Dansyl appended Cu^{II}-complex based Nitroxyl (HNO) sensing with living cell application and DFT studies

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Supporting Information

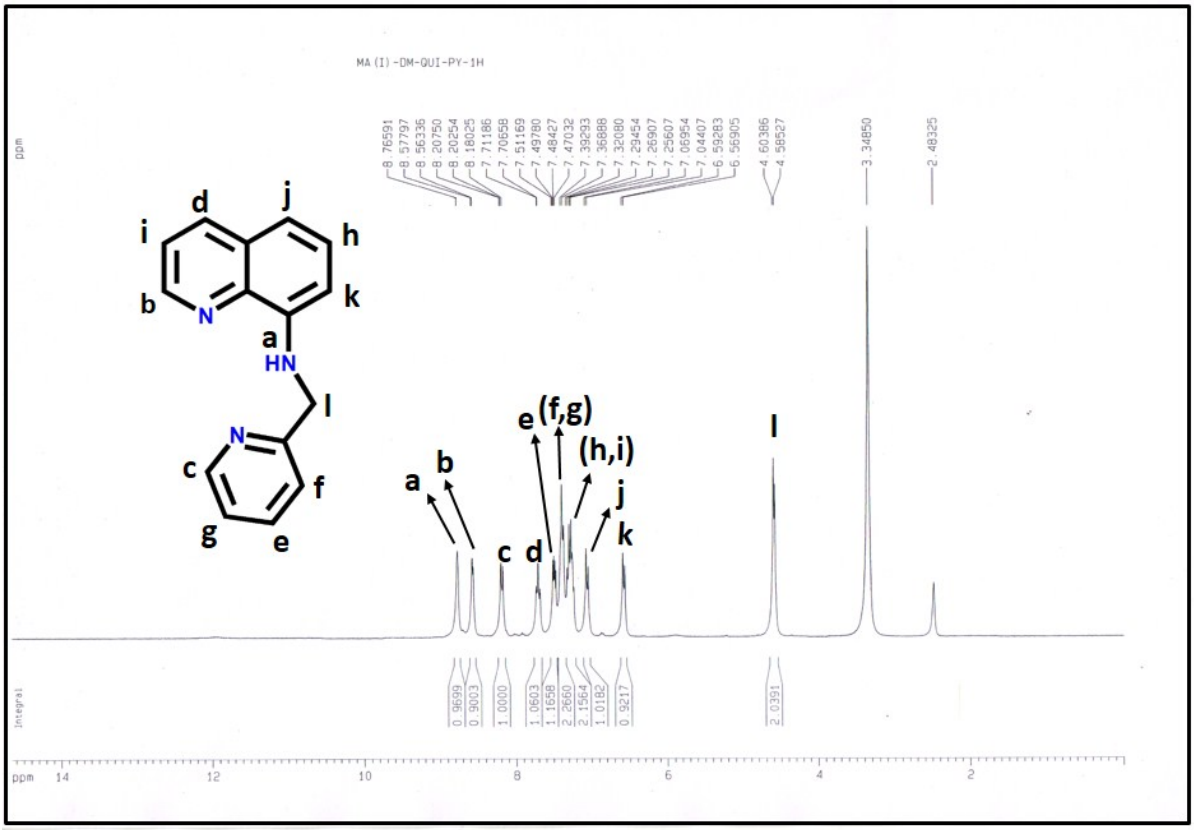


Fig.S1.^{1}H NMR spectrum of (**L^{1}**) in DMSO-$d_{6.}$

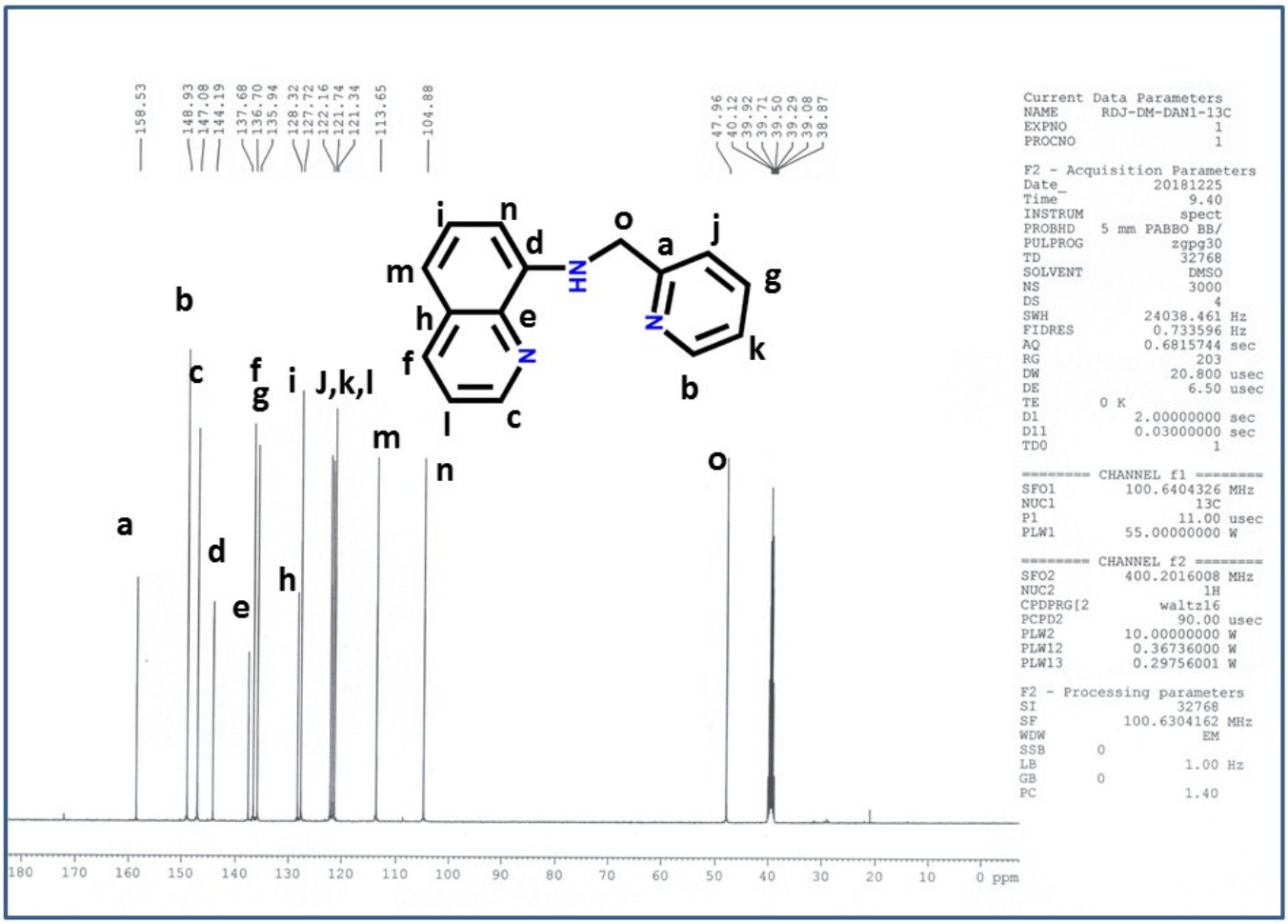


Fig. S2. ^{13}C NMR of (**L^{1}**) in DMSO-$d_{6.}$

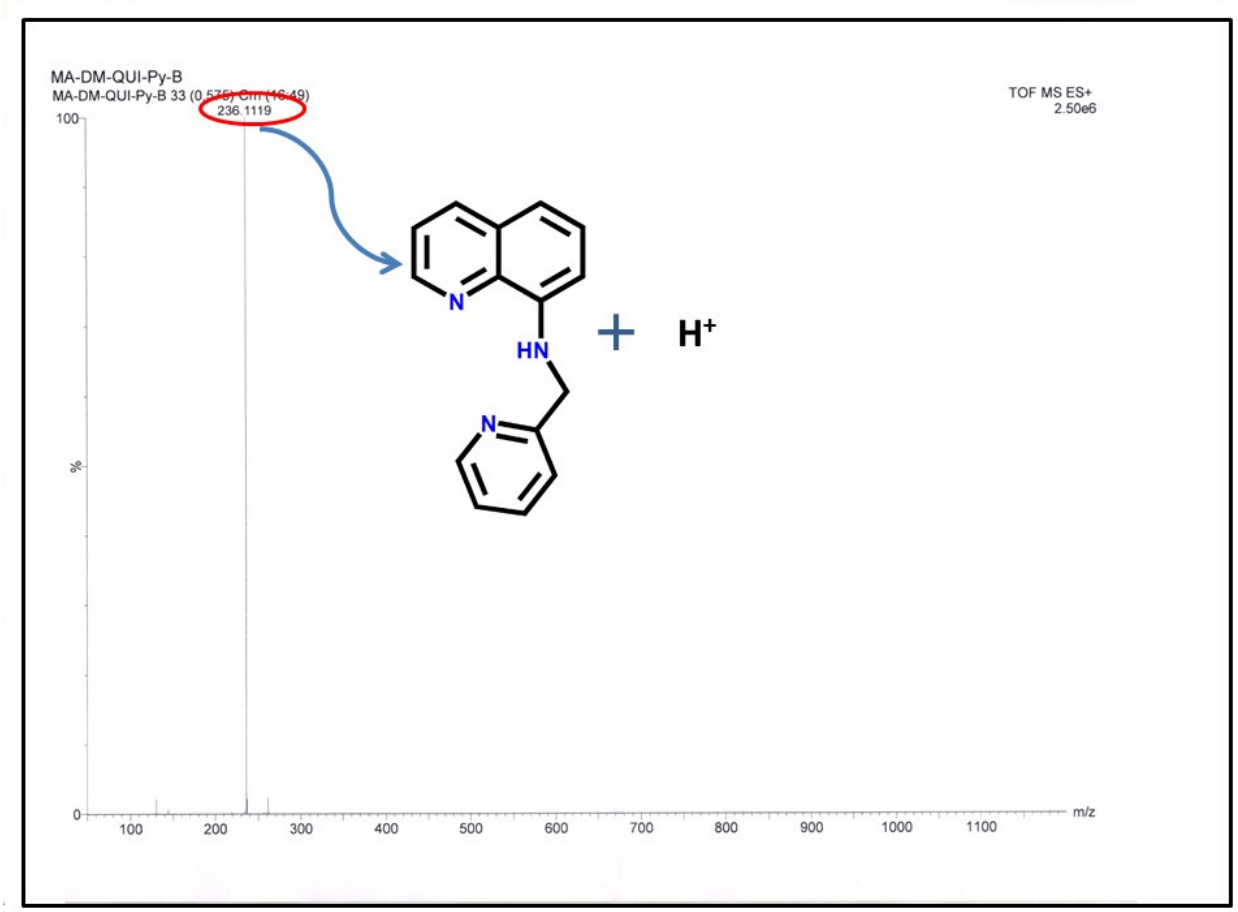


Fig. S3. Mass spectrum of spectrum of (**L**[1]) in MeCN.

