Supporting Information

for

Strategic Design of a 2,6-Disubstituted Pyridine-based Probe having Hard-Soft Centres: Responsive Divergence from One Core

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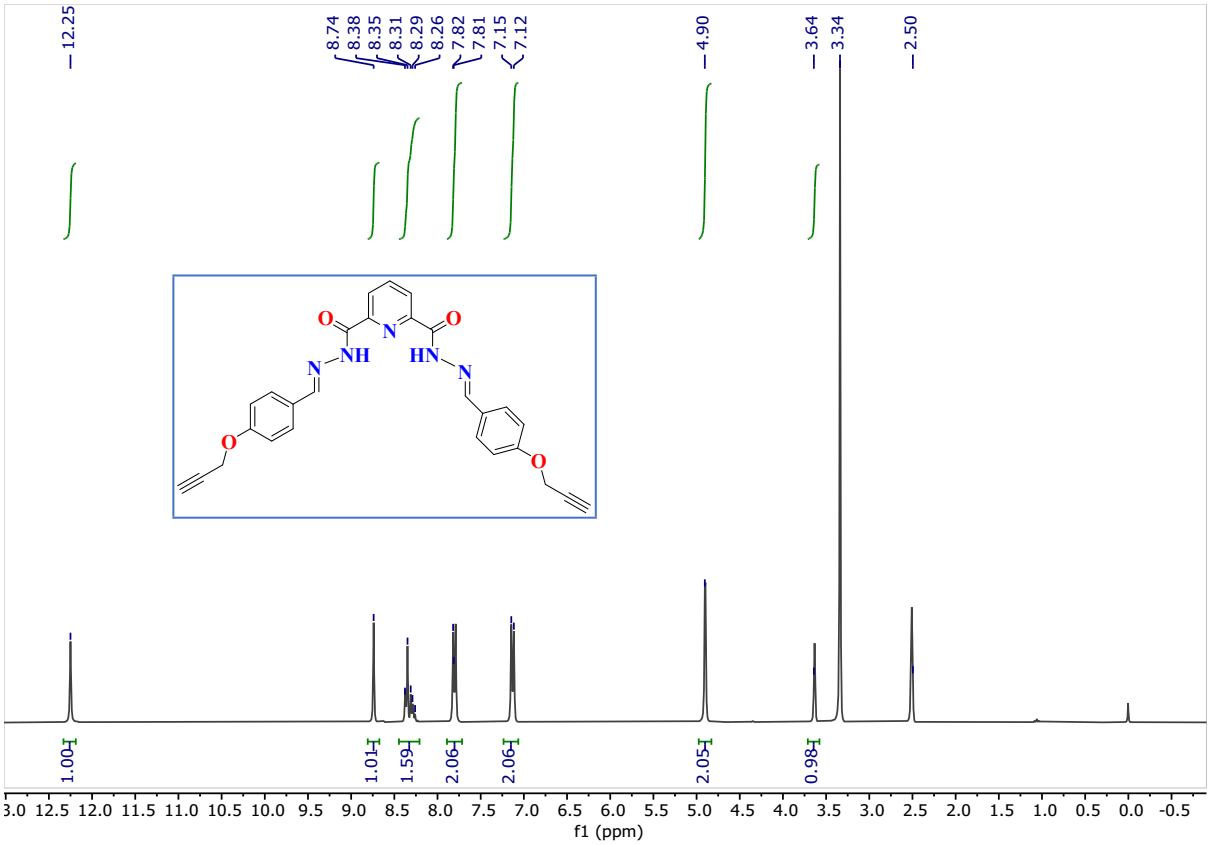


Fig. S1 ^{1}H NMR spectra of compound **5** in DMSO-d_6 as a solvent.

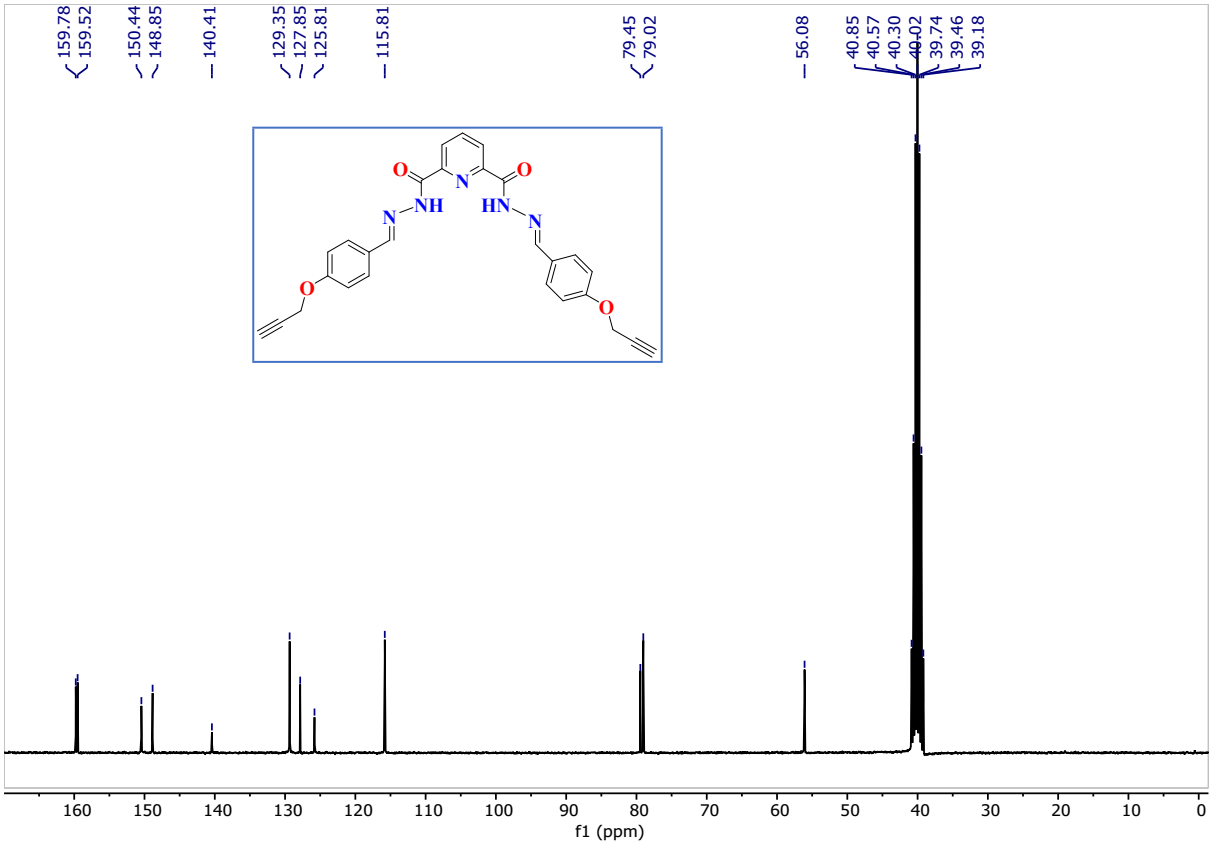


Fig. S2 ^{13}C NMR spectra of compound **5** in DMSO-d_6 as a solvent.

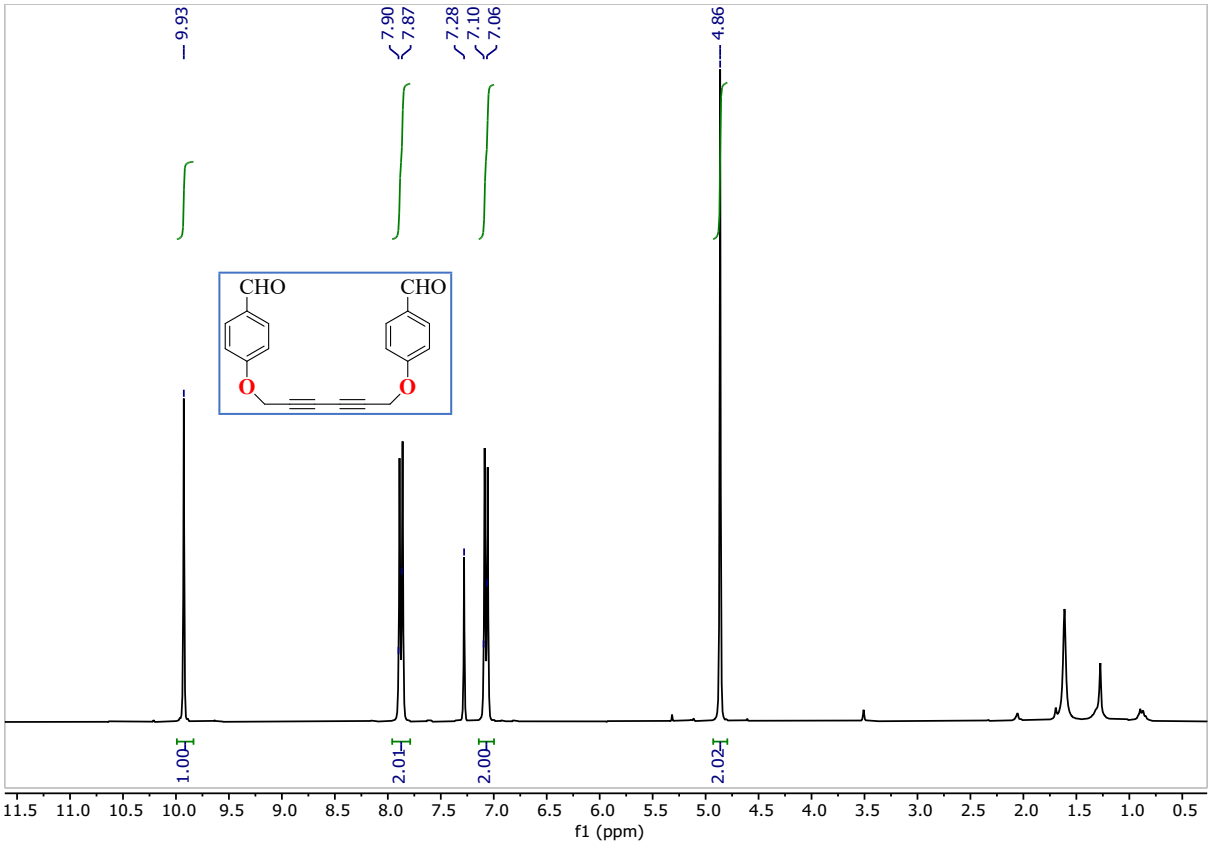


Fig. S3 ^{1}H NMR spectra of compound **6** in $CDCl_3$ as a solvent.

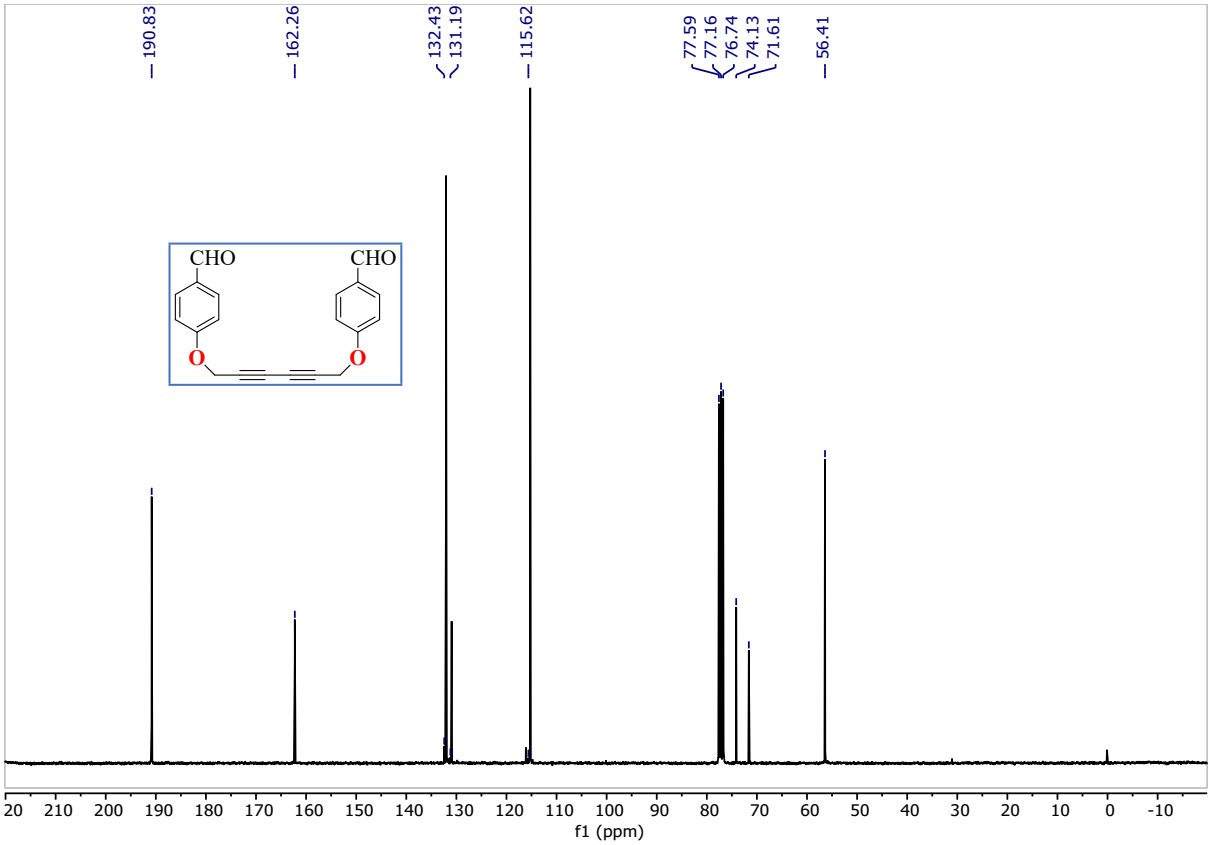


Fig. S4 ^{13}C NMR spectra of compound **6** in $CDCl_3$ as a solvent

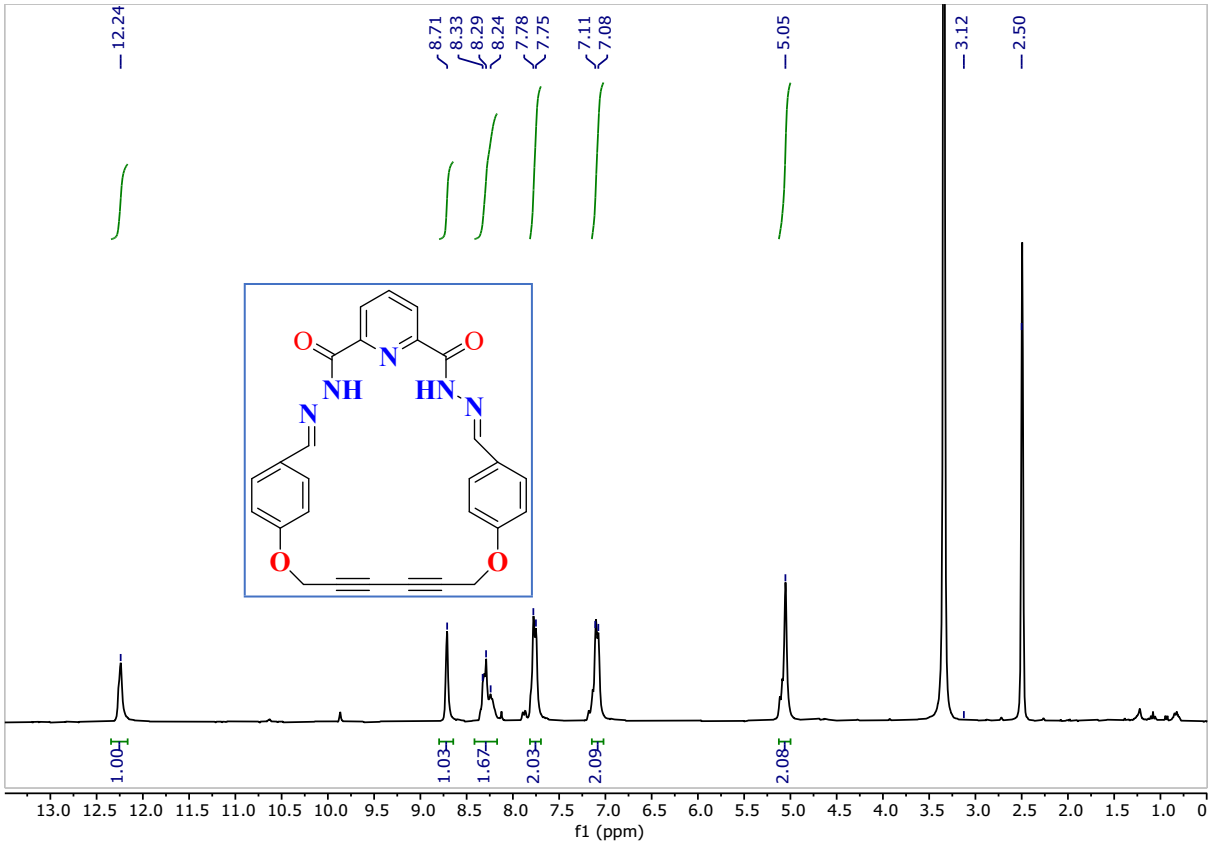


Fig. S5. ^{1}H NMR spectra of compound **7** in DMSO-d_6 as a solvent.

