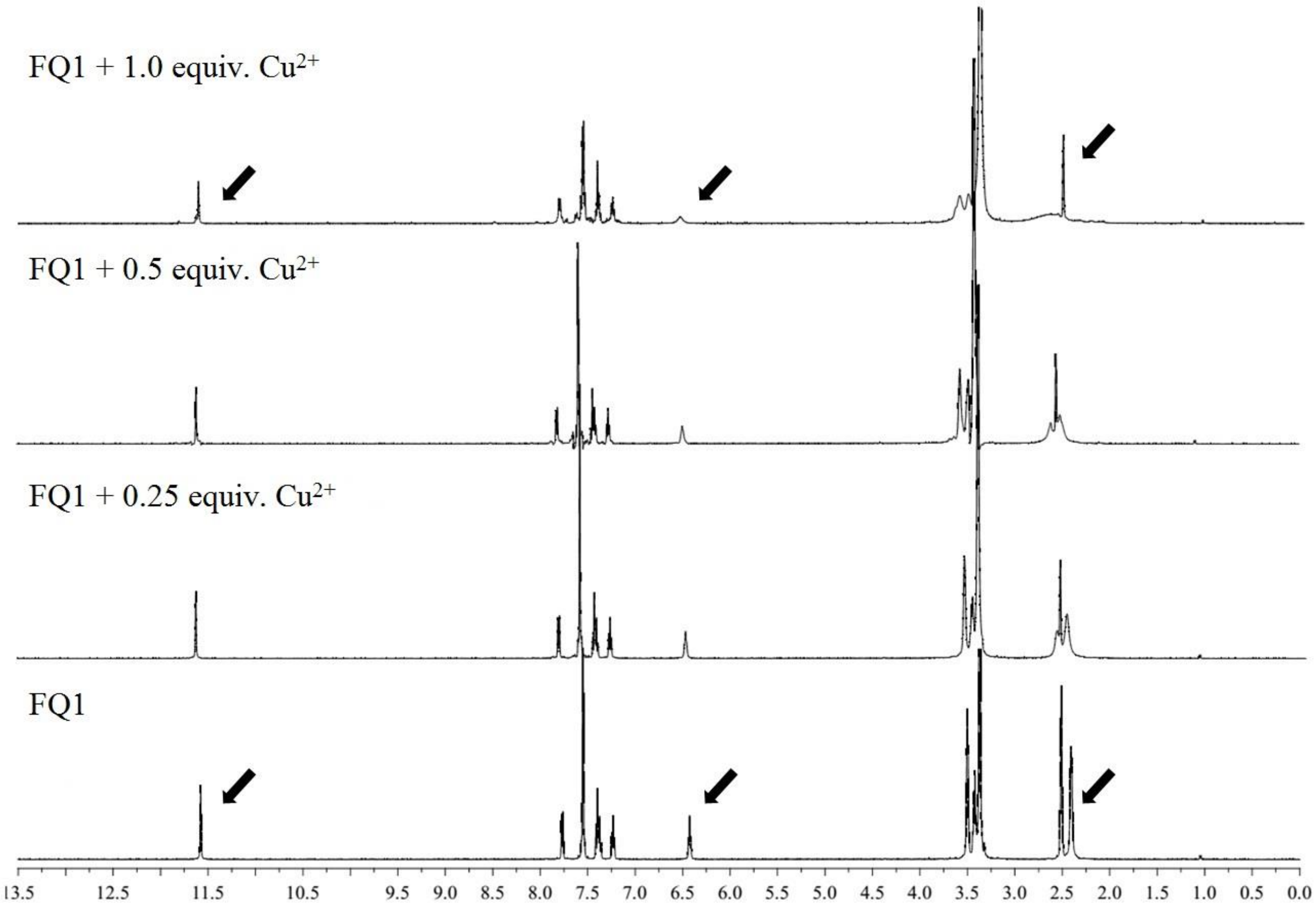


Figure SS23: NMR Titration (FQ2) in the presence of different conc. of Cu^{2+} (DMSO-d_6 was used as NMR solvent and TMS as internal standard).