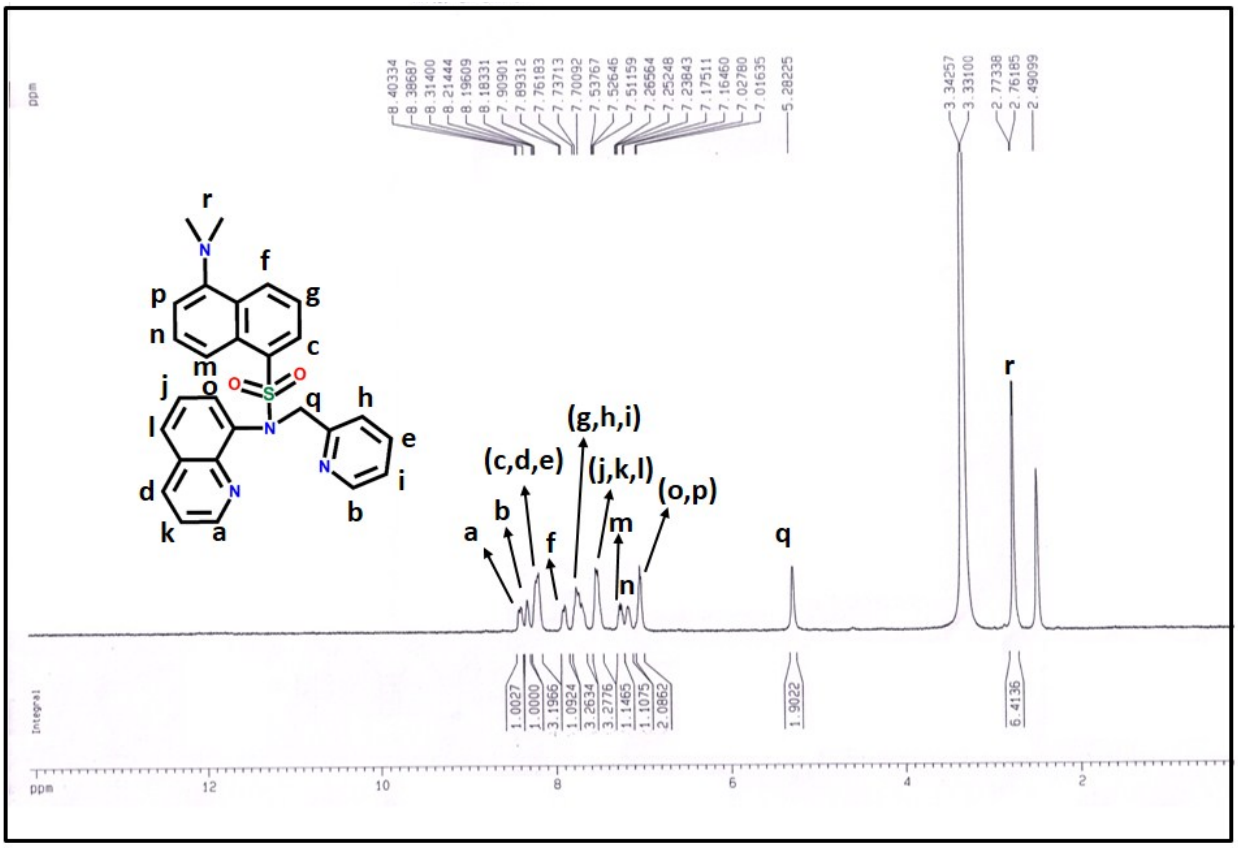


Fig.S4.[1]H NMR spectrum of **DQ$_{468}$** in DMSO-d_6 (300Mz).

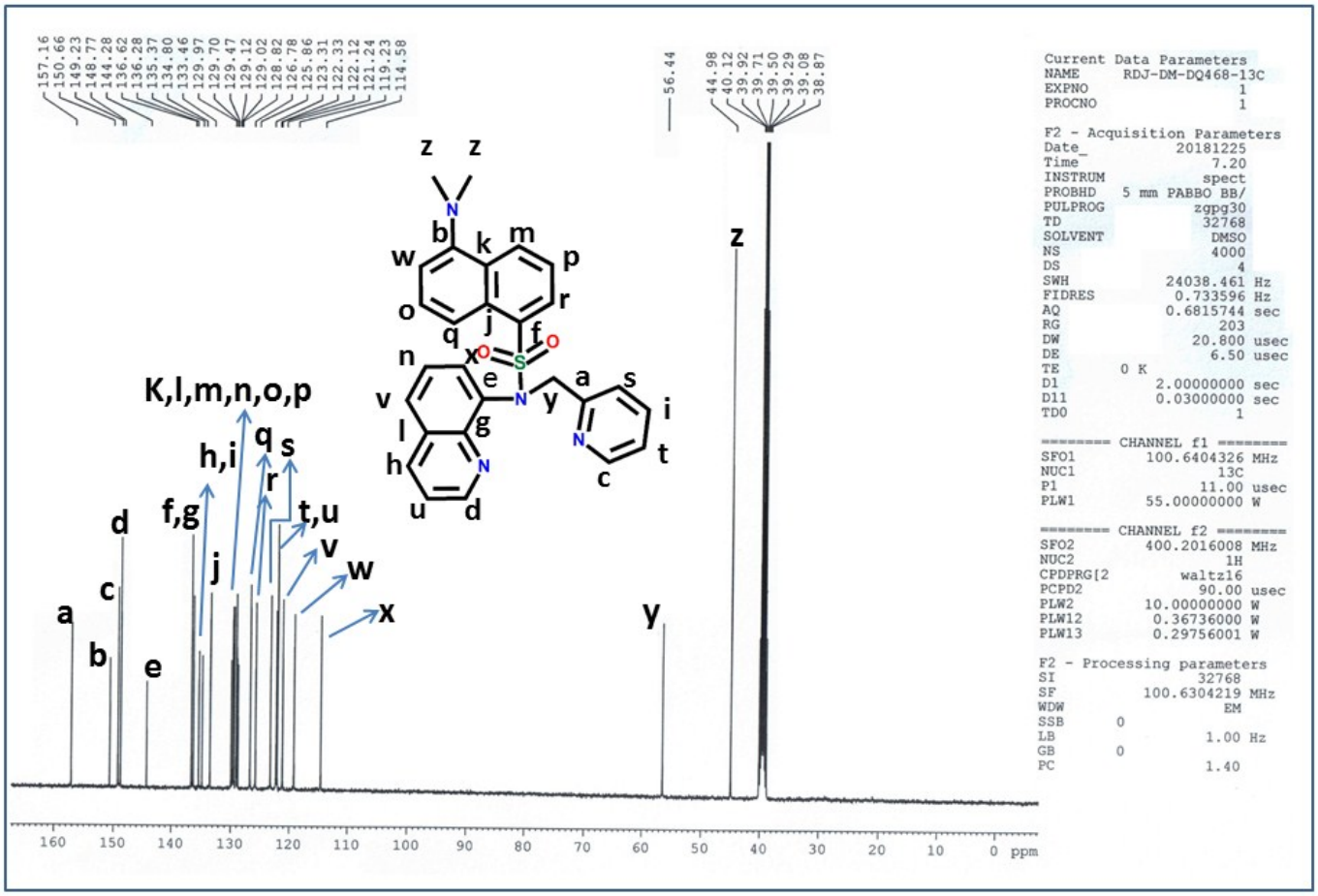


Fig. S5. ^{13}C NMR of (**DQ$_{468}$**) in DMSO-d_6.

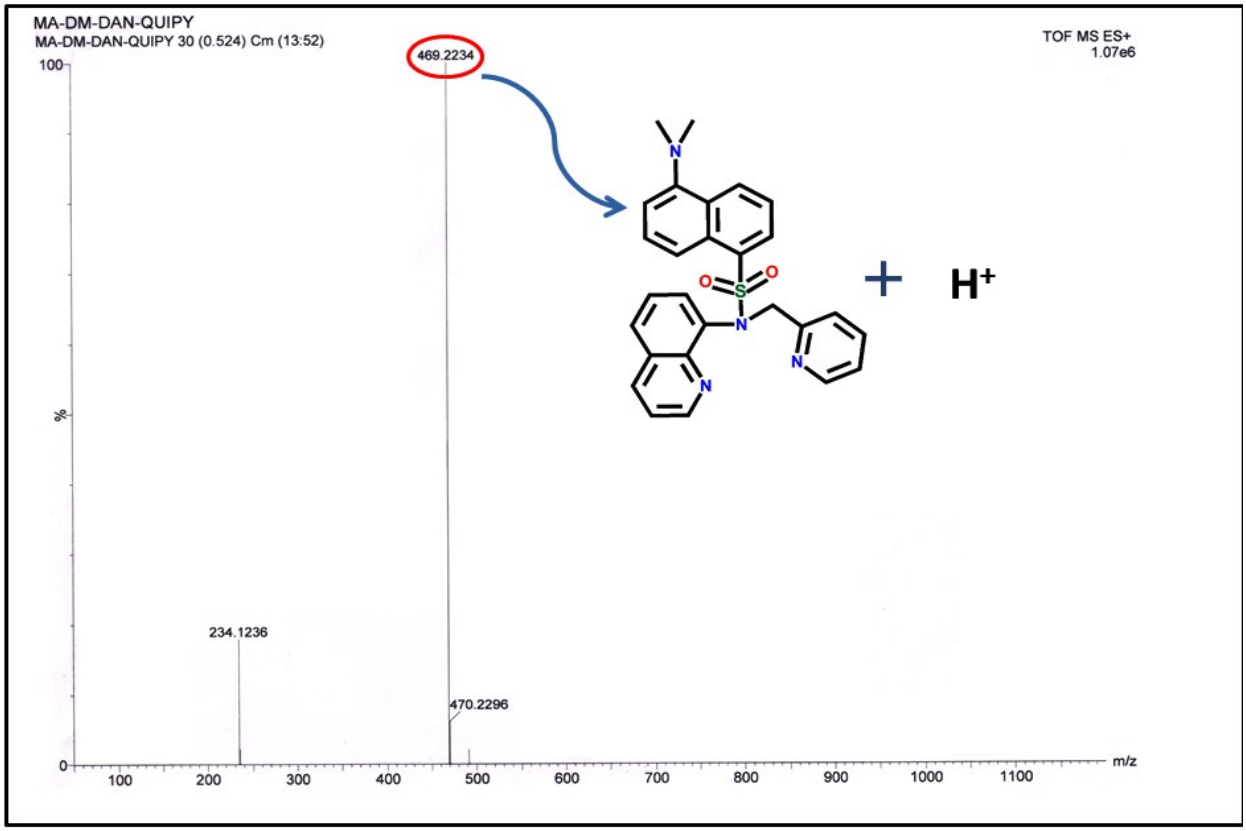


Fig. S6. Mass spectrum of **DQ_{468}** in MeCN.