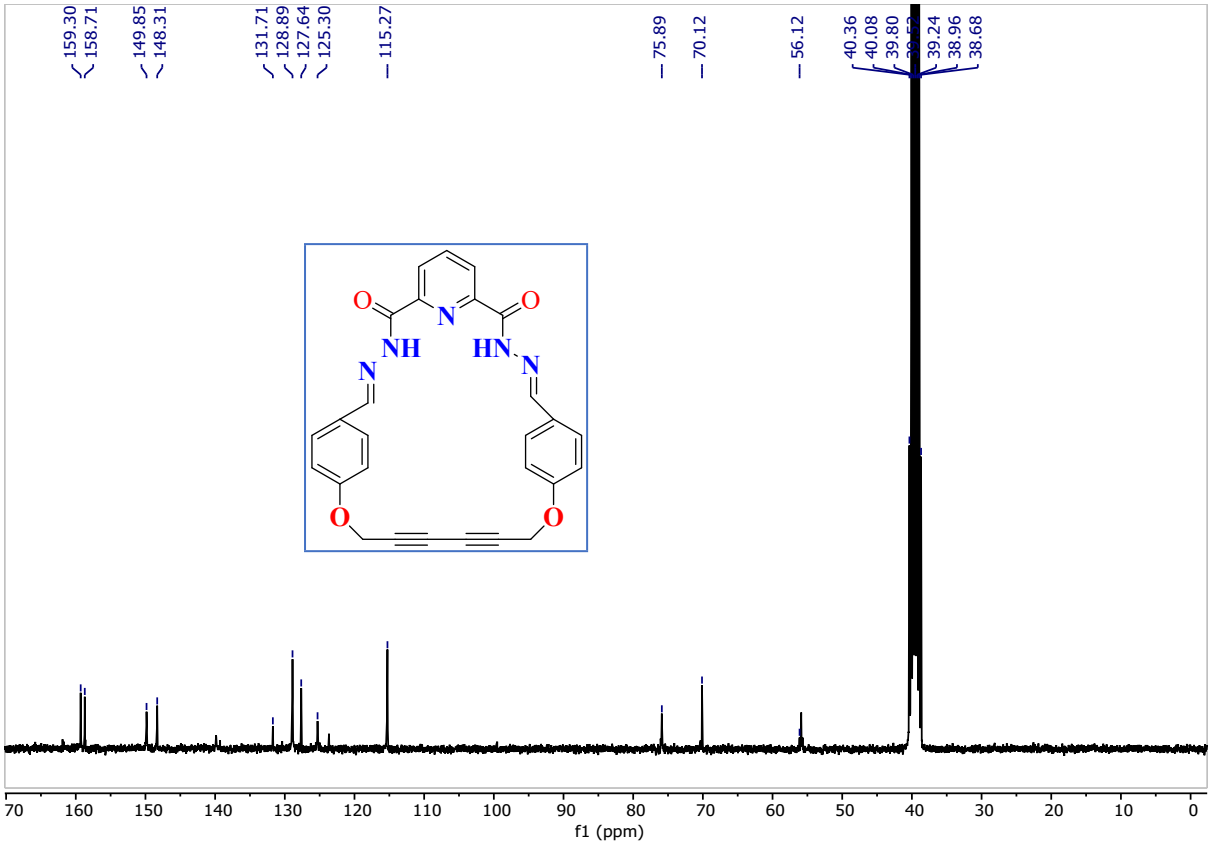


Fig. S6. ^{13}C NMR spectra of compound **7** in DMSO-d_6 as a solvent.

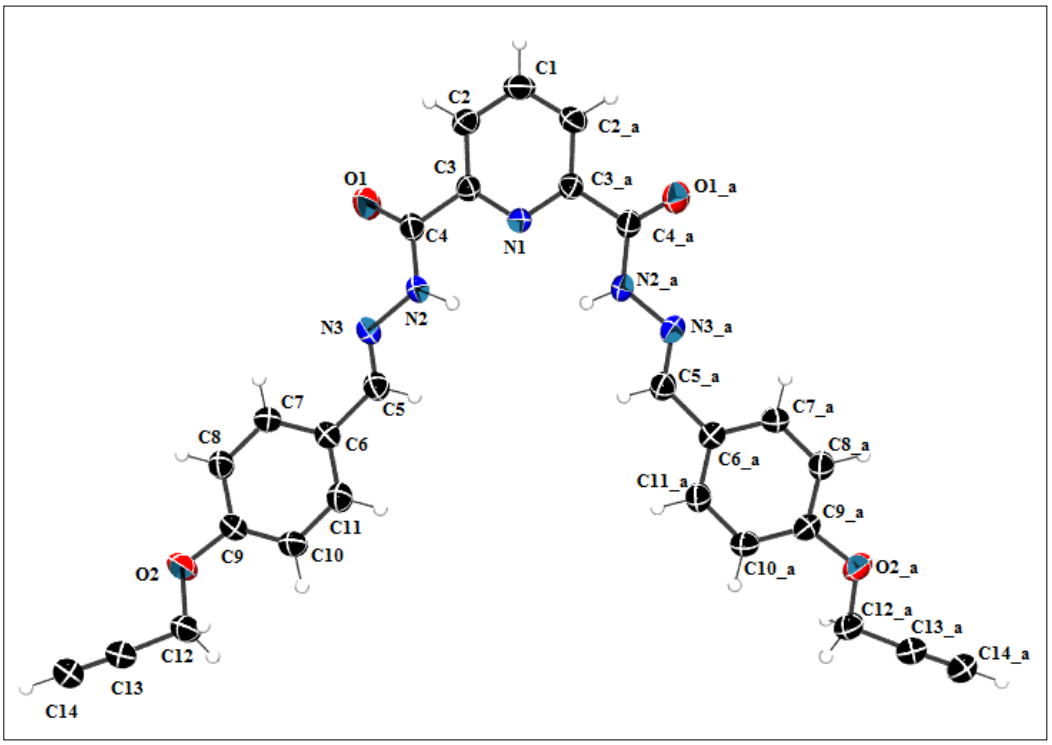


Fig. S7 ORTEP representation of the molecular structure of **5** with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg) for 5: C3-N1 1.337(2), C4-O1 1.220(2), C4-N2 1.348(2), N2-N3 1.381(2), N3-C5 1.227(3), C5-C6 1.459(3), C9-O2 1.366(2), C13-C14 1.171(3); N1-C3-C4 116.74(17), N1-C3-C2 123.06(18), O1-C4-N2 124.74(18), C4-N2-N3 121.29(16), C5-N3-N2 114.71(16), N3-C5-C6 121.77(18), C9-O2-C12 118.93(16), O2-C9-C10 125.50(18).

Table S1: Crystal data of **5**

Empirical formula	$C_{27}H_{21}N_5O_4$
Formula weight	479.49
Crystal size (mm)	0.36 X 0.28 X 0.12
Crystal system	monoclinic
Space group	*C*2/*c*
a [Å]	26.676(2)
b [Å]	11.1232(8)
c [Å]	8.1112(6)
α [°]	90
β [°]	103.747(4)
γ [°]	90
volume [Å^3]	2337.9(3)
Z	1.362
F(000)	1000
μ MoK$_\alpha$ [mm^{-1}]	0.094
Temperature [K]	140(2)
R_{int}	0.0316
Range of h, k, l	–34/34, –14/14, –10/10
$\theta_{min/max}$ (°)	1.992/27.113
Reflections collected/Unique/observed [I > 2σ(I)]	27987/2588/2043
Data/restraints/parameters	2588/0/ 164
GOF on F^2	1.126
Final R indices [I > 2σ(I)]	*R*1 = 0.0570 *wR*2 = 0.1222
R indices [all data]	*R*1 = 0.0762 *wR*2 = 0.1316

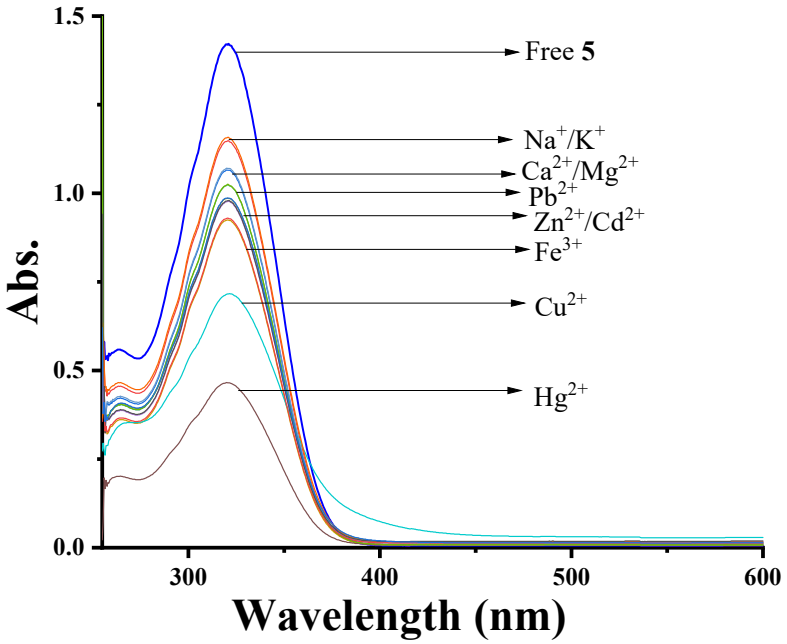


Fig. S8 Absorption spectra of compound **5** (3.1×10^{-5} M) with all metals in DMSO:H_2O (7:3, *v/v*) at 22 ˚C.

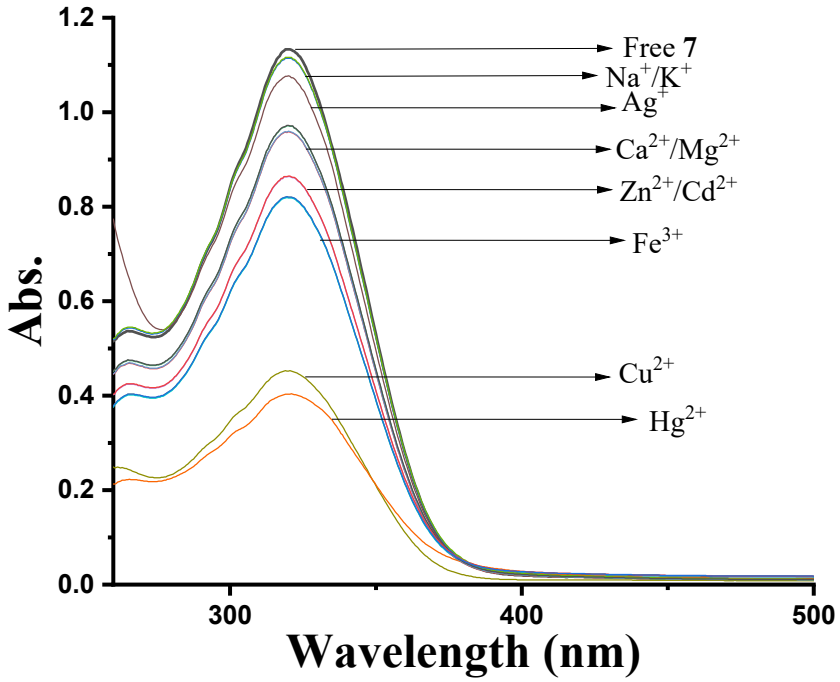


Fig. S9 Absorption spectra of compound **7** (3.1×10^{-5} M) with all metals in DMSO:H_2O (7:3, *v/v*) at 22 ˚C.

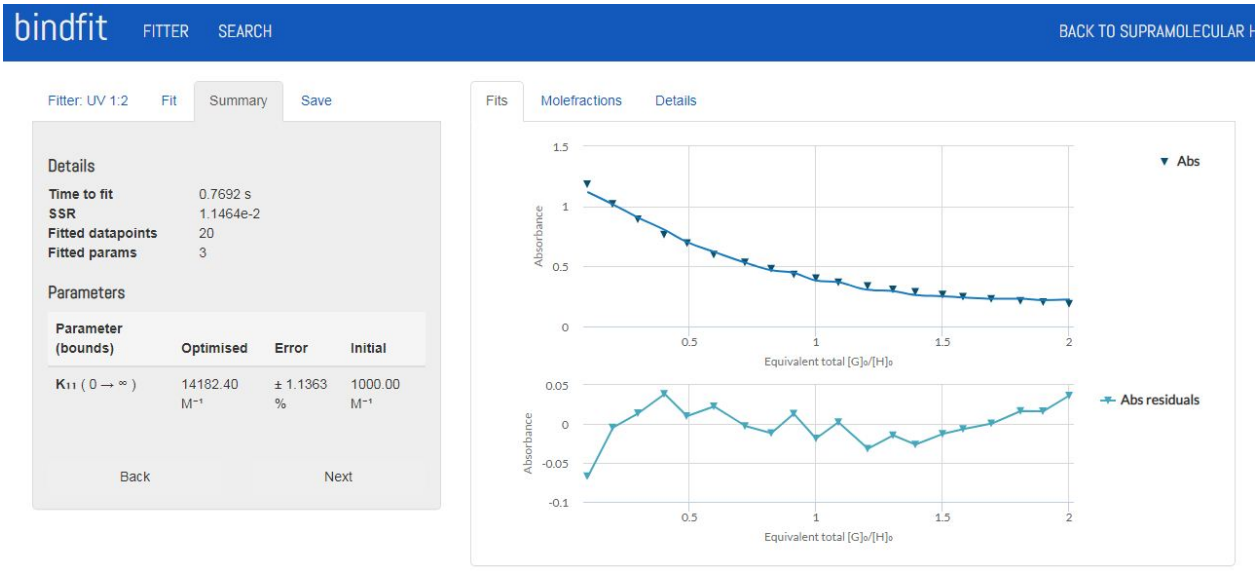


Fig. S10 Fitting of absorption titration data of compound **5** with Hg^{2+} ion into 1:2 Nelder-Mead model in Bindfit software. Screenshots taken from the website supramolecular.org. This fitting for 1:2 fitter with a minimum error of ±1.1363 % justifies the 1:2 binding of **5** with Hg^{2+} ion with an association constant of 14182.40 M^{-1}. 20 data points have been used as input in this fitting with 3 factors viz., host concentration, guest concentration and the change in fluorescence intensity. The optimised value is the actual binding constant obtained.