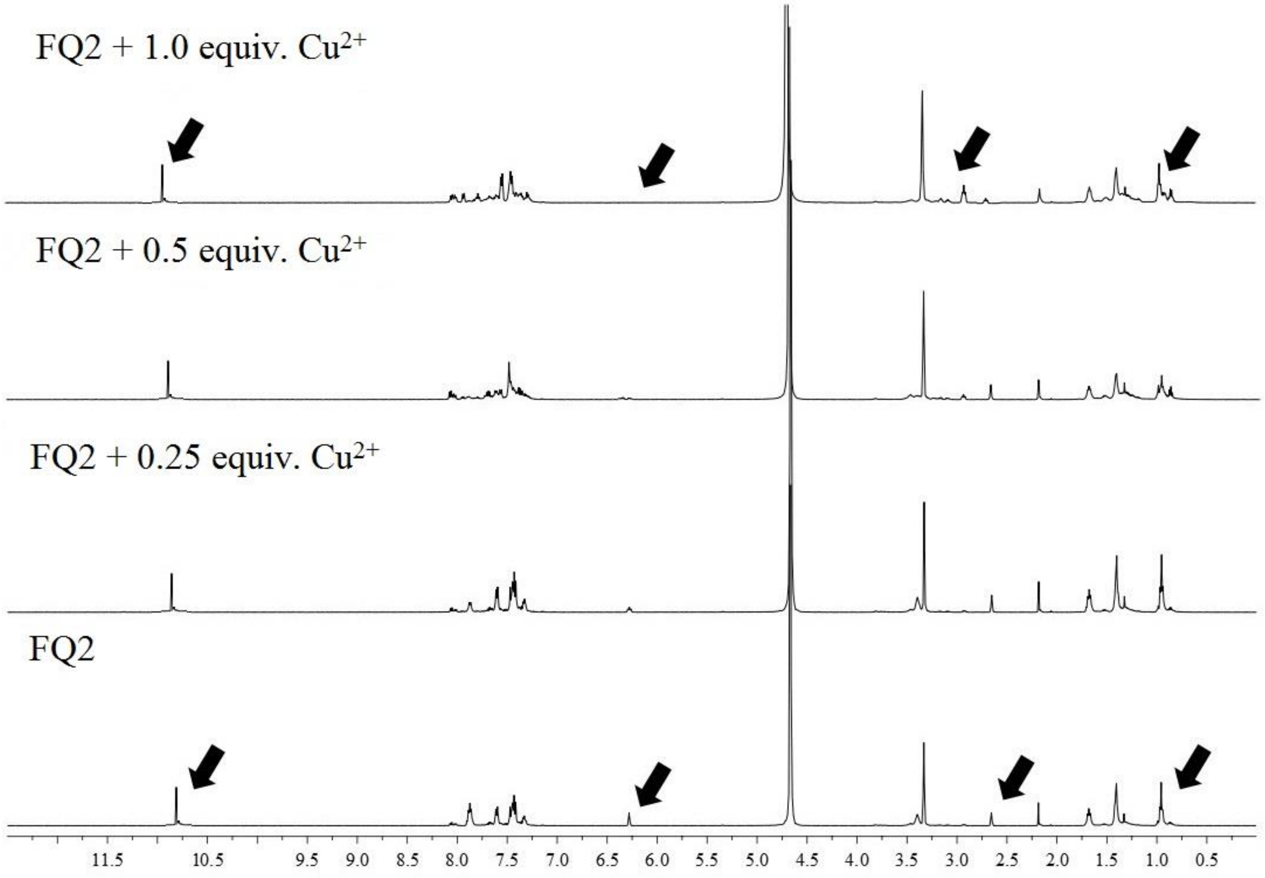


Figure SS24: Effect of pH on Fluorescence quenching

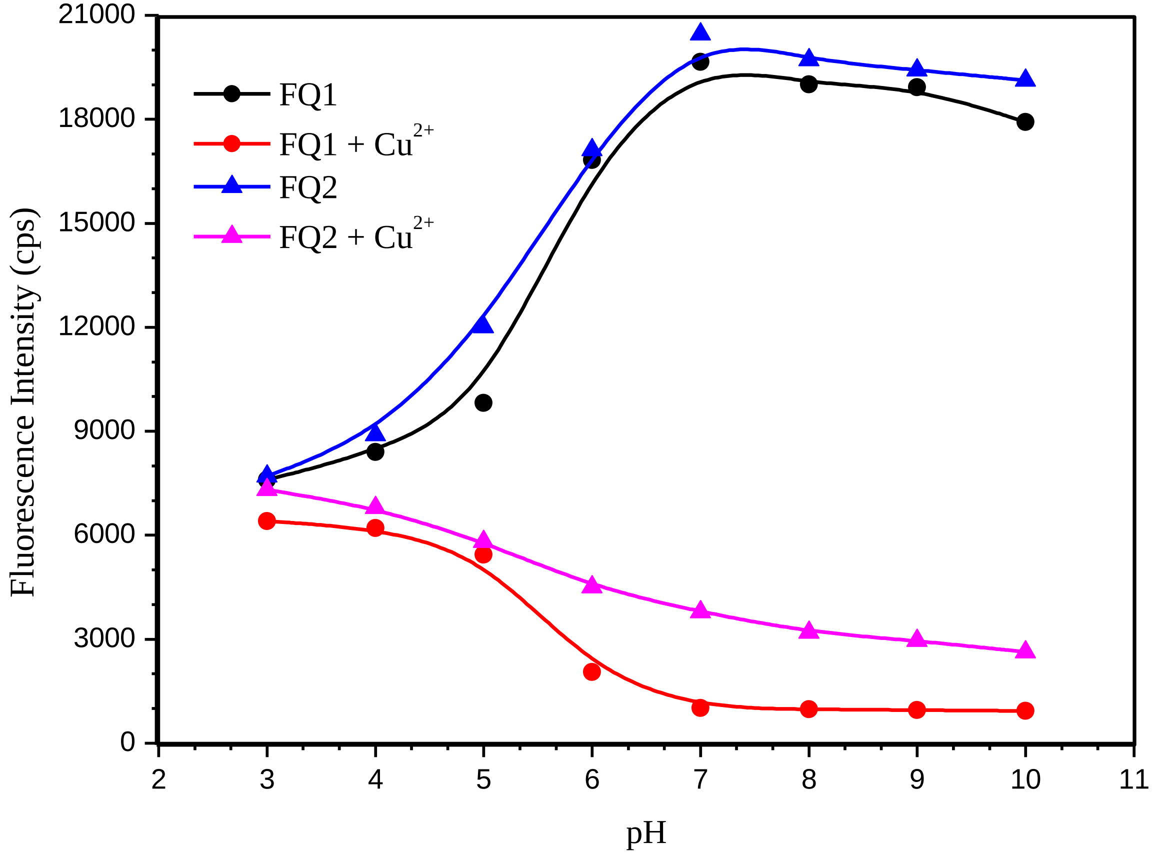
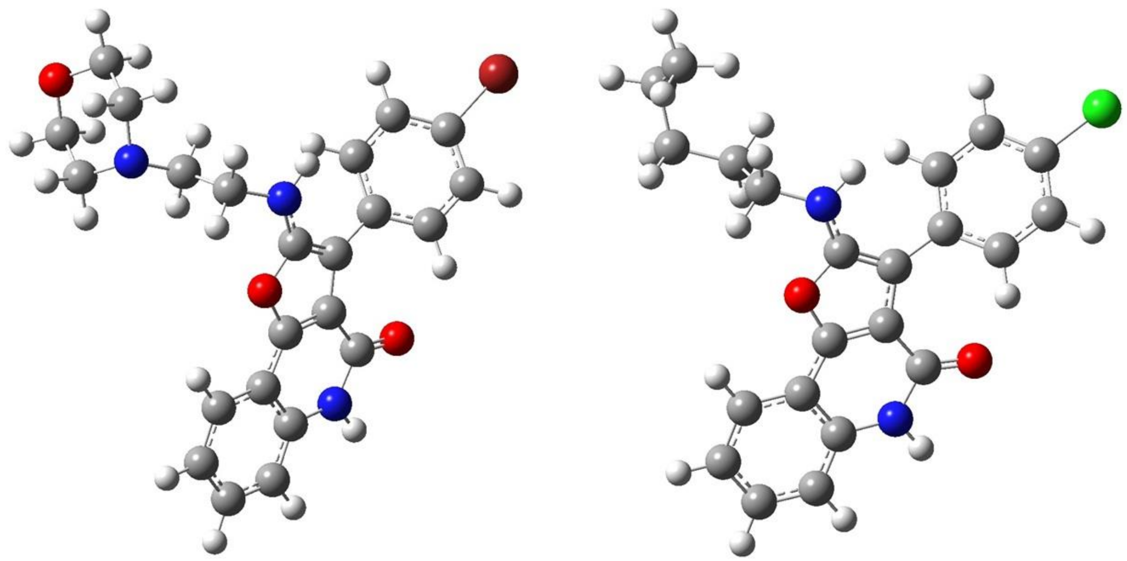
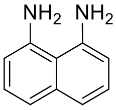
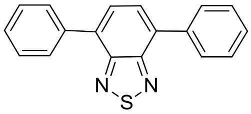
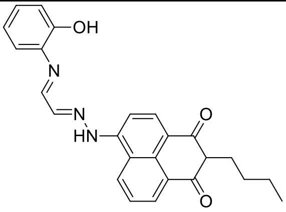
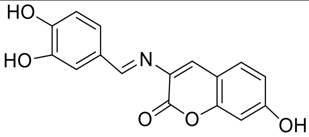
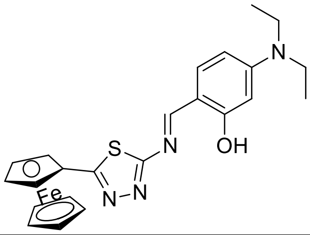