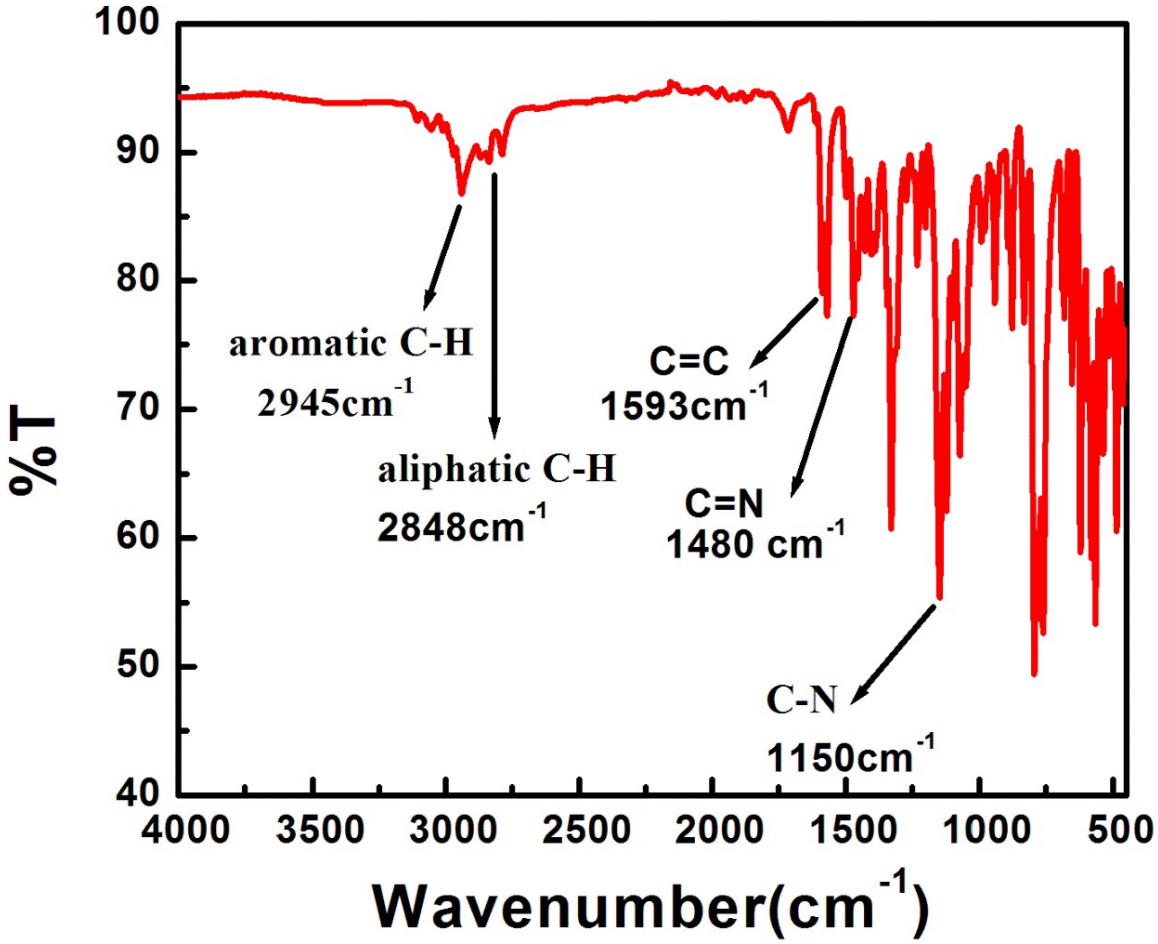


Fig. S7. Ir spectrum of DQ_{468} .

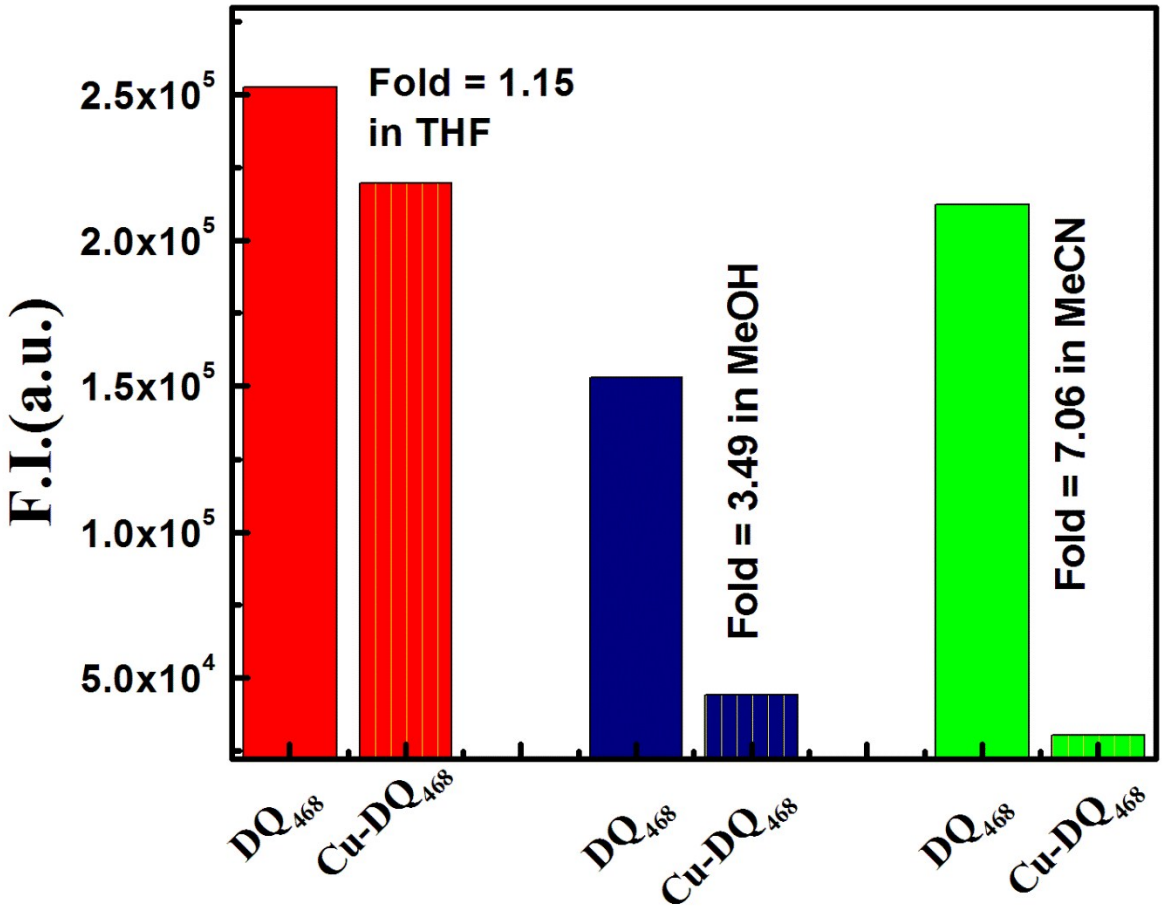


Fig. S8. Solvent selectivity of Cu(II)-complex formation.