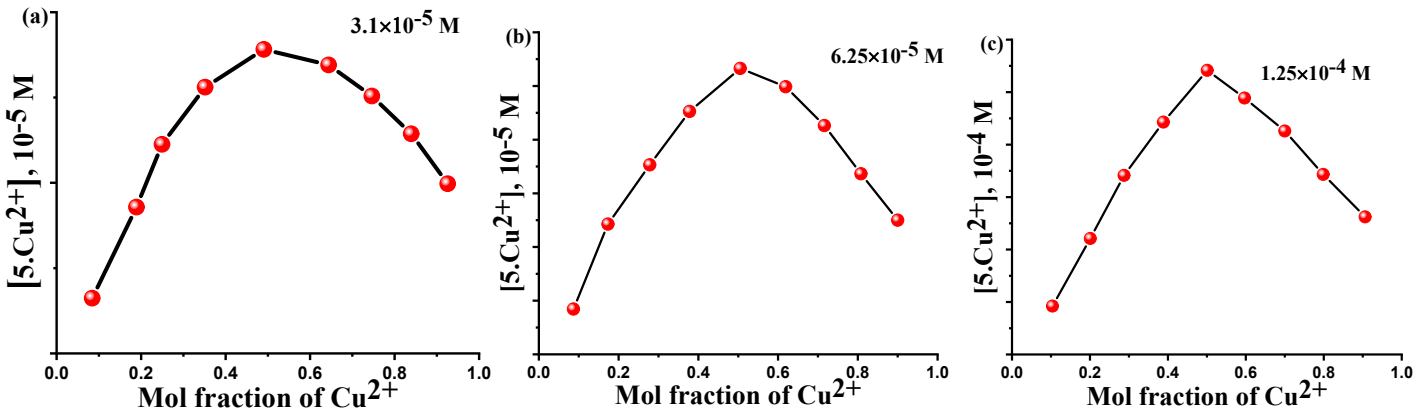


Fig. S11 Jobs plot of compound **5** with Cu^{2+} metal ion at various concentration.

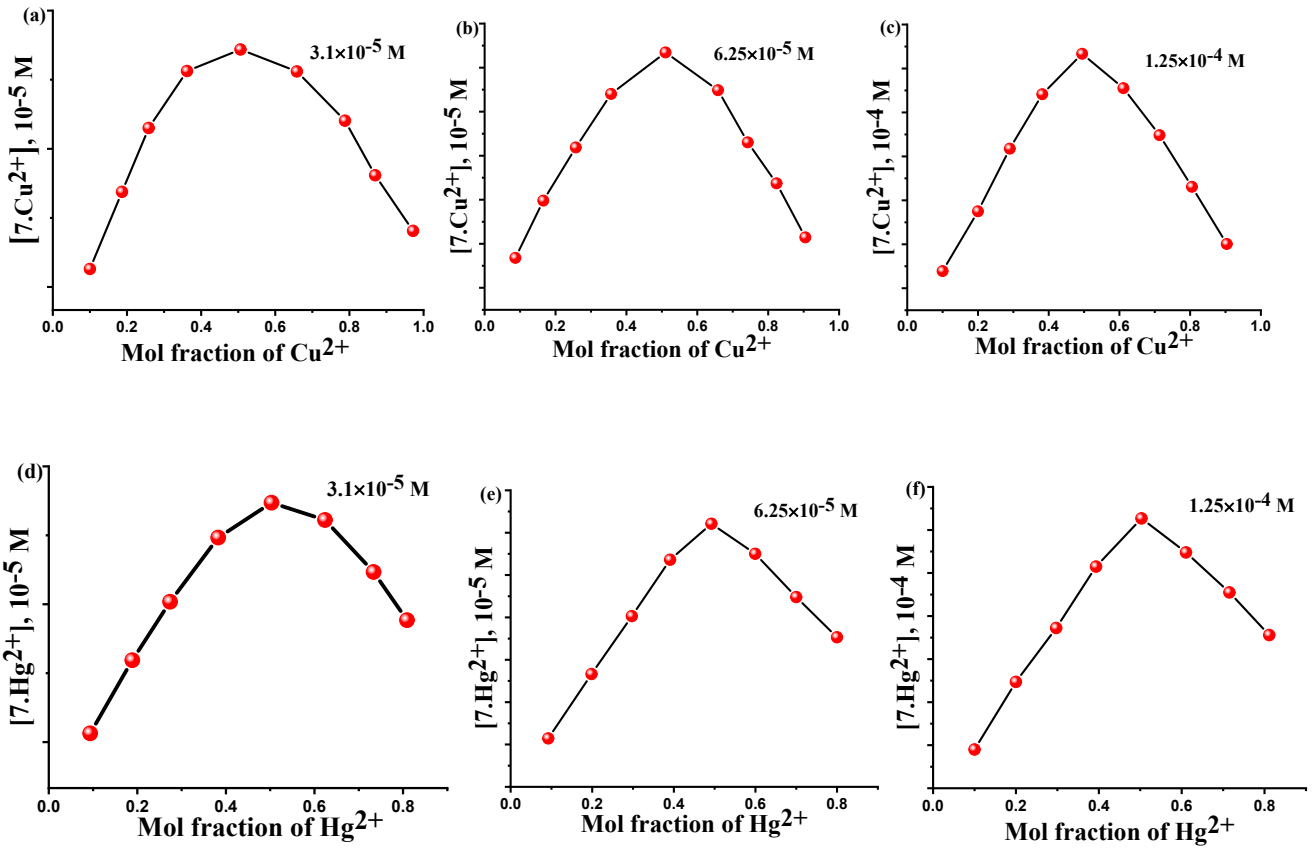


Fig. S12 Jobs plot of compound **7** with (a)-(c) Cu^{2+} and (d)-(f) Hg^{2+} metal ions at various concentration.

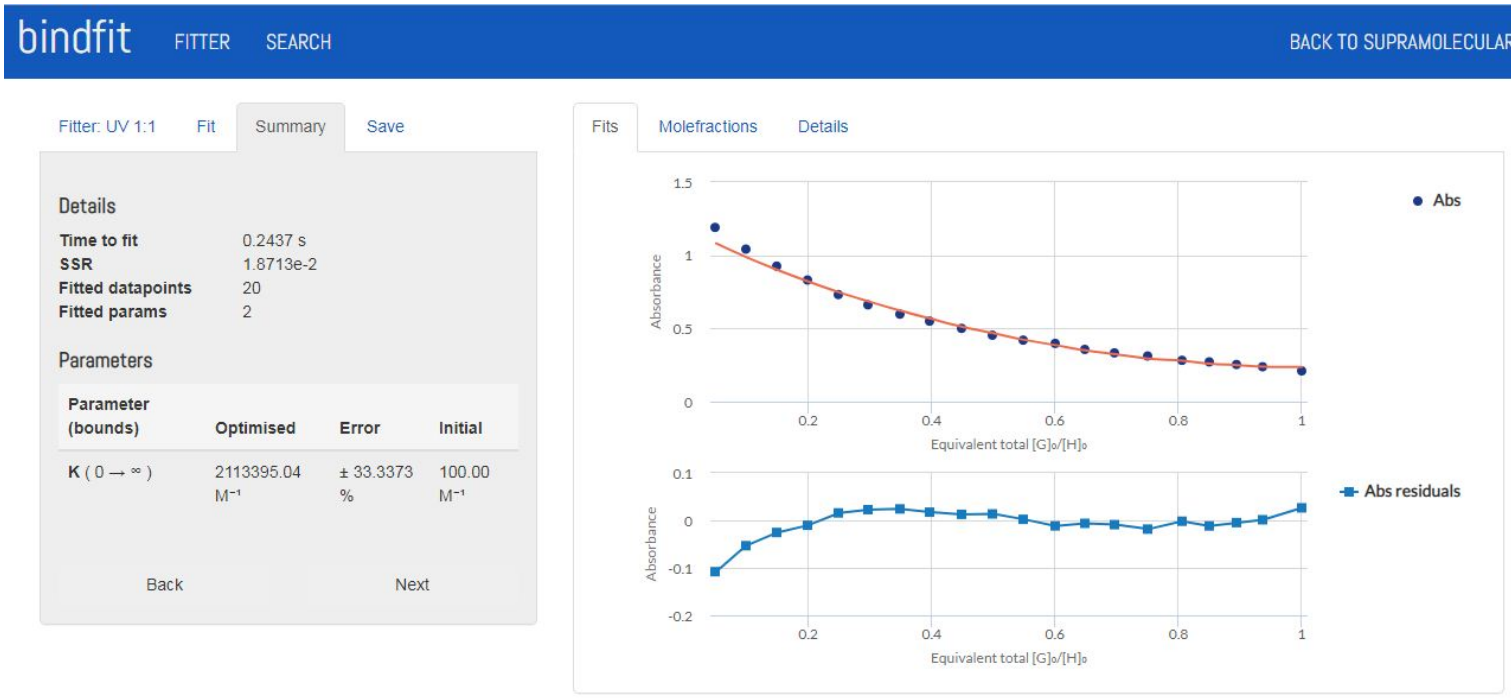


Fig. S13 Association constant of compound **5** with Cu^{2+} ion obtained from fitting the UV-vis absorbance titration data into 1:1 Nelder-Mead model in Bindfit software. Screenshots taken from the website supramolecular.org. This fitting for 1:1 fitter with an error of ±33.3373 % (< 40 %) justifies the 1:1 binding of **5** with Cu^{2+} ion with an association constant of 2113395.04 M^{-1}. 20 data points have been used as input in this fitting with 3 factors viz., host concentration, guest concentration and the change in fluorescence intensity. The optimised value is the actual binding constant obtained.

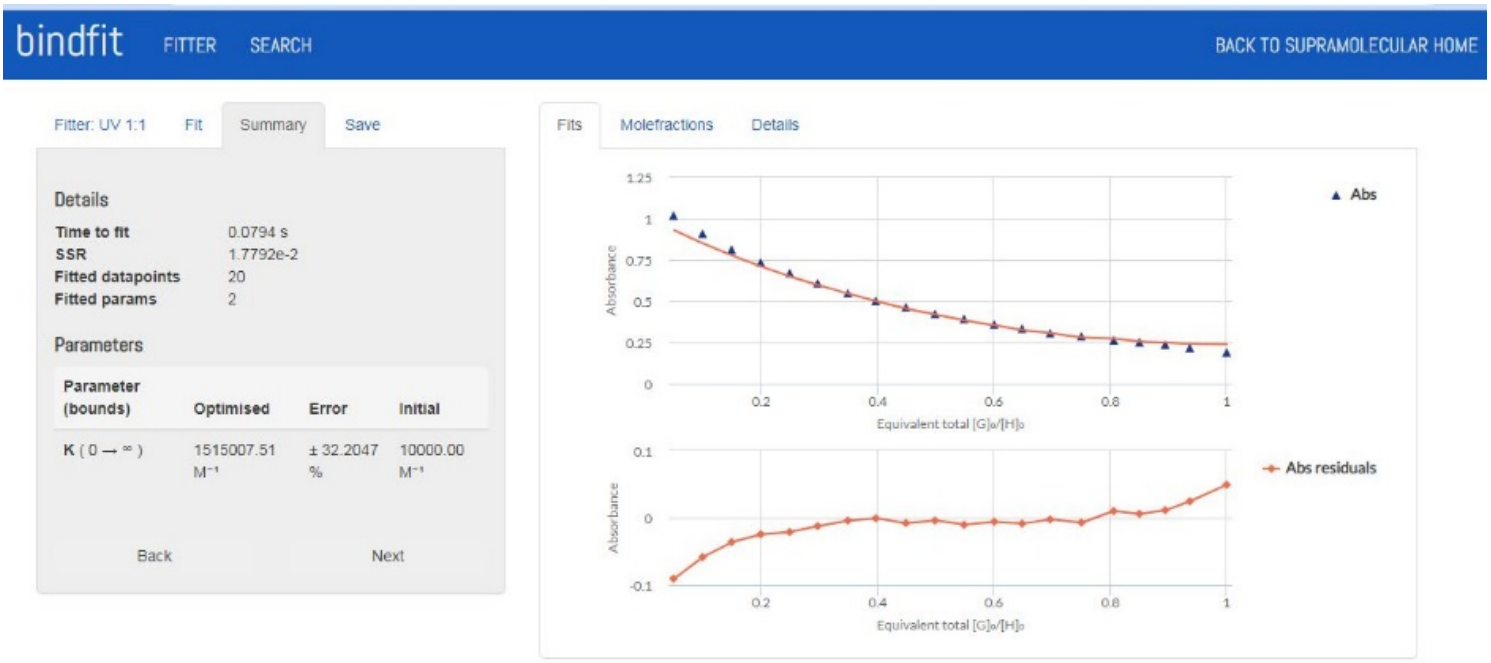


Fig. S14 Association constant of compound **7** with Cu^{2+} ion obtained from fitting the UV-vis absorbance titration data into 1:1 L-BFGS-B model in Bindfit software. Screenshots taken from the website supramolecular.org. This fitting for 1:1 fitter with an error of ±32.2047 % (< 40 %) justifies the 1:1 binding of **7** with Cu^{2+} ion with an association constant of 1515007.51 M^{-1}. 20 data points have been used as input in this fitting with 3 factors viz., host concentration, guest concentration and the change in fluorescence intensity. The optimised value is the actual binding constant obtained.