Figure SS25: DFT study (Optimized structure of FQ1 and FQ2)



FQ1 FQ2

Table SS1: Comparison of reported FQs with some of the recently developed sensors for Cu^{2+}

S.No.	Sensor/probe	Interaction	Association constant (K_a) M^{-1}	LOD in M	pH range
1	**FQs (This work)**	**Turn off (flur) Reversible**	**2.11×10^4 1.87×10^4**	**1.52×10^{-7} 2.13×10^{-7}**	**5.5-11**
2[4h]		Turn off (flur) Irreversible	NM	0.5×10^{-7}	5-7
3[4i]		Conc. dependent Turn off (flur)	6.82×10^4	4.0×10^{-7}	NM
4[8a]	P-Qs	Turn on (flur) irreversible	NM	1.5×10^{-6}	7-9
6[4j]		Turn on (flur)	1.1×10^{10}	0.15×10^{-6}	NM
7[4k]		Turn off (flur)	NM	1.27×10^{-4}	NM
8[8b]		Turn off (flur)	5.0×10^4	1.5×10^{-6}	4-11

(flur = fluorescence, NM = Not Mentioned)

Table SS2: Photophysical properties of FQ1 and FQ2

Comp.	Emission		Quantum Yield	Detection Limit (M)	Binding Constant (M^{-1})	R^2	I/I_0	Response Time (Min.)
	λ_{ex}/nm	**λ_{em}/nm**						
FQ1	370	465	0.3915	1.52 x 10^{-7}	2.11 x 10^{4}	0.984	0.027	2-3 min.
FQ1 +Cu^{2+}	370	459	0.0253					
FQ2	370	460	0.3856	2.13 x 10^{-7}	1.87 x 10^{4}	0.985	0.159	2-3 min.
FQ + Cu^{2+}	370	452	0.0597					