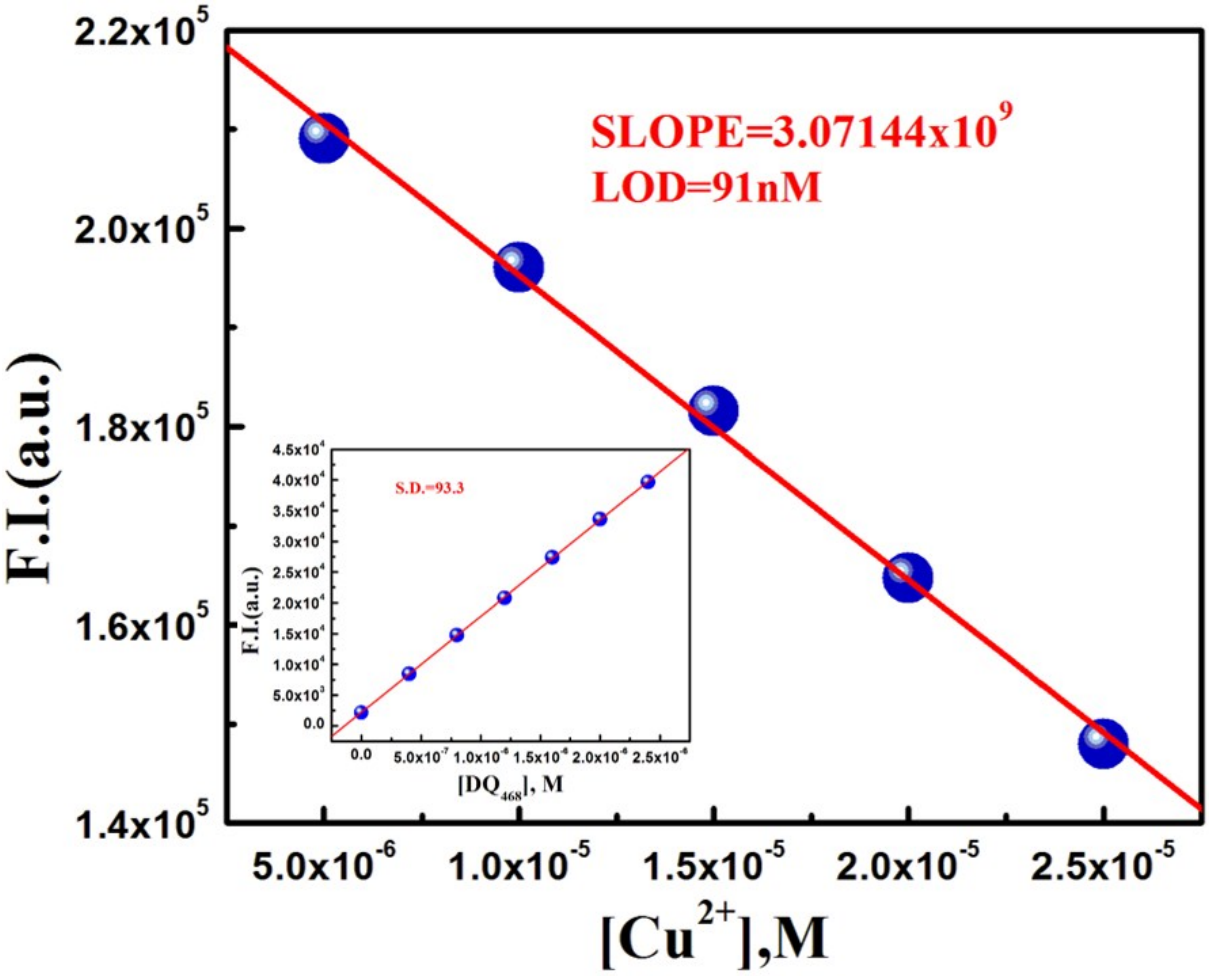


Fig. S9. LOD of **DQ_{468}** to Cu^{2+}

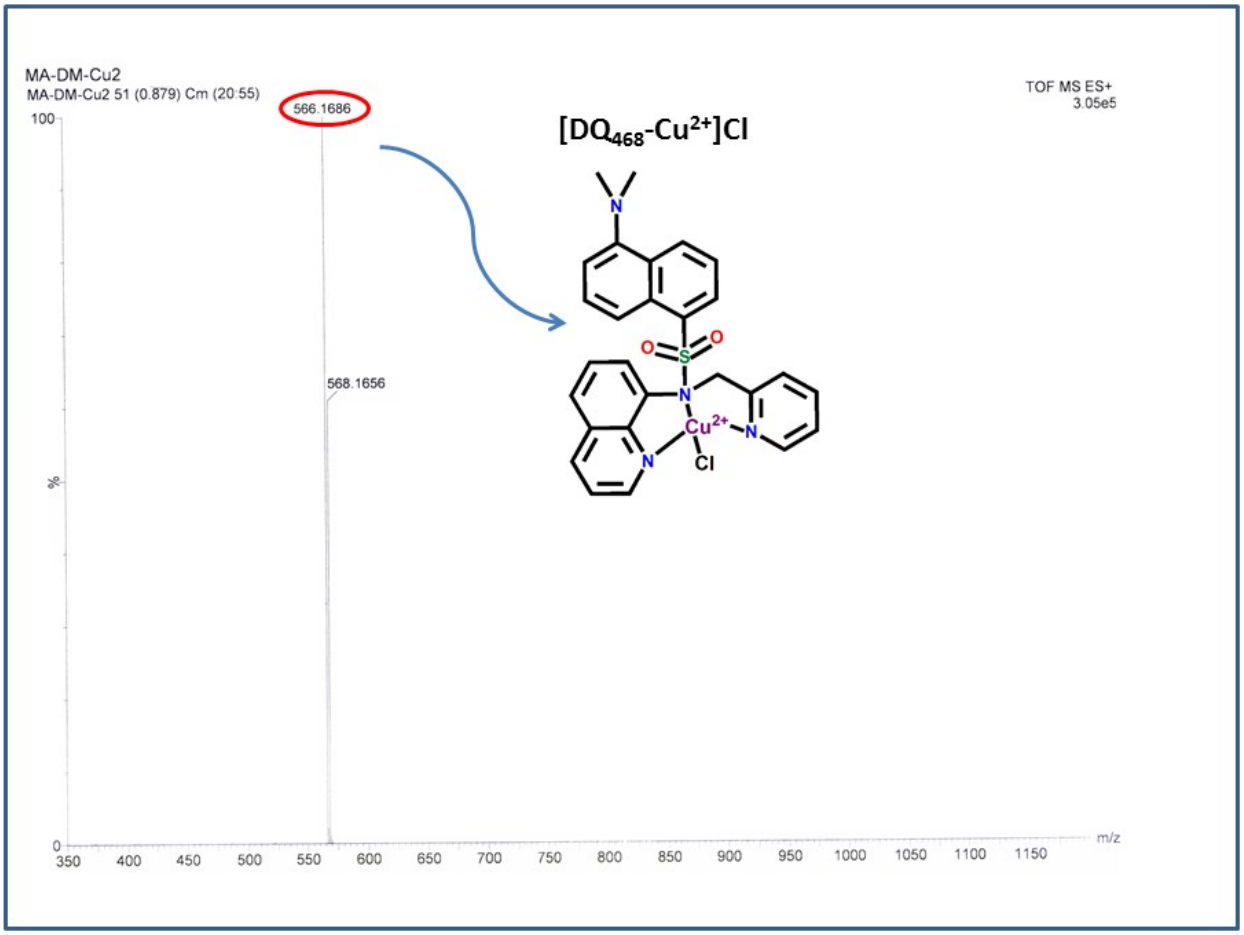


Fig. S10. Mass spectrum of [**$Cu^{II}(DQ_{468})Cl$**].

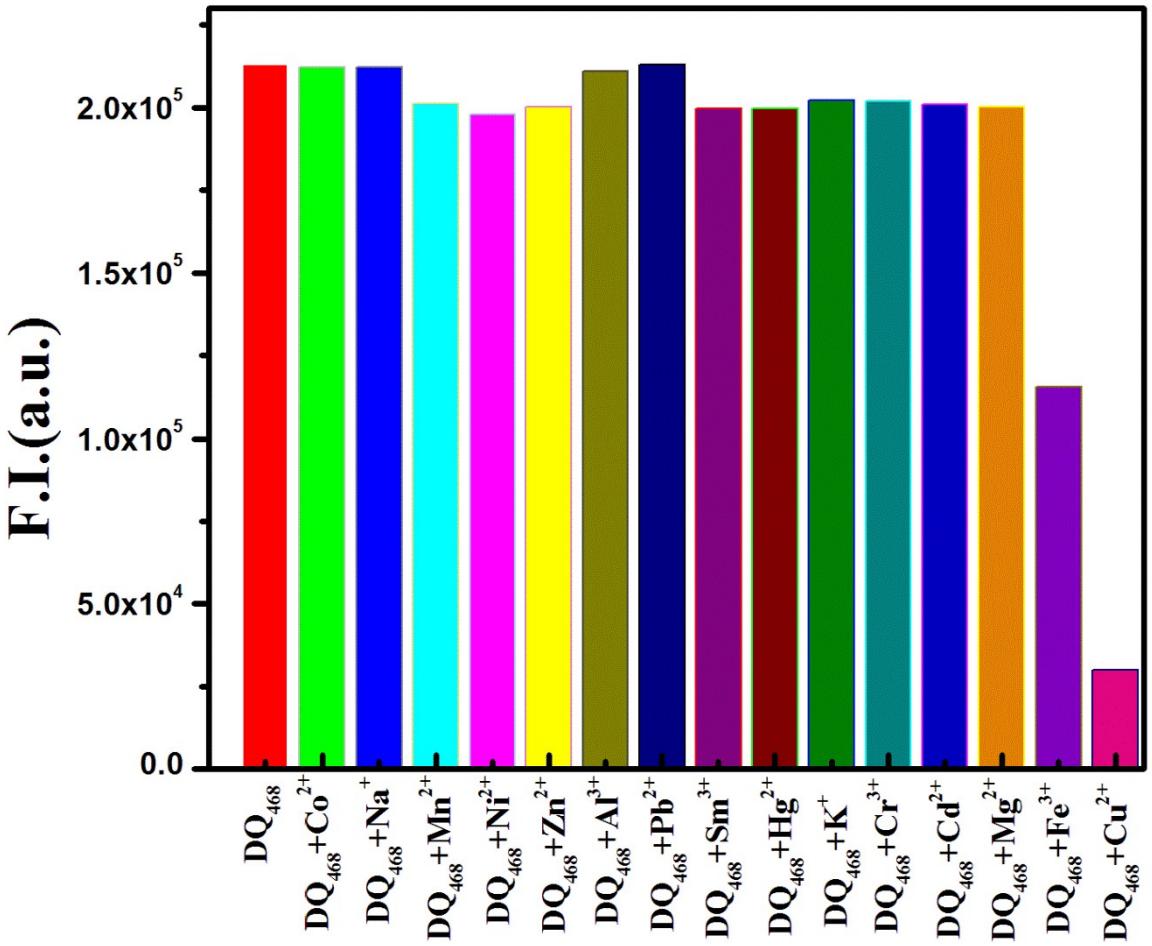


Fig. S11. Metal ion selectivity test of **DQ_{468}**

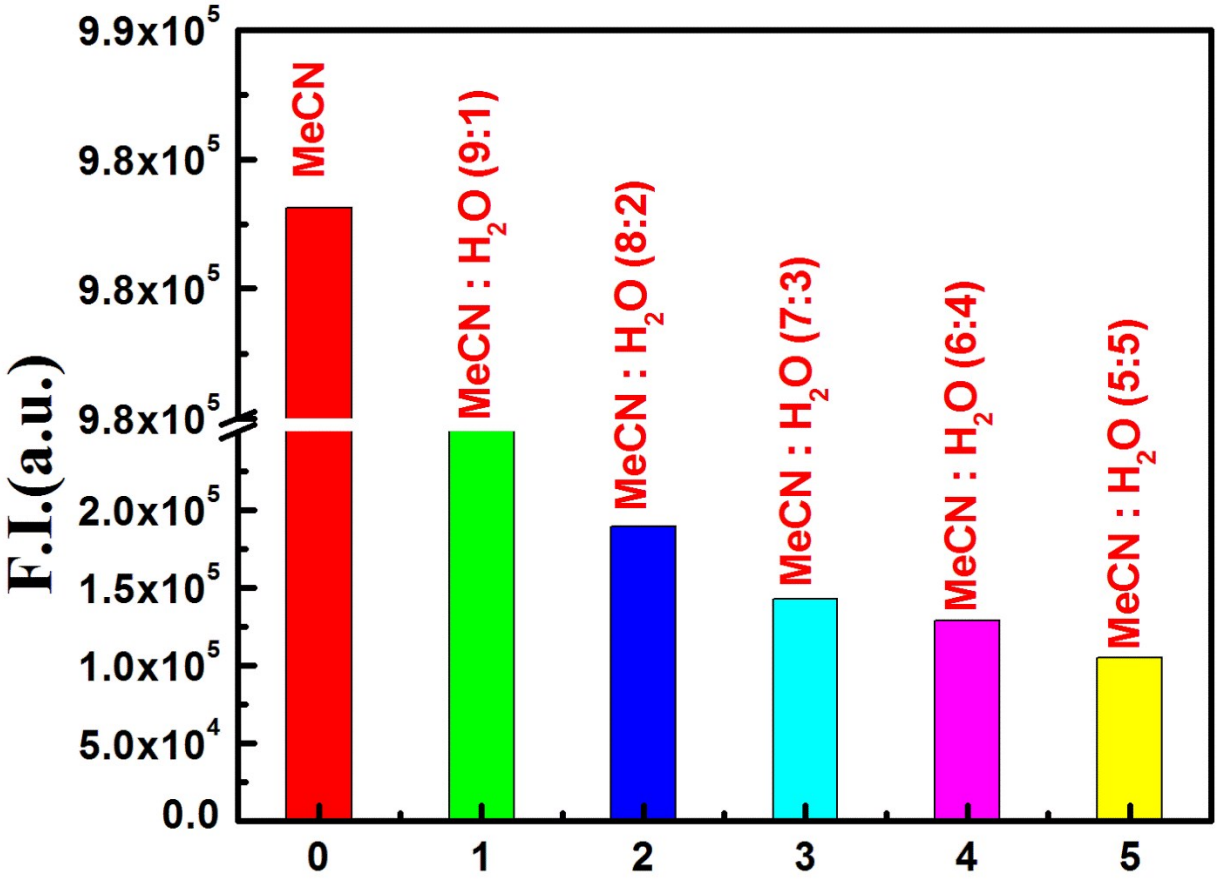


Fig. S12. Water variation on HNO induced reduction of Cu(II)-complex.