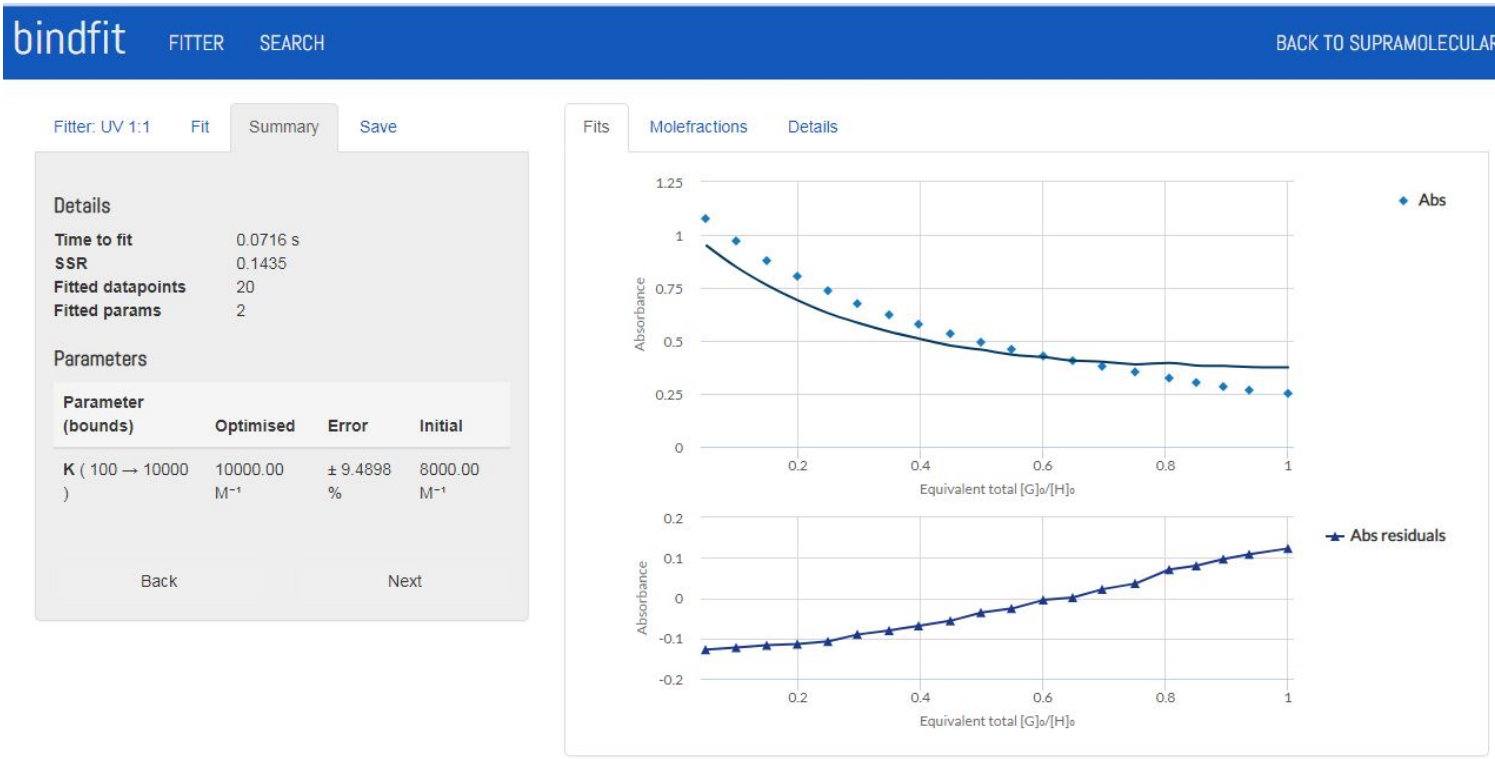


Fig. S15 Association constant of compound **7** with Hg^{2+} ion obtained from fitting the UV-vis absorbance titration data into 1:1 L-BFGS-B model in Bindfit software. Screenshots taken from the website supramolecular.org. This fitting for 1:1 fitter with an error of ±9.4898 % (< 40 %) justifies the 1:1 binding of **7** with Hg^{2+} ion with an association constant of 10000 M^{-1}. 20 data points have been used as input in this fitting with 3 factors viz., host concentration, guest concentration and the change in fluorescence intensity. The optimised value is the actual binding constant obtained.

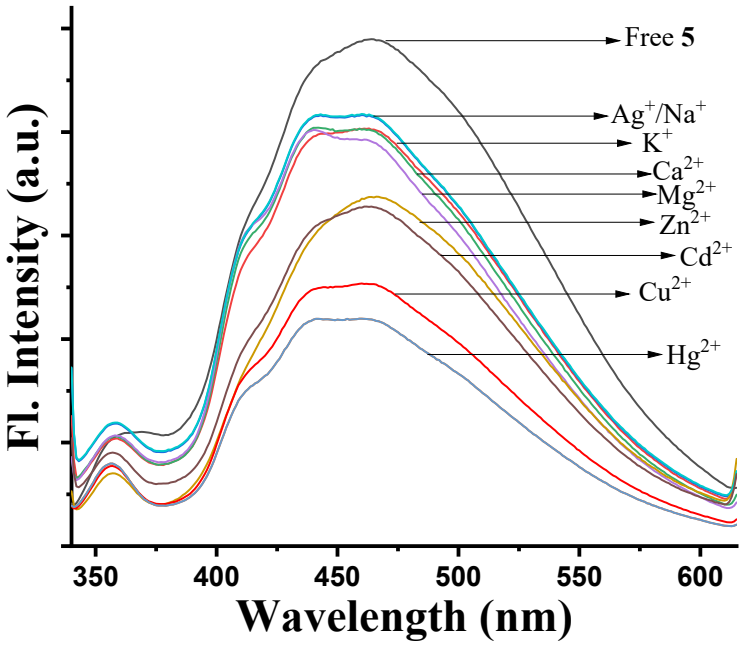


Fig. S16 Fluorescence emission spectra of compound **5** (7.8×10^{-6} M) with all metals in DMSO:H_2O (7:3, *v/v*) solvent at 22 ˚C.

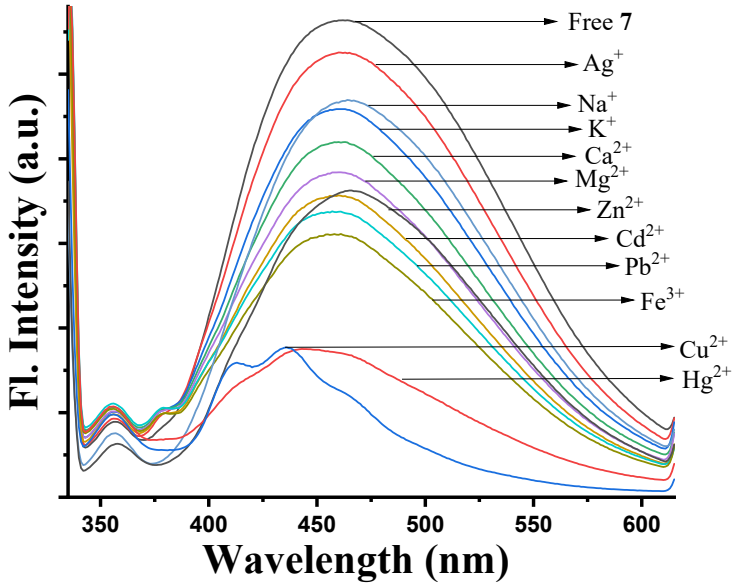


Fig. S17 Fluorescence emission spectra of compound **7** (7.8×10^{-6} M) with all metals in DMSO:H_2O (7:3, *v/v*) solvent at 22 ˚C.

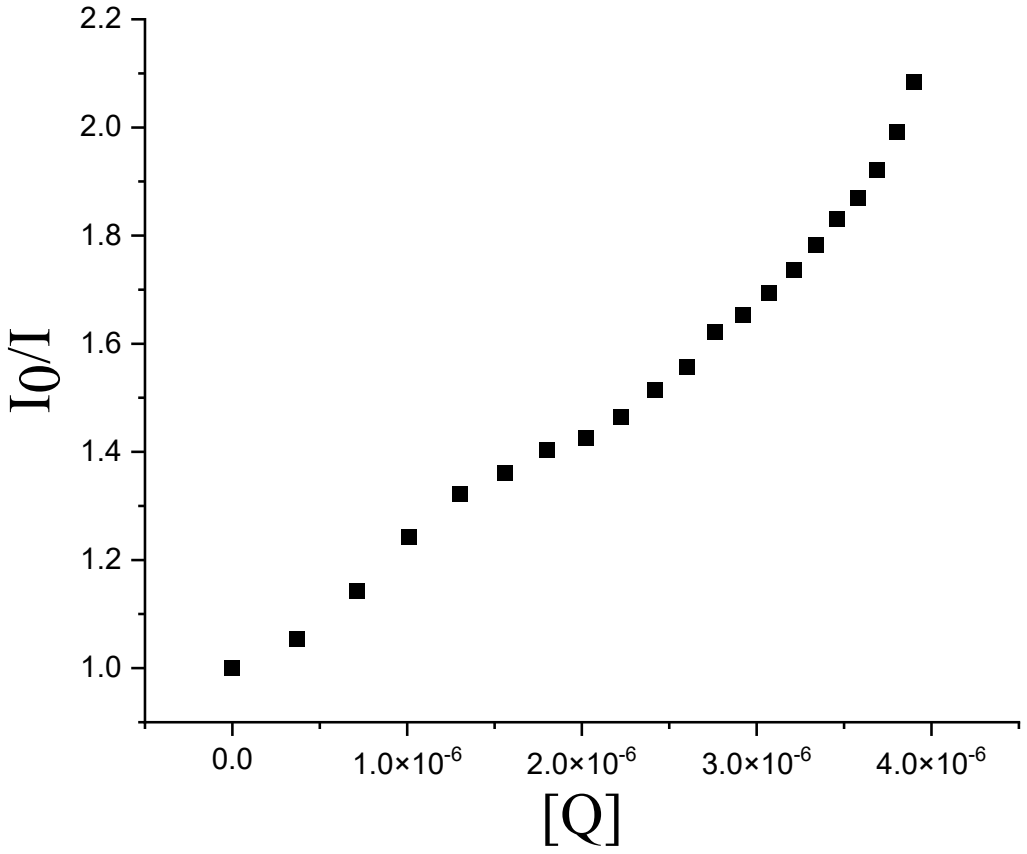


Fig. S18 Stern-Volmer plot of **5**+Cu^{2+}.

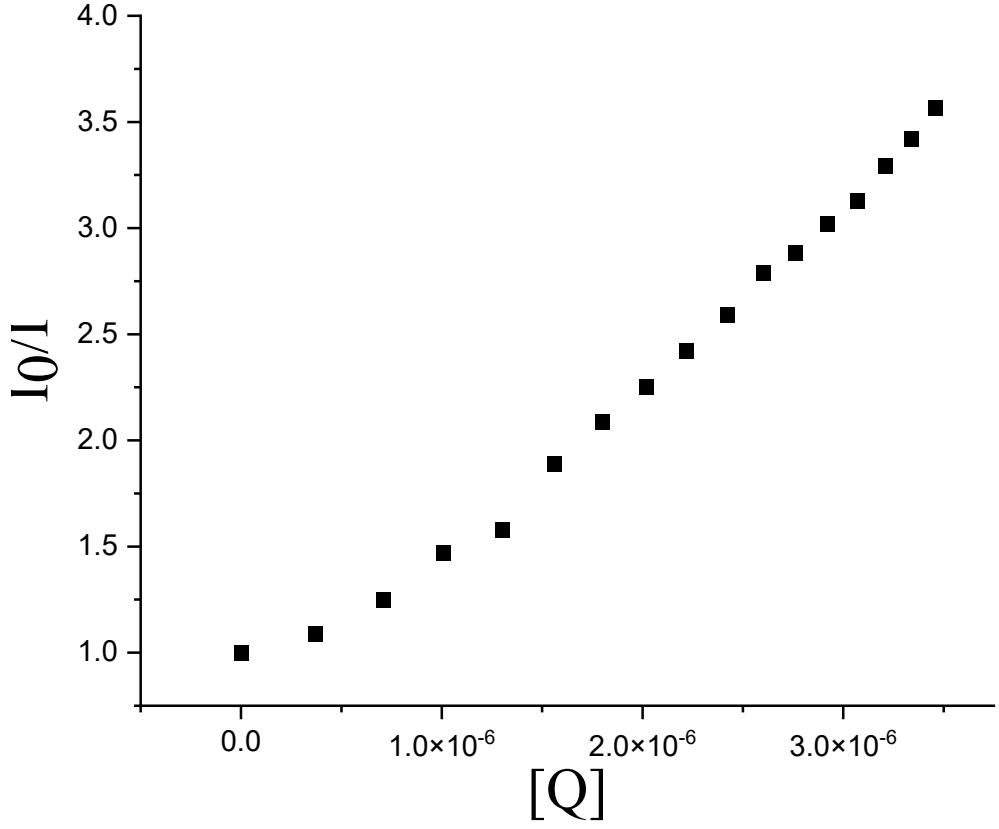


Fig. S19 Stern-Volmer plot of **7**+Cu^{2+}.

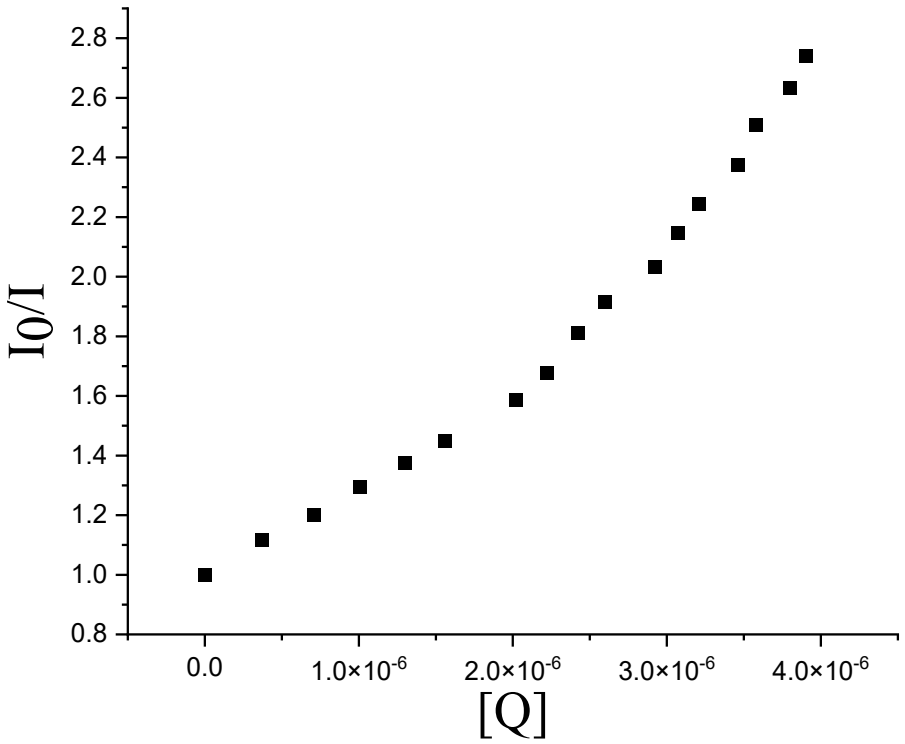


Fig. S20 Stern-Volmer plot of **7**+Hg^{2+}.

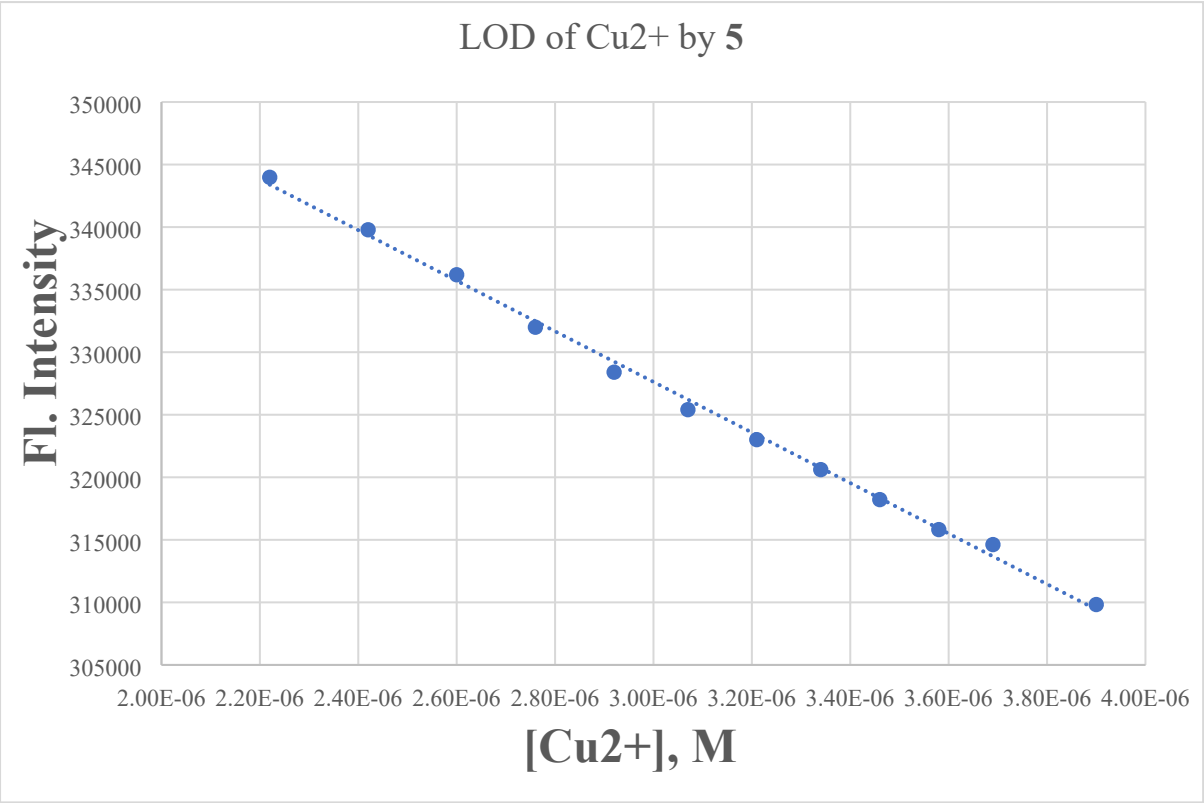


Fig. S21 Limit of detection (LOD) of compound **5** in presence of Cu^{2+} ion from fluorescence spectra by 3σ/s method.

Conc of Cu	Fl. Intensity							
2.22E-06	343980							
2.42E-06	339786							
2.60E-06	336191							
2.76E-06	331997							
2.92E-06	328401							
3.07E-06	325405							
3.21E-06	323009							
3.34E-06	320612							
3.46E-06	318215							
3.58E-06	315818							
3.69E-06	314620							
3.90E-06	309827							
SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0.998571							
R Square	0.997144							
Adjusted F	0.996858							
Standard I	597.8115							
Observatio	12							
ANOVA								
	df	*SS*	*MS*	*F*	*gnificance F*			
Regressior	1	1.25E+09	1.25E+09	3490.972	4.68E-14			
Residual	10	3573786	357378.6					
Total	11	1.25E+09						
	Coefficients	*tandard Erro*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*ower 95.0%*	*pper 95.0%*
Intercept	388266.7	1073.658	361.63	6.43E-22	385874.5	390659	385874.5	390659
X Variable	-2E+10	3.42E+08	-59.0844	4.68E-14	-2.1E+10	-1.9E+10	-2.1E+10	-1.9E+10

Fig. S22 Excel sheet for **5**+Cu^{2+} LOD calculation

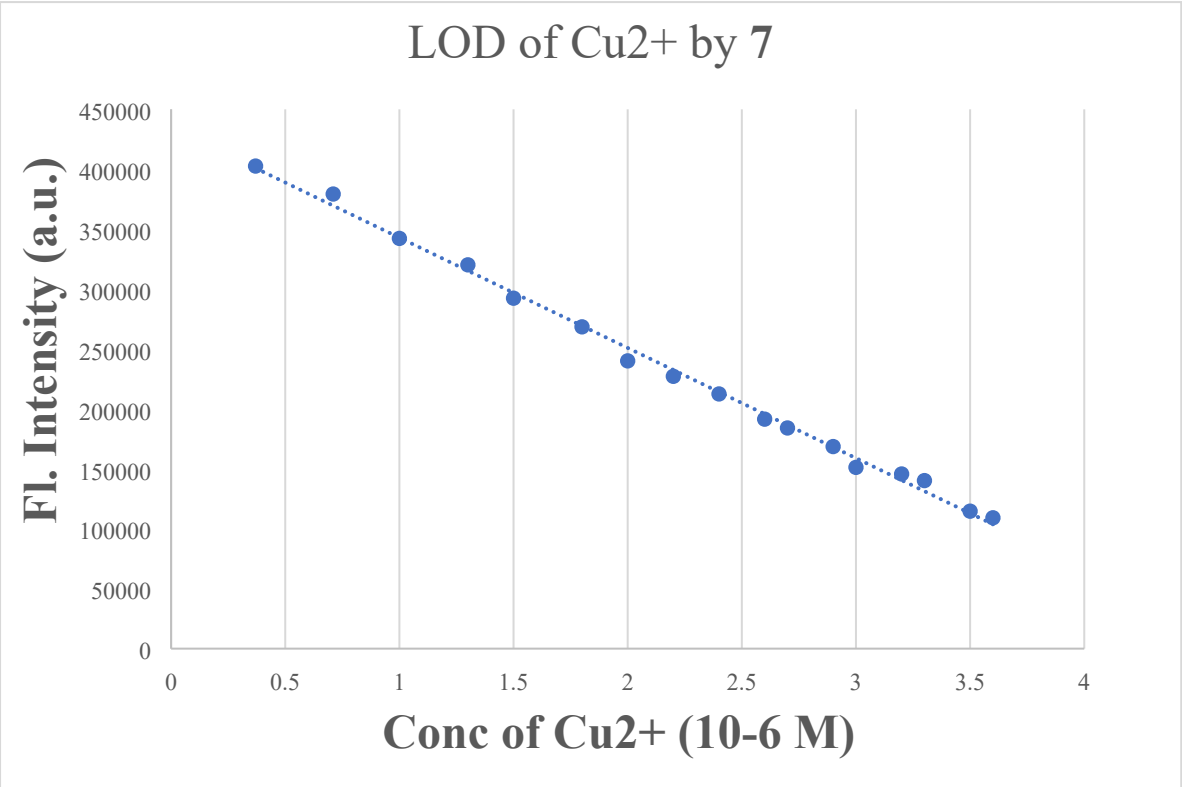


Fig. S23 Limit of detection (LOD) of compound **7** in presence of Cu^{2+} ion from fluorescence spectra by 3σ/s method.

Conc of Cu^{2+}	Fl.intensity
0.37	402654
0.71	379315
1	342297
1.3	320226
1.5	292405
1.8	268494
2	240101
2.2	227226
2.4	212512
2.6	191477
2.7	184119
2.9	168602
3	151245
3.2	145727
3.3	140209
3.5	114691
3.6	109173

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.9981031
R Square	0.9962097
Adjusted R Squ	0.9959571
Standard Error	5845.8903
Observations	17

ANOVA

	df	*SS*	*MS*	*F*	*ignificance F*
Regression	1	1.35E+11	1.35E+11	3942.516	1.4E-19
Residual	15	5.13E+08	34174434		
Total	16	1.35E+11			

	Coefficients	*andard Err*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*ower 95.0%*	*pper 95.0%*
Intercept	434909.28	3574.913	121.6559	7.03E-24	427289.5	442529	427289.5	442529
X Variable 1	-91990.145	1465.057	-62.7895	1.4E-19	-95112.8	-88867.4	-95112.8	-88867.4

Fig. S24 Excel sheet for **7**+Cu^{2+} LOD calculation.

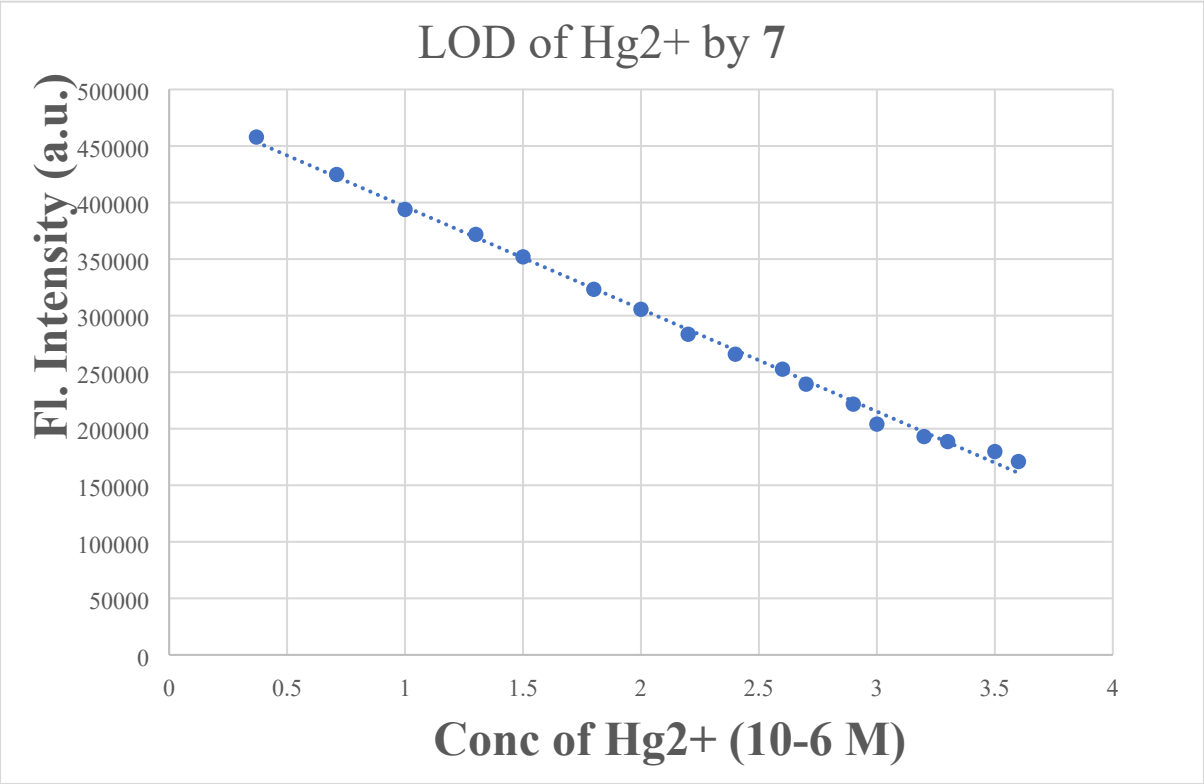


Fig. S25 Limit of detection (LOD) of compound **7** in presence of Hg^{2+} ion from fluorescence spectra by 3σ/s method.

Conc of Hg^{2+}	Fl.intensity
0.37	457894
0.71	424787
1	393887
1.3	371816
1.5	351952
1.8	323259
2	305602
2.2	283531
2.4	265874
2.6	252631
2.7	239388
2.9	221731
3	204074
3.2	193039
3.3	188624
3.5	179796
3.6	170967

SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.9983704
R Square	0.9967435
Adjusted R Squa	0.9965264
Standard Error	5333.8425
Observations	17

ANOVA

	df	*SS*	*MS*	*F*	*ignificance F*
Regression	1	1.31E+11	1.31E+11	4591.216	4.5E-20
Residual	15	4.27E+08	28449876		
Total	16	1.31E+11			

	Coefficients	*andard Err*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*	*ower 95.0%*	*pper 95.0%*
Intercept	486937.95	3261.782	149.2859	3.27E-25	479985.6	493890.3	479985.6	493890.3
X Variable 1	-90574.92	1336.731	-67.7585	4.5E-20	-93424.1	-87725.7	-93424.1	-87725.7

Fig. S26 Excel sheet for **7**+Hg^{2+} LOD calculation.

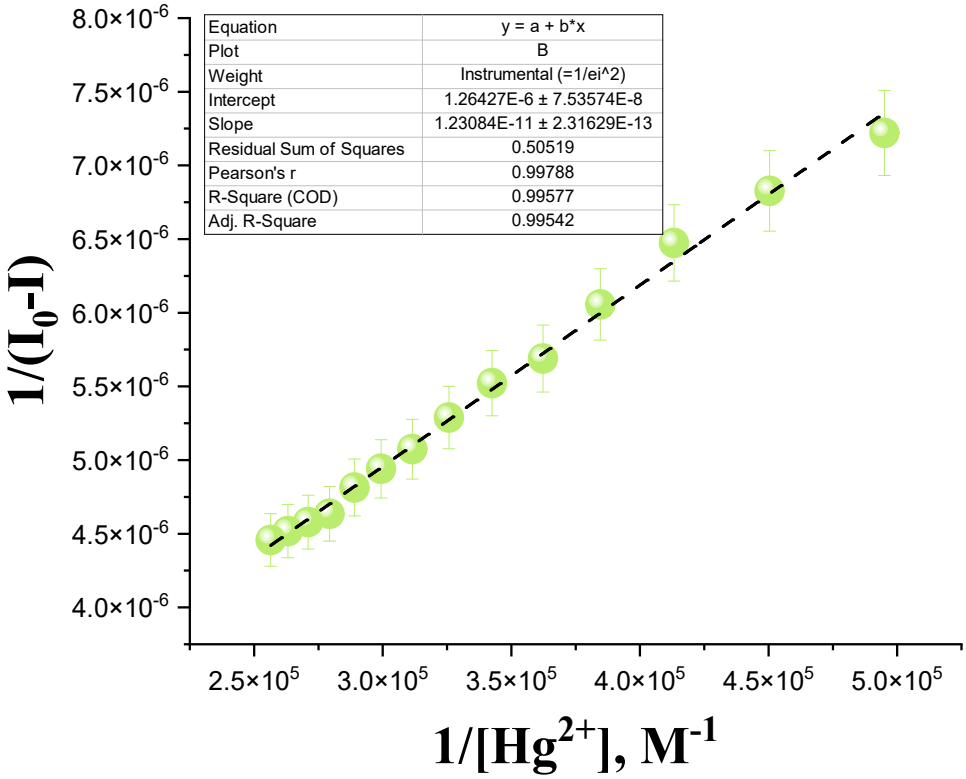


Fig. S27 Association constant of compound **5** with Cu^{2+} ion from Benesi-Hildebrand plot. Error bars represent standard deviation.

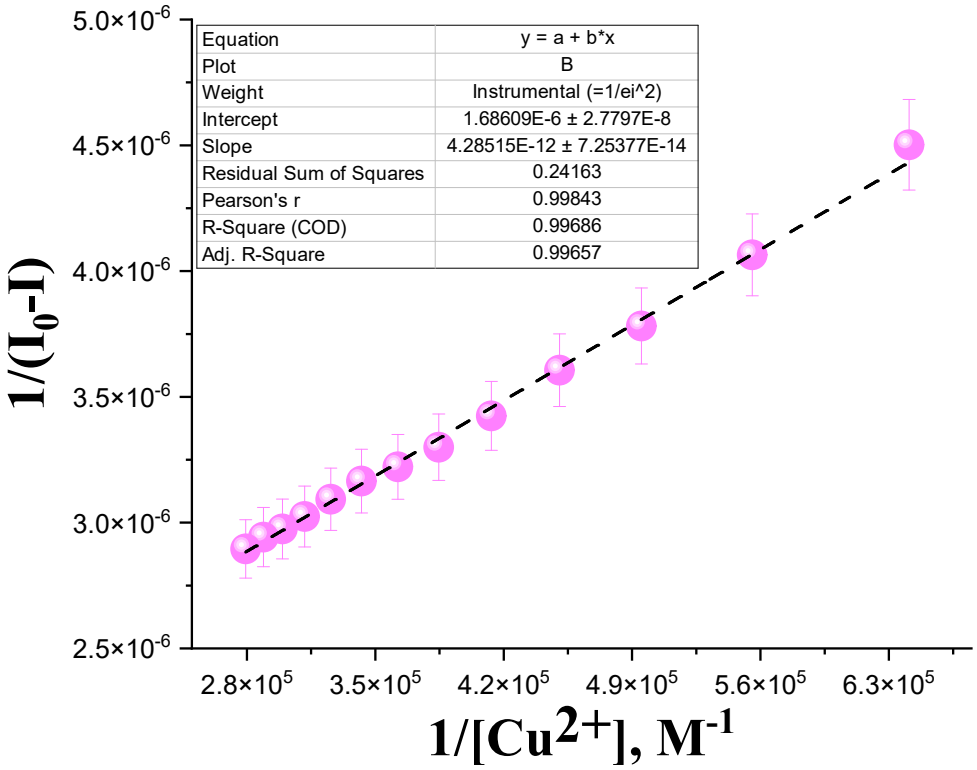


Fig. S28 Association constant of compound **7** with Cu^{2+} ion from Benesi-Hildebrand plot. Error bars represent standard deviation.