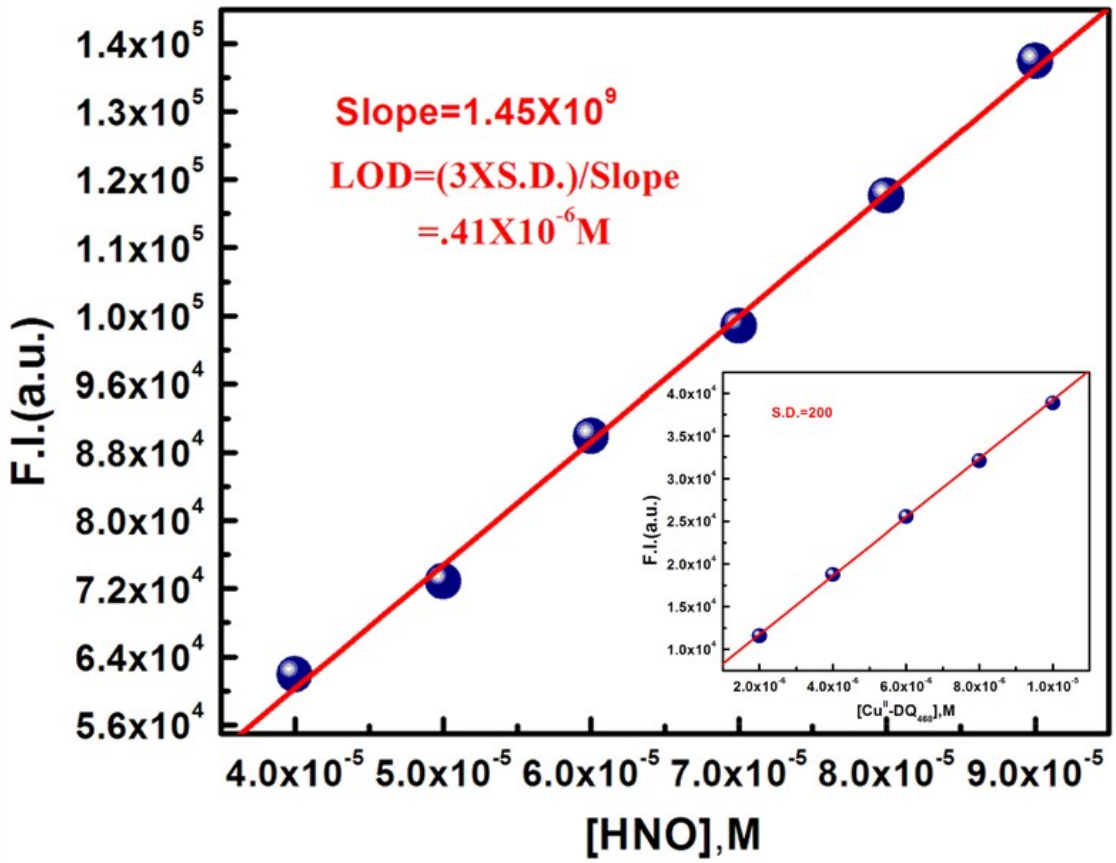


Fig. S13. LOD of **Cu^{II}-DQ_{468}** to HNO.

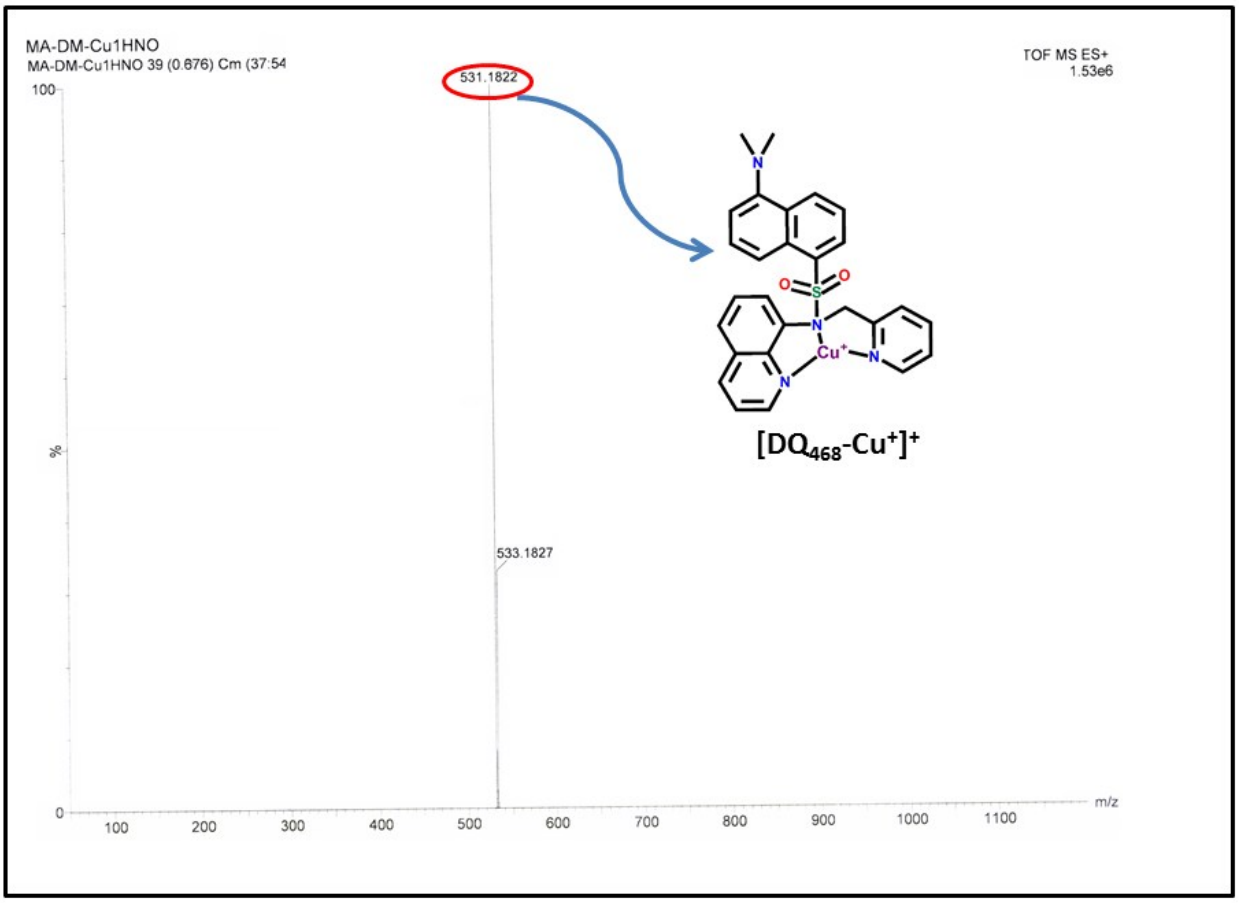


Fig. S14. Mass spectrum of [**Cu(DQ$_{468}$)Cl]+ Na$_2$N$_2$O$_3$** .

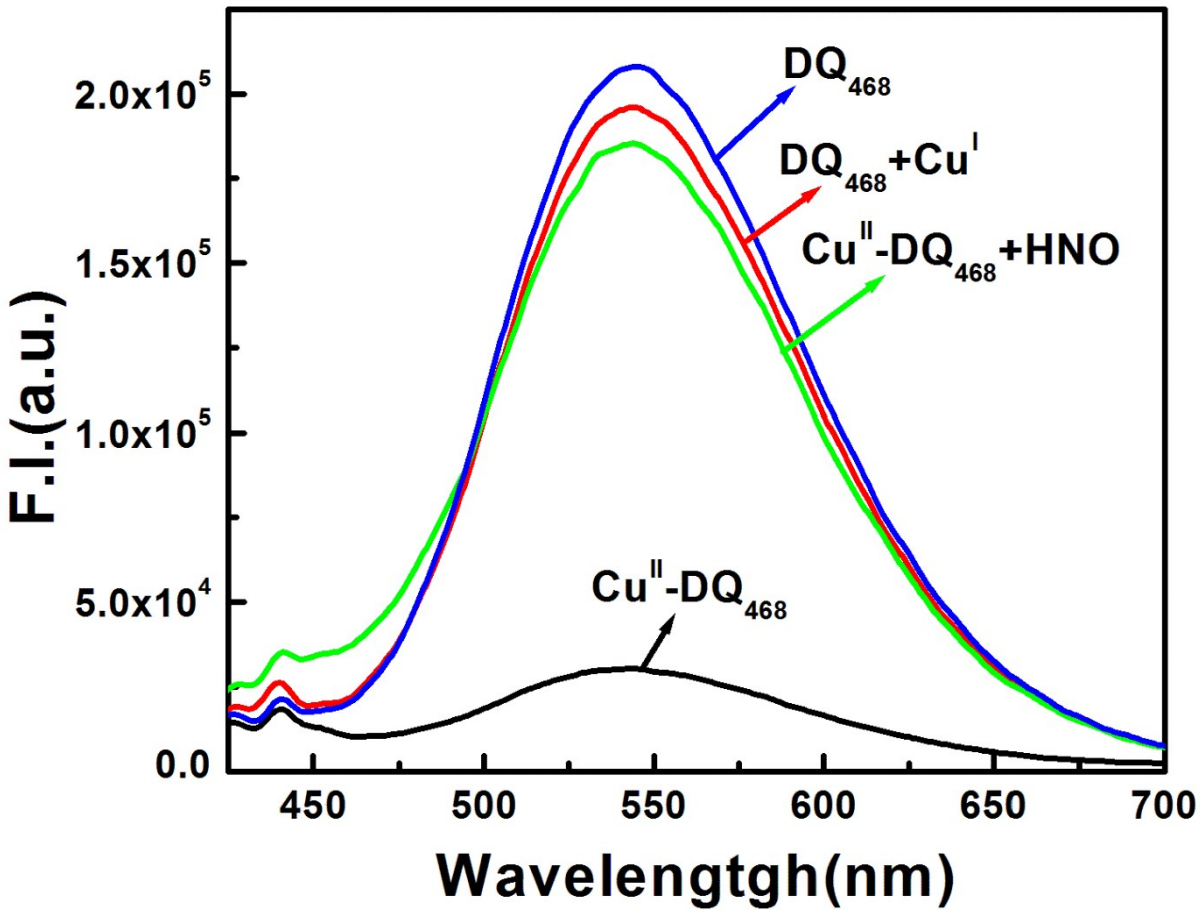


Fig. S15. Emission spectra of **DQ_{468}** in presence of Cu^{+}.

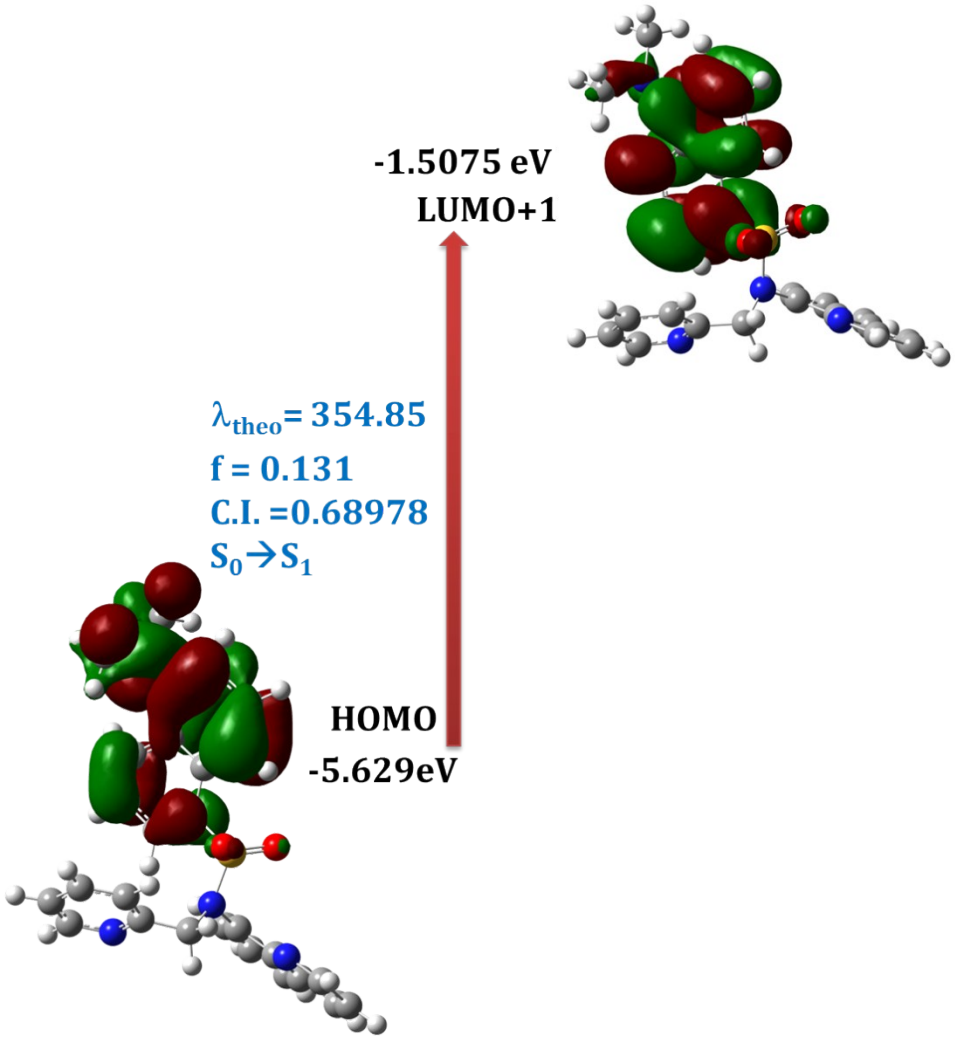


Fig.S16. Frontier molecular orbitals of **DQ_{468}** in UV-vis absorption**.**

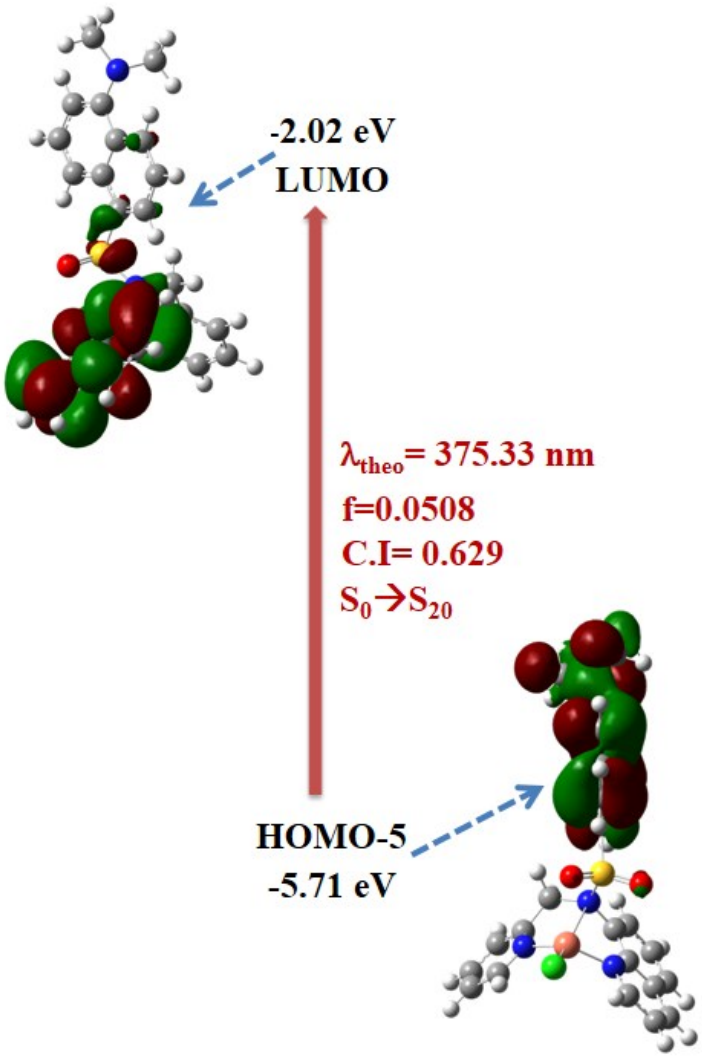


Fig.S17. Frontier molecular orbitals of **[$Cu^{II}(DQ_{468})Cl]^{+}$**in UV-vis absorption**.**

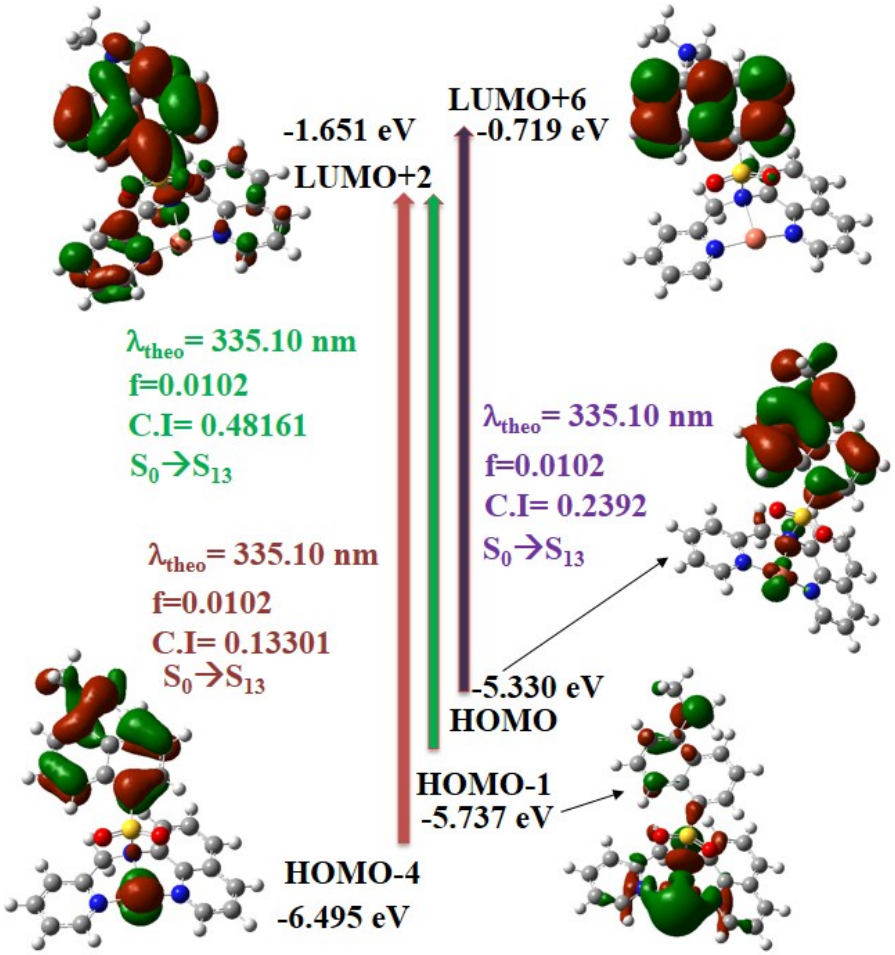


Fig.S18. Frontier molecular orbitals of **$[Cu^{I}(DQ_{468})]^{+}$** in UV-vis absorption.