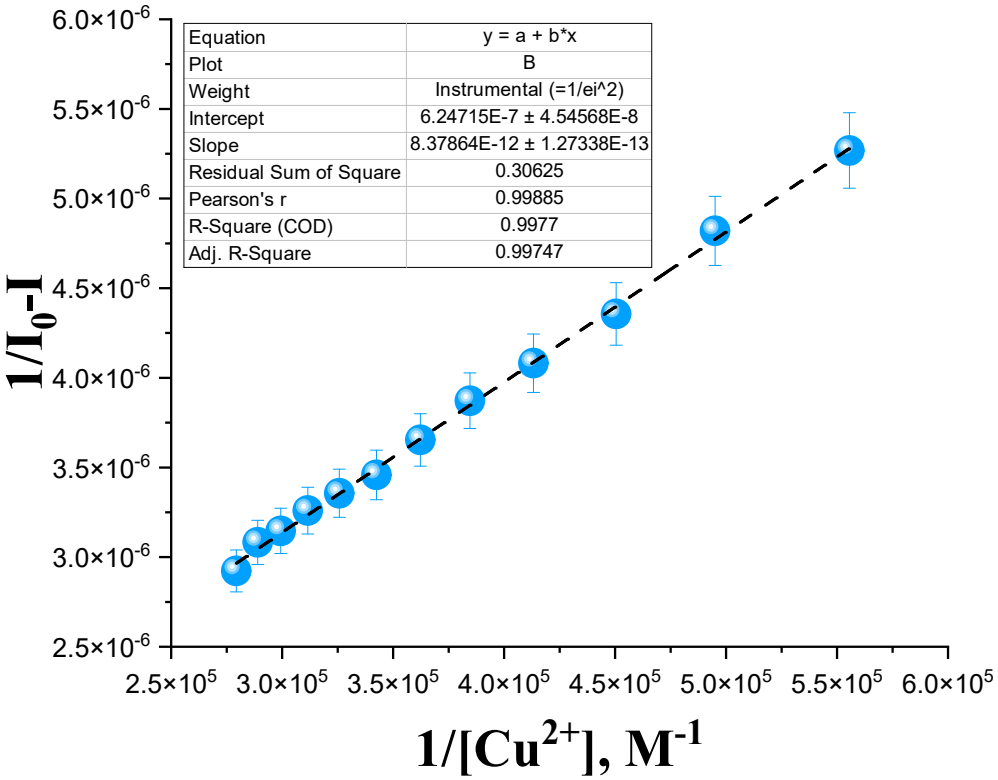


Fig. S29 Association constant of compound **7** with Hg^{2+} ion from Benesi-Hildebrand plot. Error bars represent standard deviation.

Table S2. Comparison table for LOD and association constant.

Entry	Ligand molecular formula	Solvent	LOD	Association Constant	Method of detection	Ref
1	$C_{31}H_{37}N_5O_3$	HEPES buffer (pH 7.5)	(a) 3.5×10^{-6} M for Cu^{2+} (b) 6.11×10^{-8} M for Hg^{2+}	(a) 3.51×10^{6} M^{-1} for Cu^{2+} (b) 6.06×10^{6} M^{-1} for Hg^{2+}	(a) Turn-Off fluorescence (b) Turn-On fluorescence	1
2	$C_{15}H_{12}N_6O$	CH_3OH/H_2O (1:1)	(a) 50×10^{-9} M for Cu^{2+} (b) 0.8×10^{-8} M for Hg^{2+}	(a) 1.3×10^{5} M^{-1} for Cu^{2+} (b) 0.05×10^{5} M^{-1} for Hg^{2+}	(a) Turn-On fluorescence (b) Turn-On fluorescence	2
3	$C_{47}H_{48}N_4OS_2$	THF/HEPES buffer (8:2, *v/v*, pH 7.4)	(a) 97×10^{-9} M for Cu^{2+} (b) 80×10^{-8} M for Hg^{2+}	(a) 3.5×10^{6} M^{-1} for Cu^{2+}	(a) Turn-Off fluorescence (b) Turn-Off fluorescence	3
4	$C_{47}H_{48}N_4O$	THF/HEPES buffer (*v/v*, 7:3, pH 7.4)	(a) 2.1×10^{-8} M for Cu^{2+} (b) 1.8×10^{-8} M for Hg^{2+}	(a) 1.6×10^{7} M^{-1} for Cu^{2+}	(a) Ratiometric in fluorescence (b) Ratiometric in fluorescence	4
5	$C_{260}H_{491}N_5O_{117}S$	H_2O	(a) 5.92×10^{-7} M for Cu^{2+} (b) 2.85×10^{-6} M for Hg^{2+}	(a) 5.38×10^{4} M^{-1} for Cu^{2+} (b) 1.63×10^{5} M^{-1} for Hg^{2+}	(a) Turn-On fluorescence (b) Turn-On fluorescence	5
6	$C_{32}H_{33}FeN_3O_2S_2$	CH_3CN/H_2O (7:3, *v/v*)	(a) 6.17×10^{-7} M for Cu^{2+} (b)7.94×10^{-7} M for Hg^{2+}	(a) 9.06×10^{4} M^{-1} for Cu^{2+} (b) 3.01×10^{4} M^{-1} for Hg^{2+}	(a) Turn-On fluorescence (b) Turn-Off fluorescence	6
7	$C_{24}H_{22}N_2O_5S$	HEPES buffer	(a) 2.02×10^{-6} M for Cu^{2+} (b) 1.24×10^{-6} M for Hg^{2+}	(a) 2.4×10^{5} M^{-1} for Cu^{2+} (b) 7.46×10^{5} M^{-1} for Hg^{2+}	(a) Turn-Off fluorescence (b) Turn-Off fluorescence	7

8	$C_{23}H_{20}N_2O$	CH_3CN/H_2O	(a) 7.74×10^{-6} M for Cu^{2+} (b) 7.67×10^{-6} M for Hg^{2+}	(a) log β=5.23 M^{-1} for Cu^{2+} (b) logβ=5.49 M^{-1} for Hg^{2+}	(a) Turn-Off fluorescence (b) Turn-Off fluorescence	8
9	$C_{22}H_{20}FeS$ and $C_{22}H_{20}FeO_2S$	CH_3CN	(a) 5.22×10^{-7} M for Cu^{2+} (b) 6.93×10^{-7} M for Hg^{2+}	(a) 5.74×10^{4} M^{-1} for Cu^{2+} (b) 5×10^{4} M^{-1} for Hg^{2+}	(a) Absorption increases (b) Absorption increases	9
10	$C_{20}H_{13}NS_3$	THF/H_2O (7:3, *v/v*)	(a) 7.06×10^{-8} M for Cu^{2+} (b) 1.16×10^{-7} M for Hg^{2+}	(a) 9.4×10^{4} M^{-1} for Cu^{2+} (b) 8.69×10^{4} M^{-1} for Hg^{2+}	(a) Turn-Off fluorescence (b)Turn-On fluorescence	10
11	$C_{56}H_{67}N_6O_2$	CH_3CN/H_2O (1:1, *v/v*)	(a) 1.3×10^{-6} M for Cu^{2+} (b) 1.45×10^{-6} M for Hg^{2+}	(a) 3.25×10^{7} M^{-1} for Cu^{2+} (b) 6.88×10^{6} M^{-2} for Hg^{2+}	(a) Turn-Off fluorescence (b) Turn-Off fluorescence	11
12	$C_{21}H_{22}N_3O_2S$	DMSO/H_2O (9:1, *v/v*)	(a) 2.9×10^{-6} M for Cu^{2+} (b) 2×10^{-9} M for Hg^{2+}	(a) 5.69×10^{5} M^{-1} for Cu^{2+} (b) 1.85×10^{4} M^{-2} for Hg^{2+}	(a) Turn-Off fluorescence (b) Turn-Off fluorescence	12
13	$C_{27}H_{21}N_5O_4$ (**5**) & $C_{27}H_{19}N_5O_4$ (**7**)	DMSO/H_2O (7:3, *v/v*)	(a) 5.5×10^{-7} M for (**5**-Cu^{2+}) and 5.2×10^{-7} M for (**7**-Cu^{2+}) (b) 4.4×10^{-7} M for (**7**-Hg^{2+})	(a) 1.02×10^{5} M^{-1} (**5**-Cu^{2+}) and 3.9×10^{5} M^{-1} (**7**-Cu^{2+}) (b) 7.4×10^{4} M^{-1} (**7**-Hg^{2+})	(a) Turn-Off fluorescence (b) Turn-Off fluorescence	This work

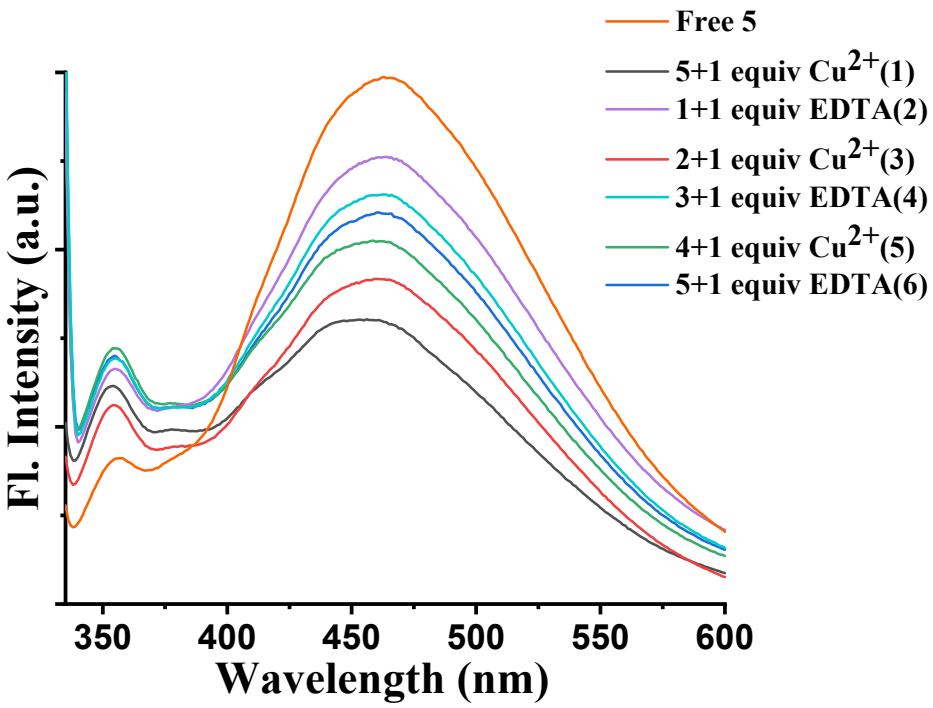


Fig. S30 Reversibility test of compound **5** (7.8×10^{-6} M) with Cu^{2+} ion in presence of EDTA in DMSO:H_2O (7:3, v/v) solvent at 22 ˚C.

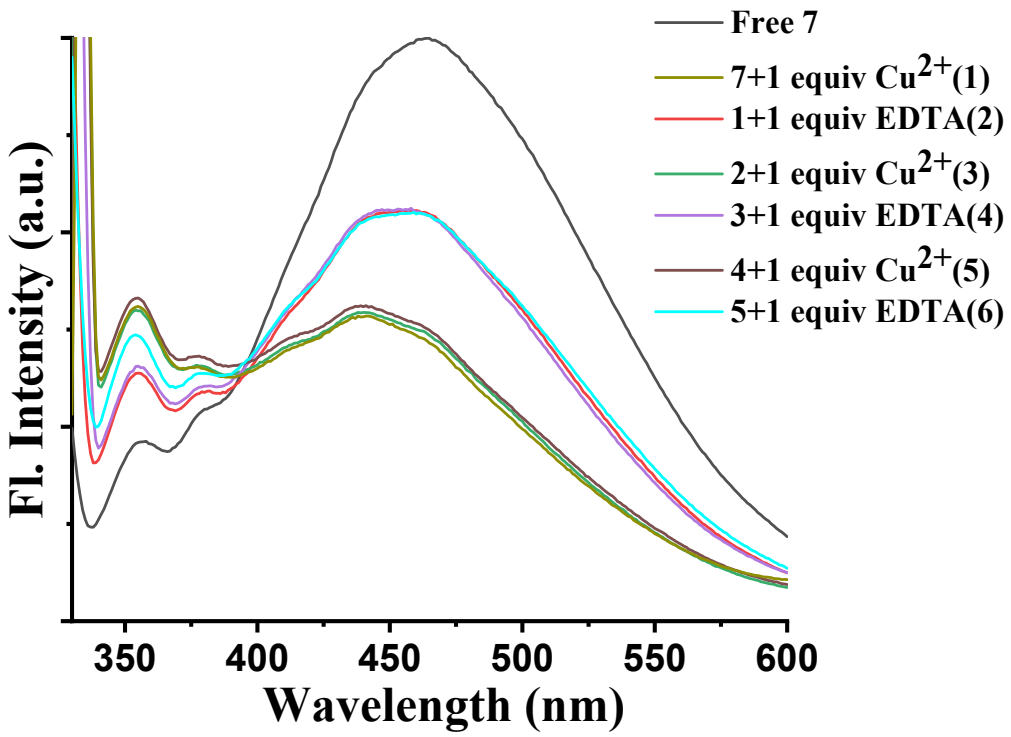


Fig. S31 Reversibility test of compound **7** (7.8×10^{-6} M) with Cu^{2+} ion in presence of EDTA in DMSO:H_2O (7:3, v/v) solvent at 22 ˚C.

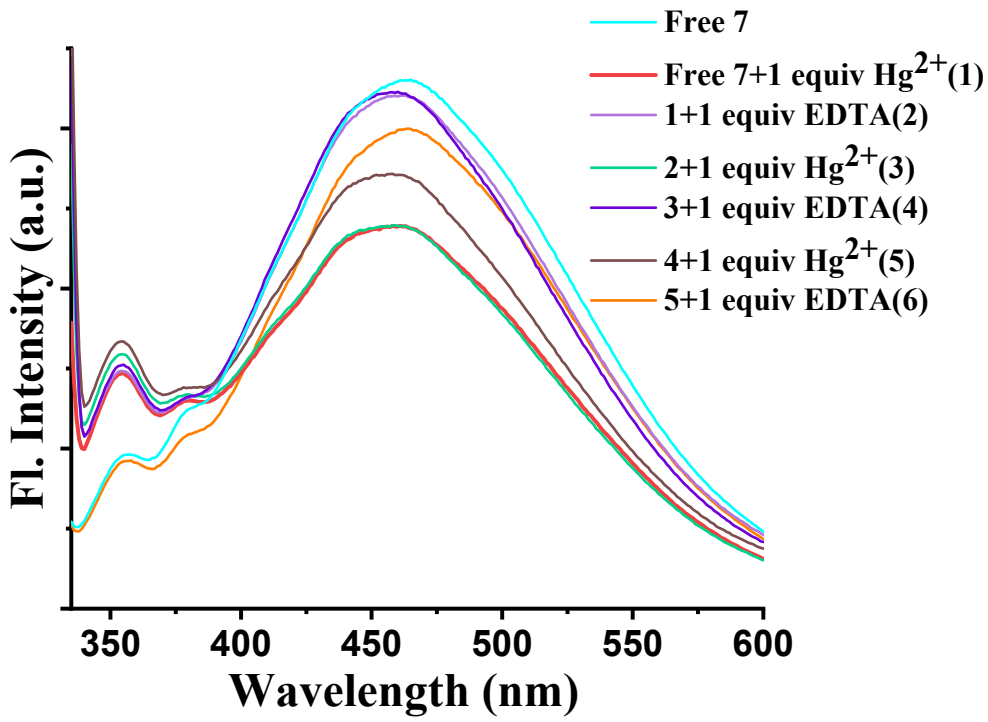


Fig. S32 Reversibility test of compound **7** (7.8×10^{-6} M) with Hg^{2+} ion in presence of EDTA in DMSO:H_2O (7:3, v/v) solvent at 22 ˚C.