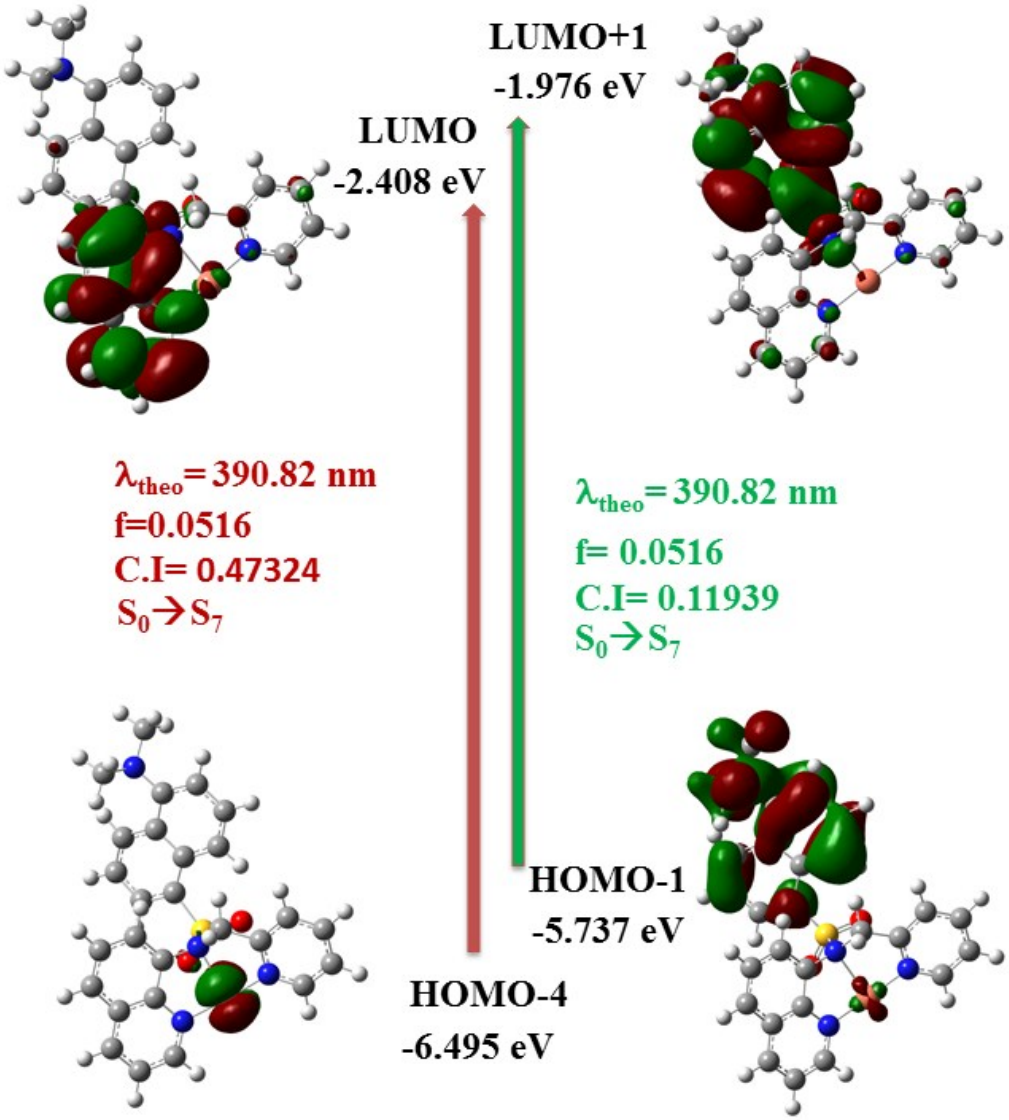


Fig.S19. Frontier molecular orbitals of **$[Cu^{I}(DQ_{468})]^{+}$** in UV-vis absorption.

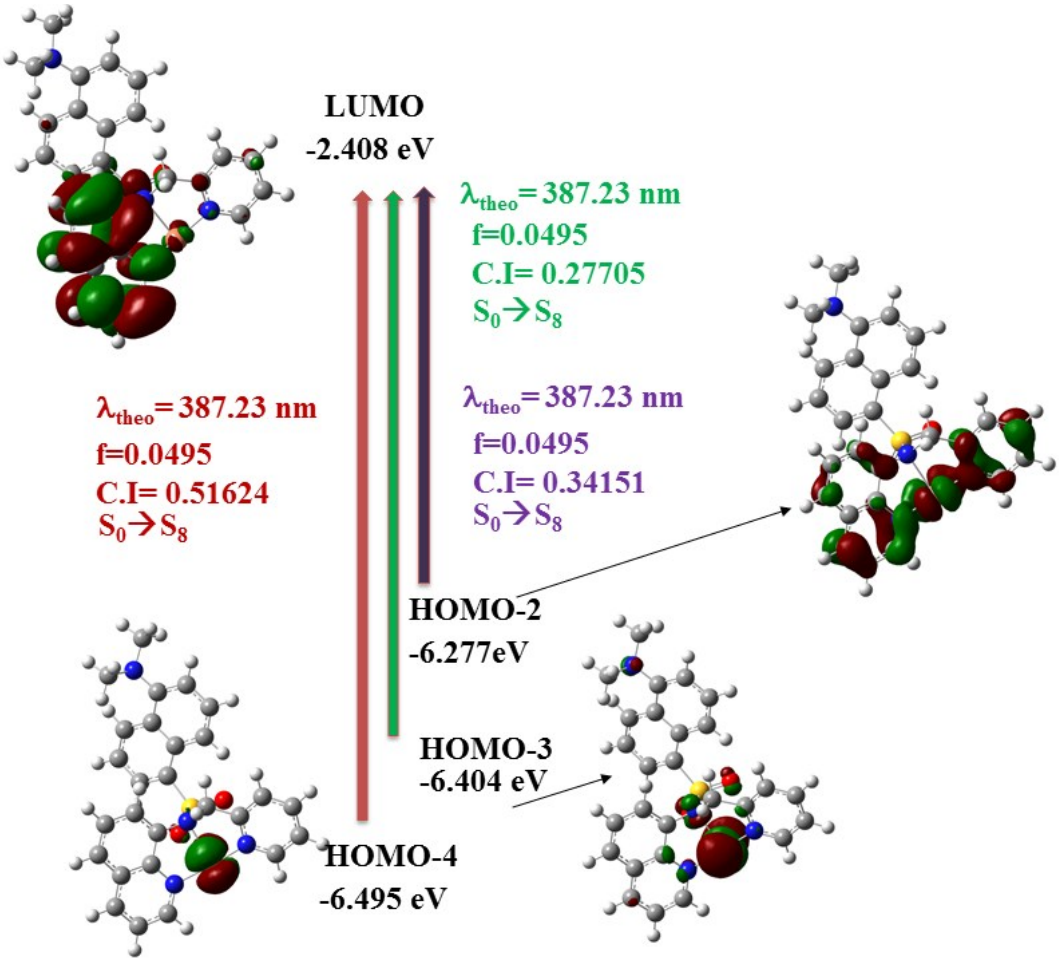


Fig.S20. Frontier molecular orbitals of **$[Cu^{I}(DQ_{468})]^{+}$** in UV-vis absorption

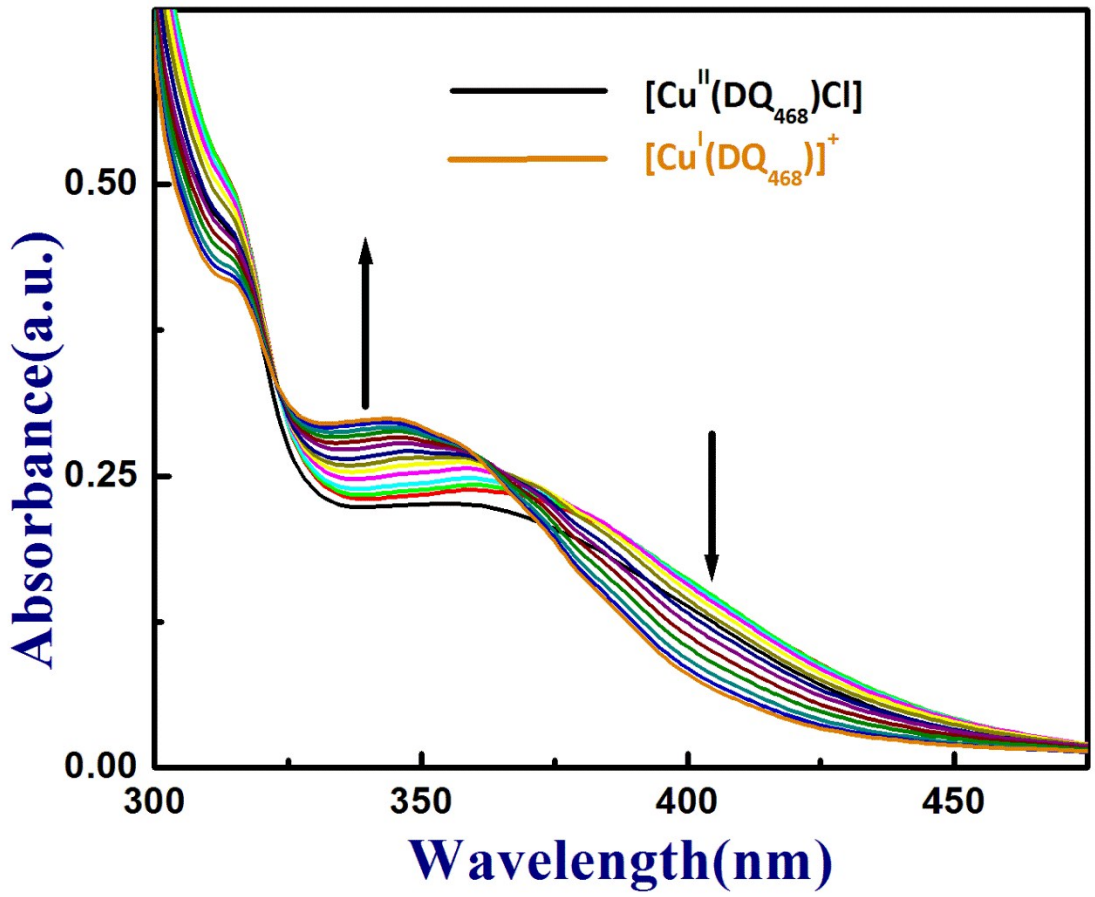


Fig. S21. UV-vis spectra of **[Cu^{II}(DQ$_{468}$)Cl]** towards HNO.

Table S1. Some selected geometrical parameters (bond lengths and bond angles) of **DQ$_{468}$** in ground state calculated at B3LYP/6-31G (d) Levels.

Bond Lengths (Å)			
C6- S2	1.81	S2-N1	1.70
S2-O4	1.46	N1-C43	1.43
S2-O3	1.46	N1-C30	1.48
Bond Angles (°)			
C6-S2-N1	104.68	S2-N1-C43	116.03
O4-S2-O3	120.27	S2-N1-C30	116.48
N1-C43-C44	120.49	N1-C30-C33	113.16

Table S2. Some selected geometrical parameters (bond lengths and bond angles) for **[$Cu^{II}(DQ_{468})Cl]^+$** in the ground state calculated at B3LYP/6-31G (d) Levels.

Bond Lengths (Å)			
S2-C6	1.808	Cu33-N60	1.949
S2-N1	1.695	N1-Cu33	2.816
N1-C45	1.431	Cu33-Cl34	2.278
N1-C30	1.468	Cu33-N44	1.944
Bond Angles (°)			
S2-N1-C30	118.446	N60-Cu33-Cl34	112.665
S2-N1-C45	120.096	N44-Cu33-Cl34	114.493
N1-Cu33-N44	73.925		
N1-Cu33-N60	71.219		

Table S3. Some selected geometrical parameters (bond lengths and bond angles) for **[$Cu^{I}(DQ_{468})]^+$** in the ground state calculated at B3LYP/6-31G (d) Levels.

Bond Lengths (Å)			
C6-S2	1.7928	N43-Cu33	1.8746
S2-O4	1.4629	N1-Cu33	2.1991
S2-O3	1.4629	N59-Cu33	1.8749
S2-N1	1.7599		
Bond Angles (°)			
C6-S2-N1	108.5100	N1-Cu33-N59	86.7645
S2-N1-Cu33	98.1251	N43-Cu33-N59	156.9166
N1-Cu33-N43	87.3255		

Table S4a. Vertical excitation energy and oscillator strength (f_{cal}) of low-lying excited singlet states obtained from TDDFT// B3LYP/6-31G(d) calculations of **DQ_{468}** which is matched with the experimental one**.**

Electronic transition	Composition	Excitation energy	Oscillator strength (f_{cal})	CI	λ_{exp} (nm)
$S_0 \rightarrow S_1$	HOMO→ LUMO+1 (123 ->125)	3.494 eV (354.85nm)	0.1310	0.68978	337

Table S4b. All vertical excitation energies and oscillator strengths (f_{cal}) of some low-lying excited singlet states obtained from TDDFT// B3LYP/6-31G(d) calculations of **DQ_{468} .**

Electronic transition	Composition	Excitation energy	Oscillator strength (f_{cal})	CI	λtheo (nm)
$S_0 \rightarrow S_2$	**123 ->124**	**3.5588 eV**	**0.0009**	**0.69982**	**348.38**
$S_0 \rightarrow S_3$	**122 ->124**	**4.1961 eV**	**0.1322**	**0.62435**	**295.48**
	123 ->128			**0.14947**	
$S_0 \rightarrow S_4$	**123 ->126**	**4.2099 eV**	**0.0162**	**0.17684**	**294.51**
	123 ->128			**0.48177**	
$S_0 \rightarrow S_5$	**123 ->126**	**4.3426 eV**	**0.0002**	**0.67979**	**285.51**
$S_0 \rightarrow S_6$	**116 ->124**	**4.3549 eV**	**0.0189**	**0.51975**	**284.70**
	117 ->124			**0.15908**	
	118 ->124			**0.36919**	
	122 ->124			**0.18026**	
$S_0 \rightarrow S_7$	**122 ->125**	**4.4352 eV**	**0.0010**	**0.68757**	**279.55**
$S_0 \rightarrow S_8$	**117 ->124**	**4.5105 eV**	**0.0352**	**0.10643**	**274.88**
	119 ->124			**0.50113**	
$S_0 \rightarrow S_9$	**121 ->124**	**4.5430 eV**	**0.0066**	**0.6754**	**272.91**
$S_0 \rightarrow S_{10}$	**121 ->125**	**4.5719 eV**	**0.0394**	**0.66793**	**271.19**

Table S5a. Vertical excitation energy and oscillator strength (f_{cal}) of low-lying excited singlets obtained from TDDFT// B3LYP/6-31G (d) calculations of **$[Cu^{II}(DQ_{468})Cl]^+$** complex which is matched with the experimental one.

Electronic Transition	Composition	Excitation energy	Oscillator strength (f_{cal})	CI	λ_{exp} (nm)
$S_0 \rightarrow S_{20}$	HOMO-5 →LUMO (141→147)	3.3033 eV (375.33nm)	0.0508	0.629	370

Table S5b. All vertical excitation energies and oscillator strengths (f_{cal}) of some low-lying excited singlets obtained from TDDFT// B3LYP/6-31G (d) calculations of **$[Cu^{II}(DQ_{468})Cl]^+$** complex.

Electronic transition	Composition	Excitation energy	Oscillator strength (f_{cal})	CI	λtheo (nm)
$S_0 \rightarrow S_{10}$	144→149	2.7669 eV	0.0013	0.661	448.10
$S_0 \rightarrow S_{11}$	144 ->148	2.8810 eV	0.0021	0.667	430.36
	144 ->149			0.212	
$S_0 \rightarrow S_{12}$	146 ->150	2.9085 eV	0.0030	0.680	426.28
	146 ->151			0.114	
$S_0 \rightarrow S_{13}$	142 ->149	2.9834 eV	0.0039	0.468	415.59
	143 ->148			0.213	
$S_0 \rightarrow S_{14}$	142 ->149	3.0358 eV	0.0029	0.128	408.40
	143 ->148			0.100	
	145 ->150			0.603	
	145 ->151			0.110	
$S_0 \rightarrow S_{15}$	143 ->148	3.0578 eV	0.0049	0.13245	405.47
	145 ->150			0.29261	
	146 ->151			0.29932	
	146 ->152			0.52448	
$S_0 \rightarrow S_{16}$	143 ->148	3.0652 eV	0.0030	0.62561	404.49
$S_0 \rightarrow S_{17}$	142 ->148	3.1582 eV	0.0003	0.68404	392.58
	142 ->149			0.13745	
$S_0 \rightarrow S_{18}$	145 ->151	3.1867 eV	0.0013	0.34507	389.07
	145 ->152			0.59806	
$S_0 \rightarrow S_{19}$	142 ->149	3.2509 eV	0.0042	0.32038	381.39
	143 ->147			0.10125	
	143 ->148			0.14708	
	143 ->149			0.37583	
$S_0 \rightarrow S_{20}$	141 ->147	3.3033 eV	0.0508	0.62904	375.33

Table S6a. Vertical excitation energie and oscillator strength (f_{cal}) of low-lying excited singlets obtained from TDDFT// B3LYP/6-31G (d) calculations of **$[Cu^{I}(DQ_{468})]^{+}$** complex which is matched with the experimental one.

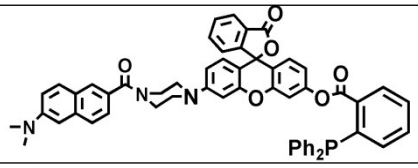
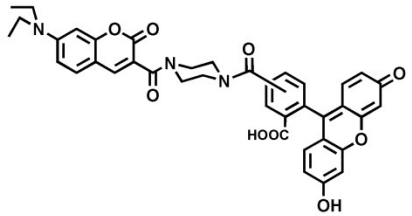
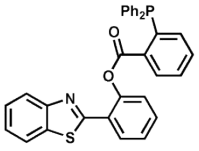
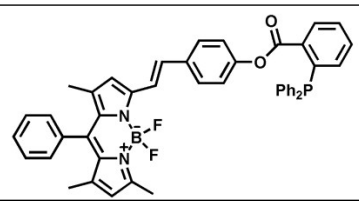
Electronic transition	Composition	Excitation energy	Oscillator strength (f_{cal})	CI	λ_{exp} (nm)
$S_0 \rightarrow S_{13}$	HOMO-4 →LUMO+2 (133→140) HOMO-1→LUMO+2 (136→140) HOMO→LUMO+6 (137 →144)	3.699 eV (335.10nm)	0.0102	0.13301 0.48161 0.23920	
$S_0 \rightarrow S_7$	HOMO-4→LUMO (133->138)	3.1724 eV (390.82 nm)	0.0516	0.47324	340
	HOMO-1 →LUMO+1 (136 ->139)			0.11939	
$S_0 \rightarrow S_8$	HOMO-4→LUMO (133 ->138)	3.2018 eV (387.23nm)	0.0495	0.51624	
	HOMO-3→LUMO (134 ->138)			0.27705	
	HOMO-2→LUMO (135 ->138)			0.34151	

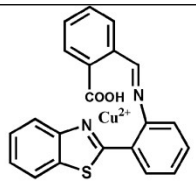
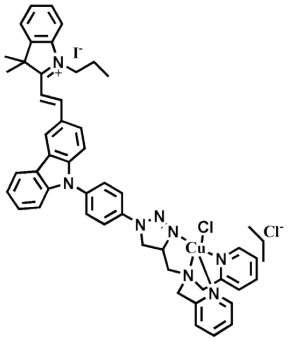
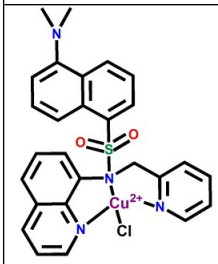
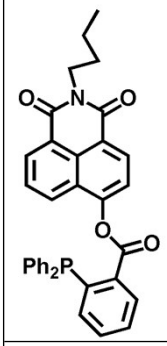
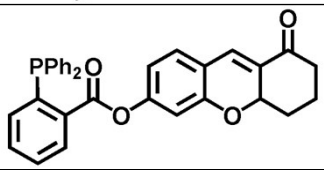
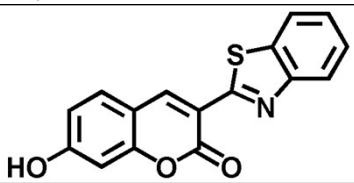
Table S6b. All vertical excitation energies and oscillator strengths (f_{cal}) of some low-lying excited singlets obtained from TDDFT// B3LYP/6-31G(d) calculations of **$[Cu^{I}(DQ_{468})]^{+}$** complex .

Electronic transition	**Composition**	**Excitation energy**	**Oscillator strength (f_{cal})**	**CI**	**λtheo (nm)**
$S_0 \rightarrow S_7$	133->138	3.1724 eV	0.0516	0.47324	390.82
	136 ->139			0.11939	
$S_0 \rightarrow S_8$	133 ->138	3.2018 eV	0.0495	0.51624	387.23
	134 ->138			0.27705	
	135 ->138			0.34151	
$S_0 \rightarrow S_9$	137 ->141	3.3675 eV	0.0002	0.67789	368.18
$S_0 \rightarrow S_{10}$	132 ->138	3.3891 eV	0.0005	0.67855	365.83
	137 ->141			0.16656	
$S_0 \rightarrow S_{11}$	137 ->142	3.5407 eV	0.0015	0.69295	350.17
	137 ->143			0.10158	
$S_0 \rightarrow S_{12}$	134 ->139	3.6471 eV	0.0032	0.14748	339.95
	134 ->140			0.37982	
	135 ->139			0.17712	
	135 ->140			0.24647	

	136 ->140			0.44043	
$S_0 \rightarrow S_{13}$	133->140	3.6999 eV	0.0102	0.13301	335.10
	136 ->140			0.48161	
	137 ->144			0.23920	
$S_0 \rightarrow S_{14}$	135 ->139	3.7298 eV	0.0015	0.37668	332.42
	135 ->140			0.14490	
	137 ->143			0.11738	
	137 ->144			0.52594	
$S_0 \rightarrow S_{15}$	134 ->139	3.7414 eV	0.0080	0.23671	331.39
	134 ->140			0.44980	
	137 ->144			0.28323	
$S_0 \rightarrow S_{16}$	133 ->139	3.7803 eV	0.0019	0.26571	327.98
	133 ->140			0.60691	
	135 ->139			0.19626	

Table S7: Comparative table for detection limit of HNO probes.

HNO Probes	λ_{em}	LOD (μM)	REFFERENCES
	541nm	0.59	1
	517nm	1.4	2
	460nm	0.98	3
	586nm	2	4

	450nm	9	5
	595nm	23	6
	543nm	0.4	THIS WORK
	546nm	0.5	7
	512nm	0.59	8
	490nm	0.64	9

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