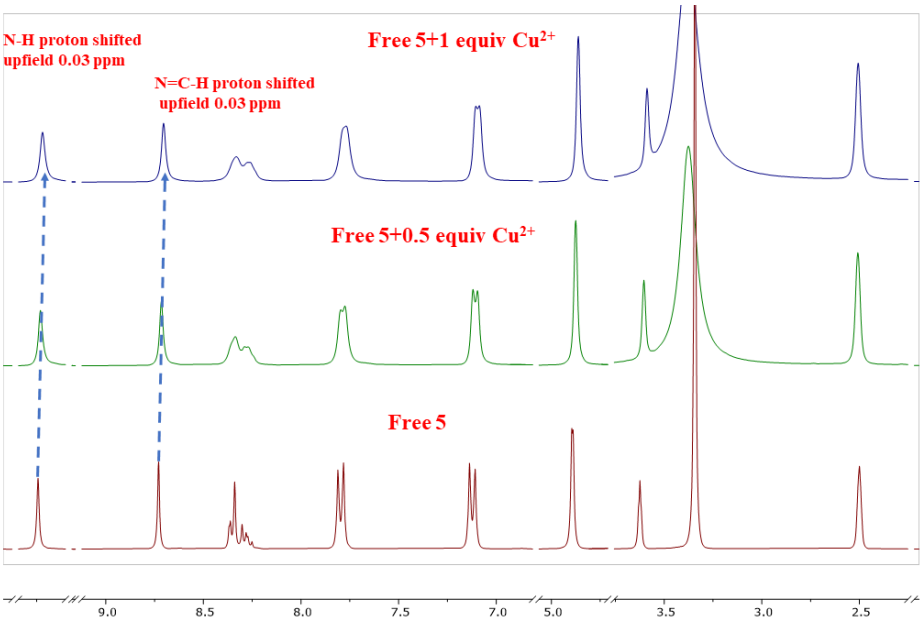


Fig. S33 ^{1}H NMR titration of ligand **5** with addition of up to 1 equiv of Cu^{2+} ion in DMSO-d_6.

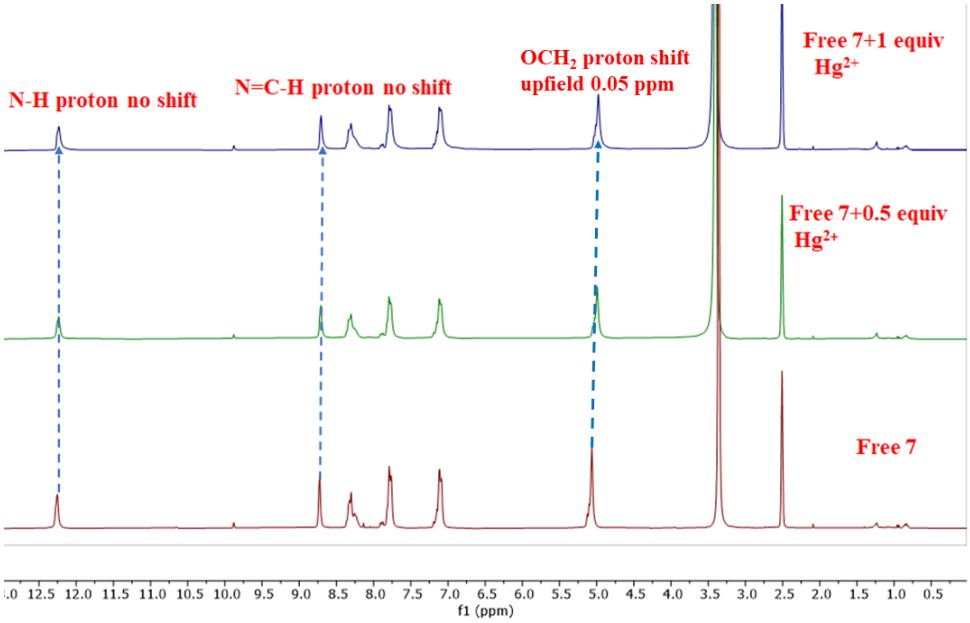
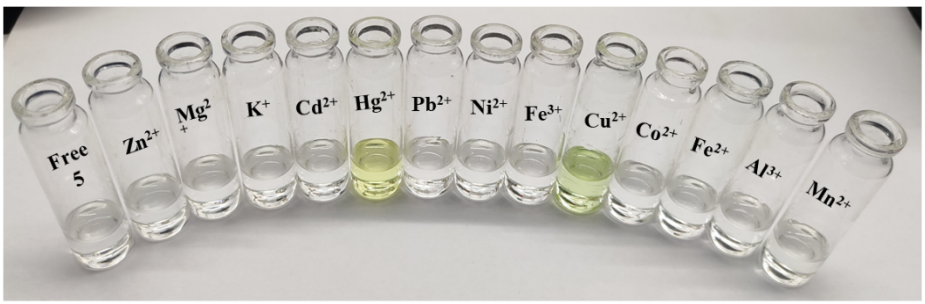


Fig. S34 ^{1}H NMR titration of ligand **7** with addition of up to 1 equiv of Hg^{2+} ion in DMSO-d_6 medium.

(a)



(b)

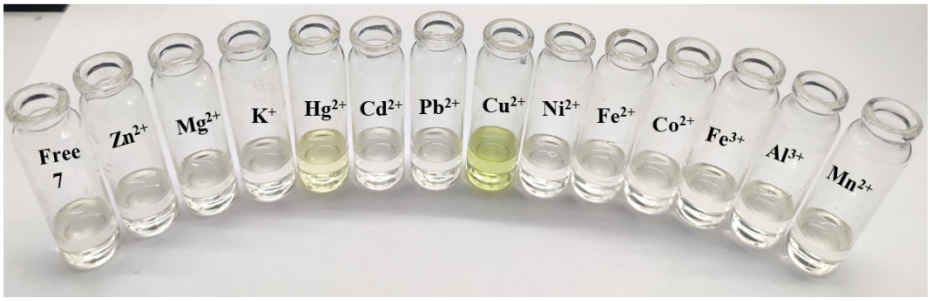


Fig. S35 Naked eye detection of Hg^{2+} and Cu^{2+} among all other metal ions (1×10^{-5} M) by compounds (a) **5** and (b) **7** (1×10^{-3} M) in DMSO solvent.

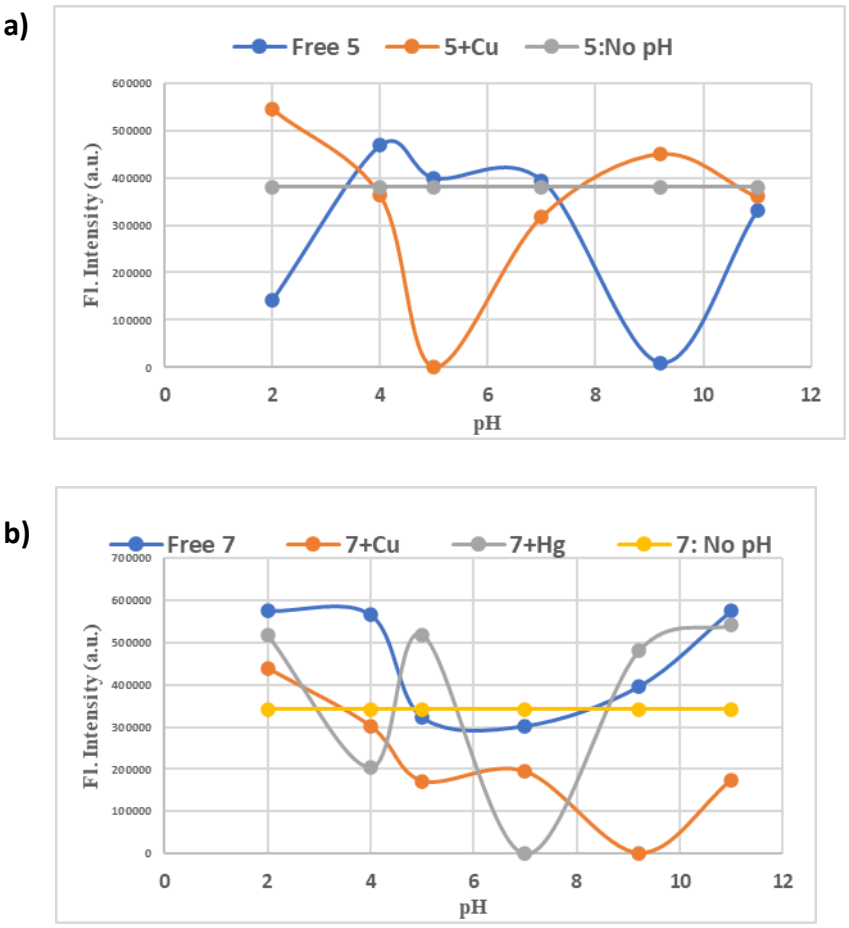


Fig. S36 Variation of fluorescence intensity with pH in (a) Free **5** and **5**+Cu^{2+}, (b) Free **7**, **7**+Cu^{2+} and **7**+Hg^{2+} in DMSO solvent at 22 ˚C.

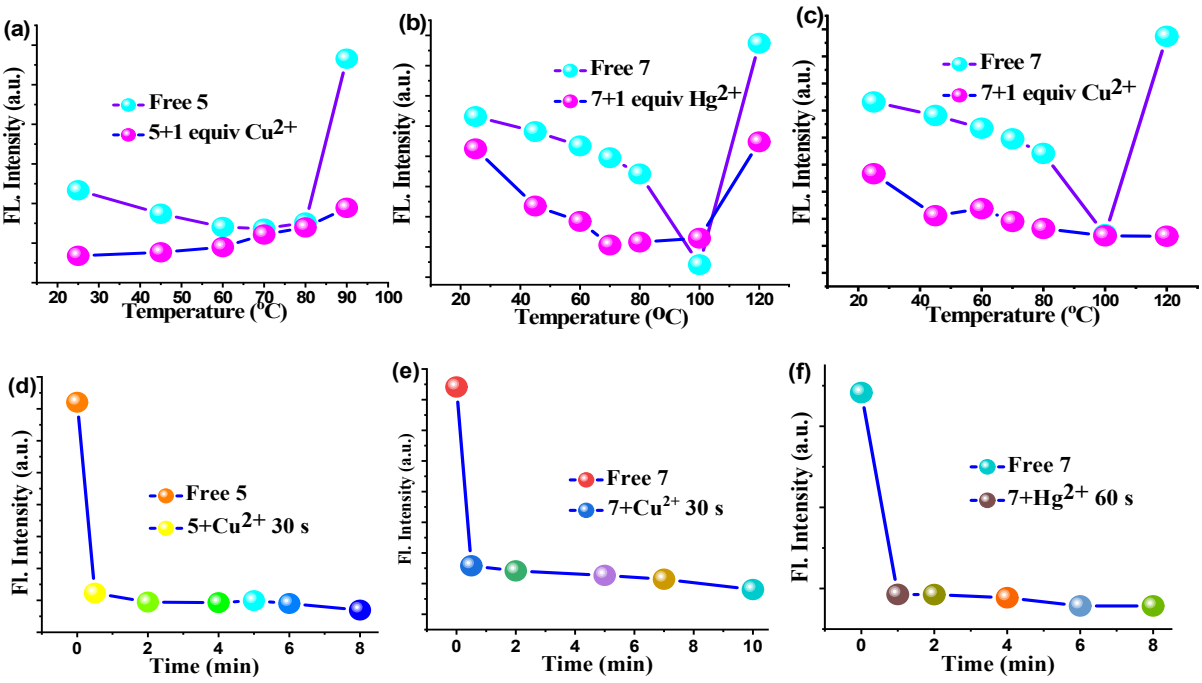


Fig. S37 Variation of fluorescence intensity with temperature in (a) Free **5** and **5**+Cu^{2+}, (b) Free **7** and **7**+Hg^{2+} in DMSO solvent at 22 ˚C and (c) Free **7** and **7**+Cu^{2+} and variation of fluorescence intensity with response time of (d) **5** for Cu^{2+}, (e) **7** for Cu^{2+} and (f) **7** for Hg^{2+} in DMSO solvent at 22 ˚C.

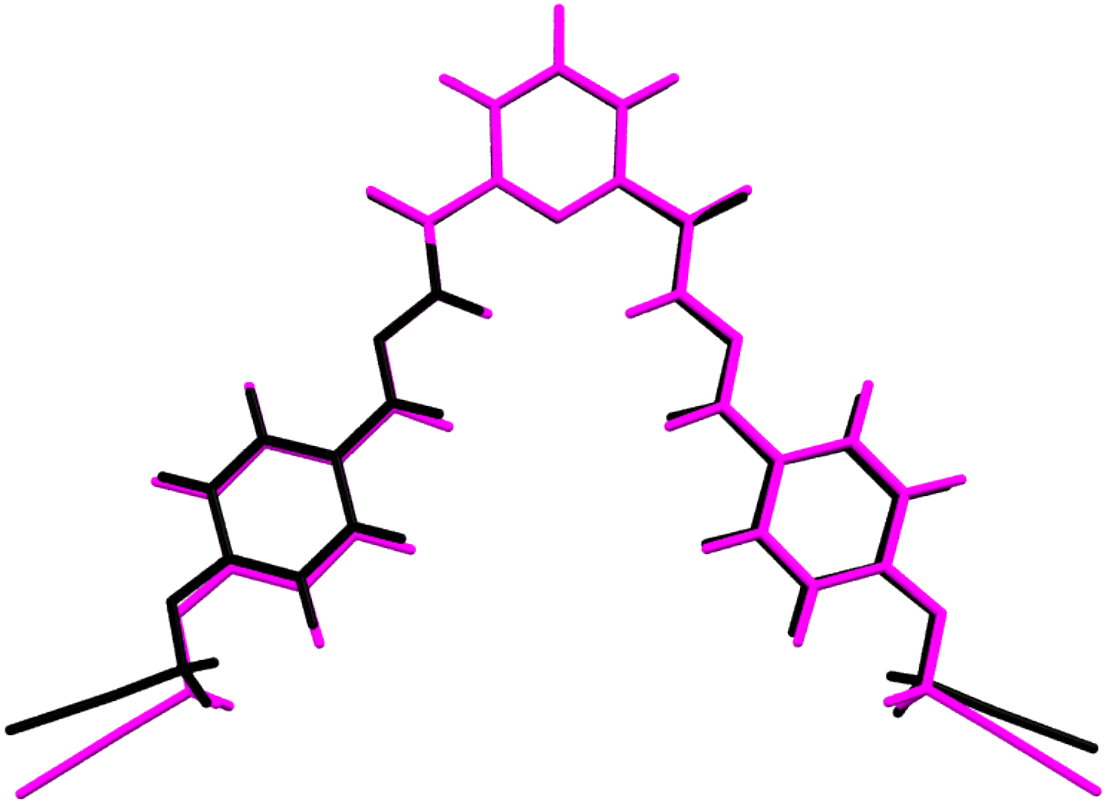
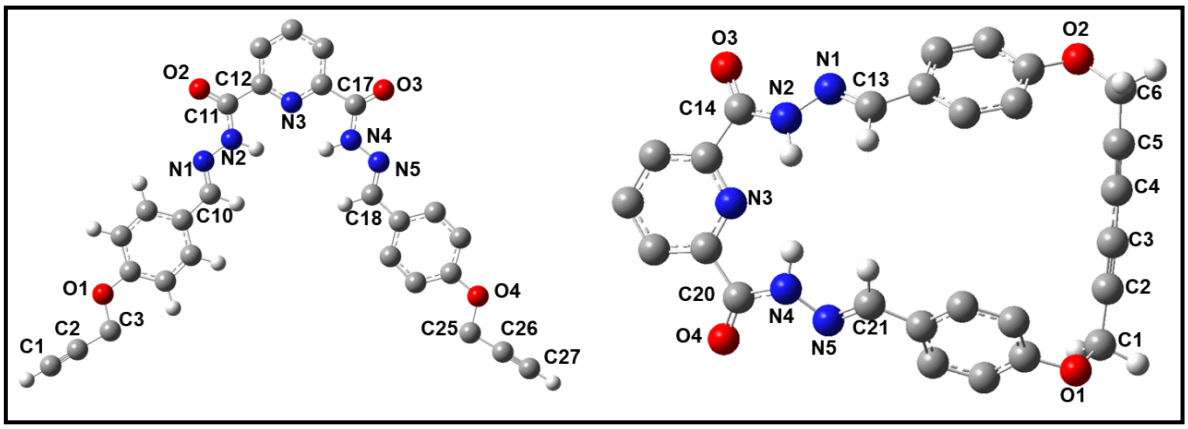


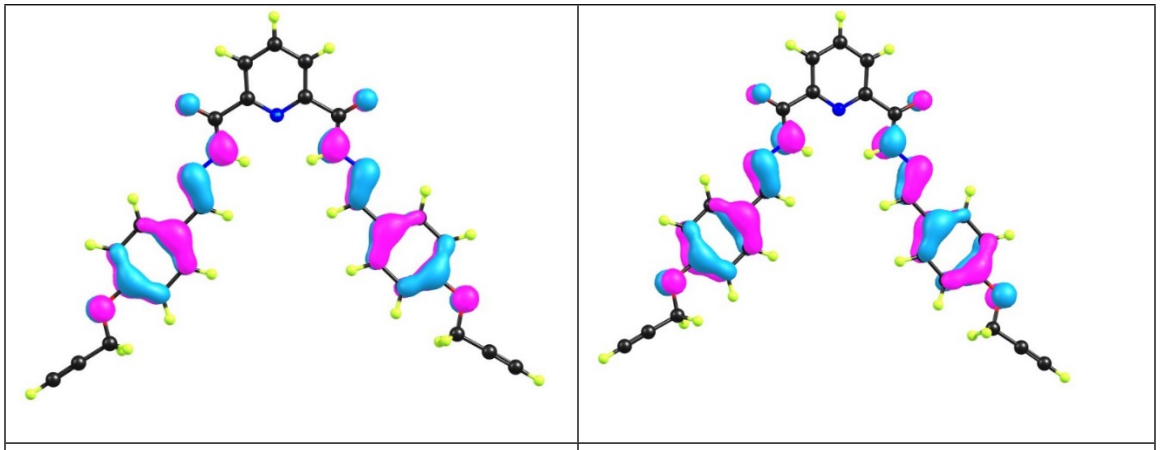
Fig. S38 Overlay of X-ray crystal structure and DFT optimized structure of receptor **5**. (Crystal structure obtained from XRD is shown in black color, and DFT optimized structure is shown in magenta color.

Table S3. The selected distances (Å) of receptors **5** and **7** calculated at B3LYP/6-311g(d)/cpcm (acetonitrile) level (The labeled primary binding core of both receptors **5** (left) and **7** (right) are shown above the table).

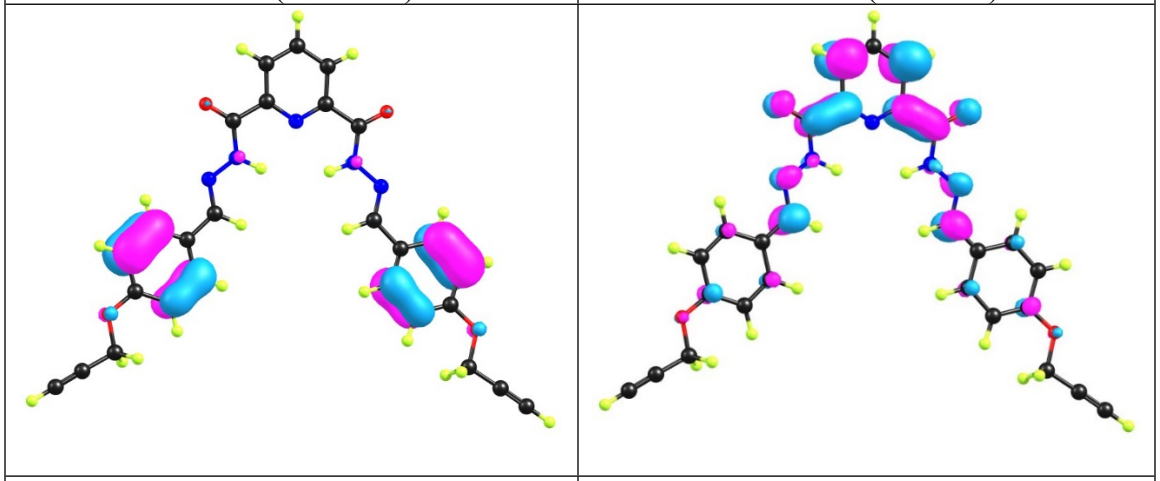


Receptor [5]	contact	Distance (Å)
	C1-C2	1.20120
	C2-C3	1.45721
	C3-O1	1.43501
	C10-N1	1.28331
	N1-N2	1.36129
	N2-C11	1.36383
	C12-N3	1.33802
	C11-O2	1.22191
	C17-N4	1.36383
	C17-O3	1.22191
	N4-N5	1.36129
	N5-C18	1.28331
	O4-C25	1.43501
	C25-C26	1.45721
	C26-C27	1.20120
	N2-N4	**4.58178**
	N2H-N4H	**2.68537**
	N2-N3	**2.70241**
	N3-N4	**2.70241**
	N1-N5	**6.72499**
	C10-C18	**6.21463**
	C10H-C18H	**4.15275**

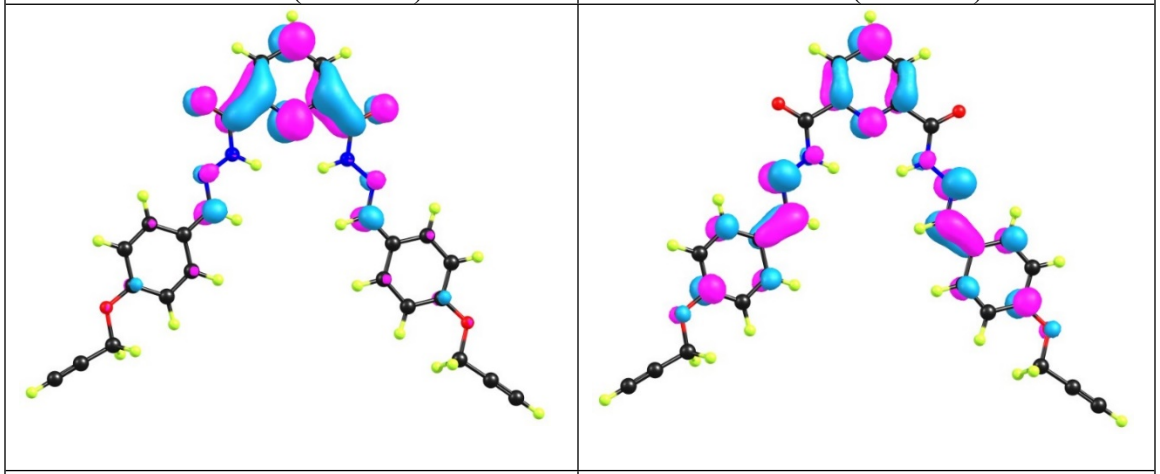
Receptor [7]	contact	Distance (Å)
	O1-C1	1.44165
	C1-C2	1.46116
	C2-C3	1.21151
	C3-C4	1.36336
	C4-C5	1.21123
	C5-C6	1.46086
	C6-O2	1.43574
	C13-N1	1.28535
	N1-N2	1.37255
	N2-C14	1.36563
	C14-O3	1.22013
	C20-N4	1.36600
	C20-O4	1.21987
	N4-N5	1.36923
	N5-C21	1.28452
	N2-N4	**4.36916**
	N2H-N4H	**2.47027**
	N2-N3	**2.64242**
	N3-N4	**2.63921**
	N1-N5	**5.93003**
	C21-C13	**5.05133**
	C10H-C18H	**3.31883**



HOMO (**- 6.07 eV**) | HOMO-1 (**-6.08 eV**)



HOMO-2 (**-7.39** eV) | LUMO (**-2.16** eV)



LUMO+1 (**-2.12** eV) | LUMO+2 (**-1.39** eV)

Fig. S39 Frontiers MOs of the acyclic receptor **5** with corresponding energy values in parenthesis. (isosurface value= 0.04)

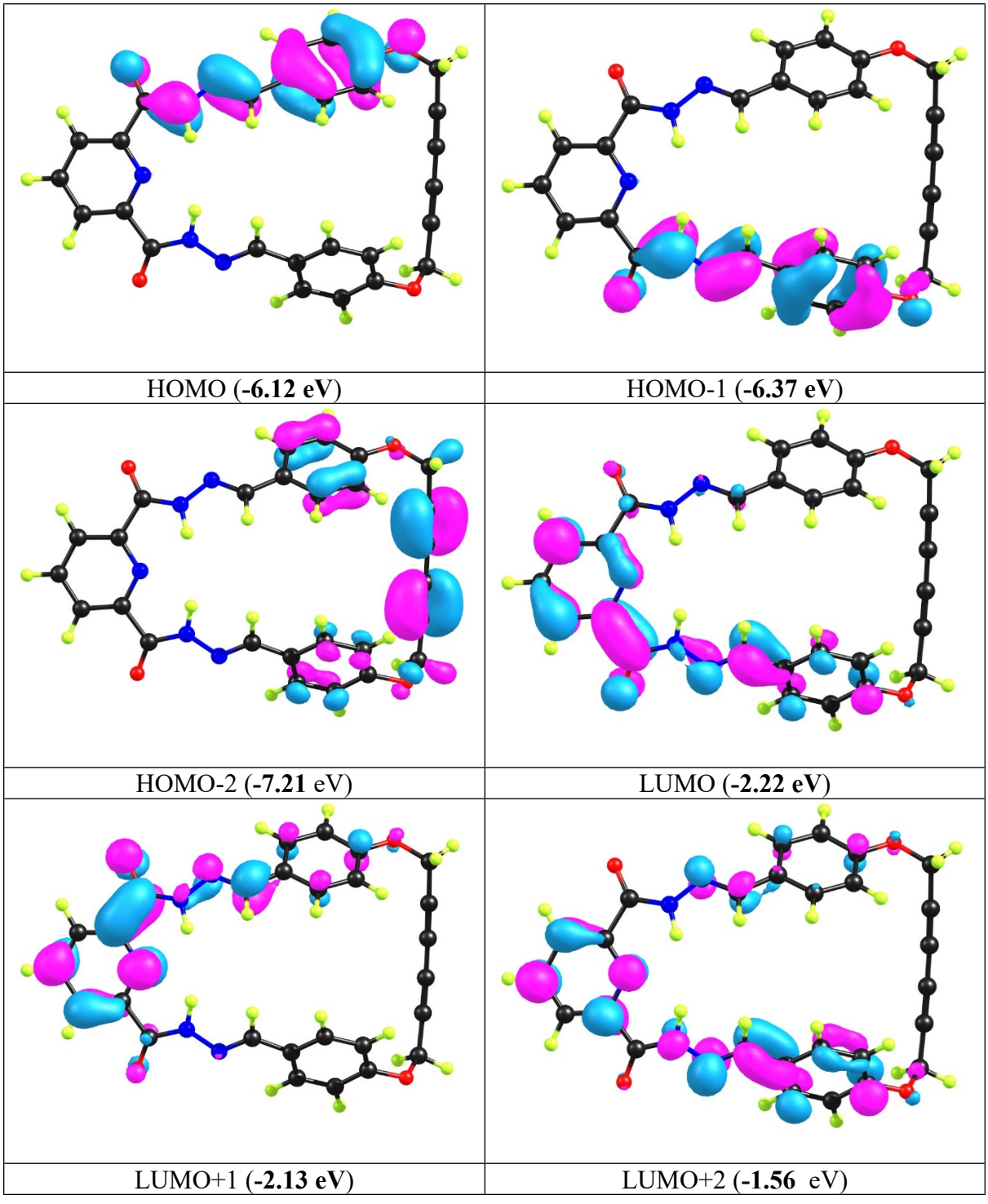
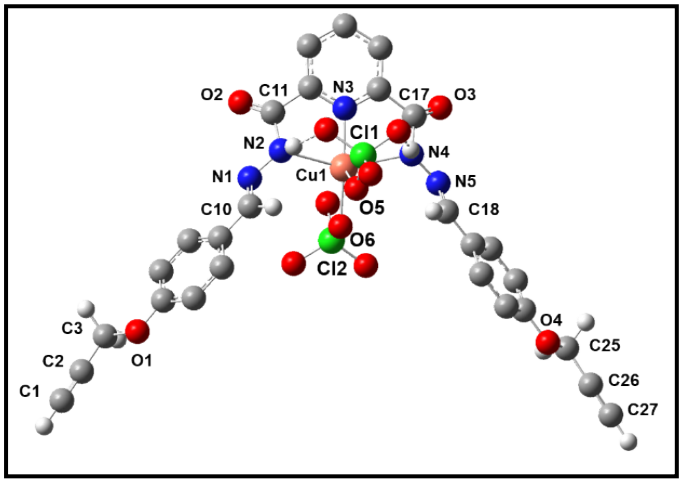


Fig. S40 Frontiers MOs of the cyclic receptor **7** with corresponding energy values in parenthesis. (isosurface value = 0.04).

Table S4. The selected distances (Å) of complex [**5**·$Cu(ClO_4)_2$] calculated at B3LYP/6-311g(d)/lanl2dz(Cu)/cpcm(acetonitrile) level (The labeled primary binding core of complex [**5**·$Cu(ClO_4)_2$] is shown at the left side of the table).



Complex [5.1Cu^{2+}·$(ClO_4)_2$]	contact	Distance (Å)
	C1-C2	1.20100
	C2-C3	1.45611
	C3-O1	1.43968
	C10-N1	1.28805
	N1-N2	1.38611
	N2-C11	1.43524
	C11-O2	1.19948
	C17-N4	1.43518
	C17-O3	1.19949
	N4-N5	1.38611
	N5-C18	1.28804
	O4-C25	1.43967
	C25-C26	1.45611
	C26-C27	1.20100
	N2-Cu1	2.29963
	N3-Cu1	1.98024
	N4-Cu1	2.30009
	O5-Cu1	2.36077
	O6-Cu1	1.97125

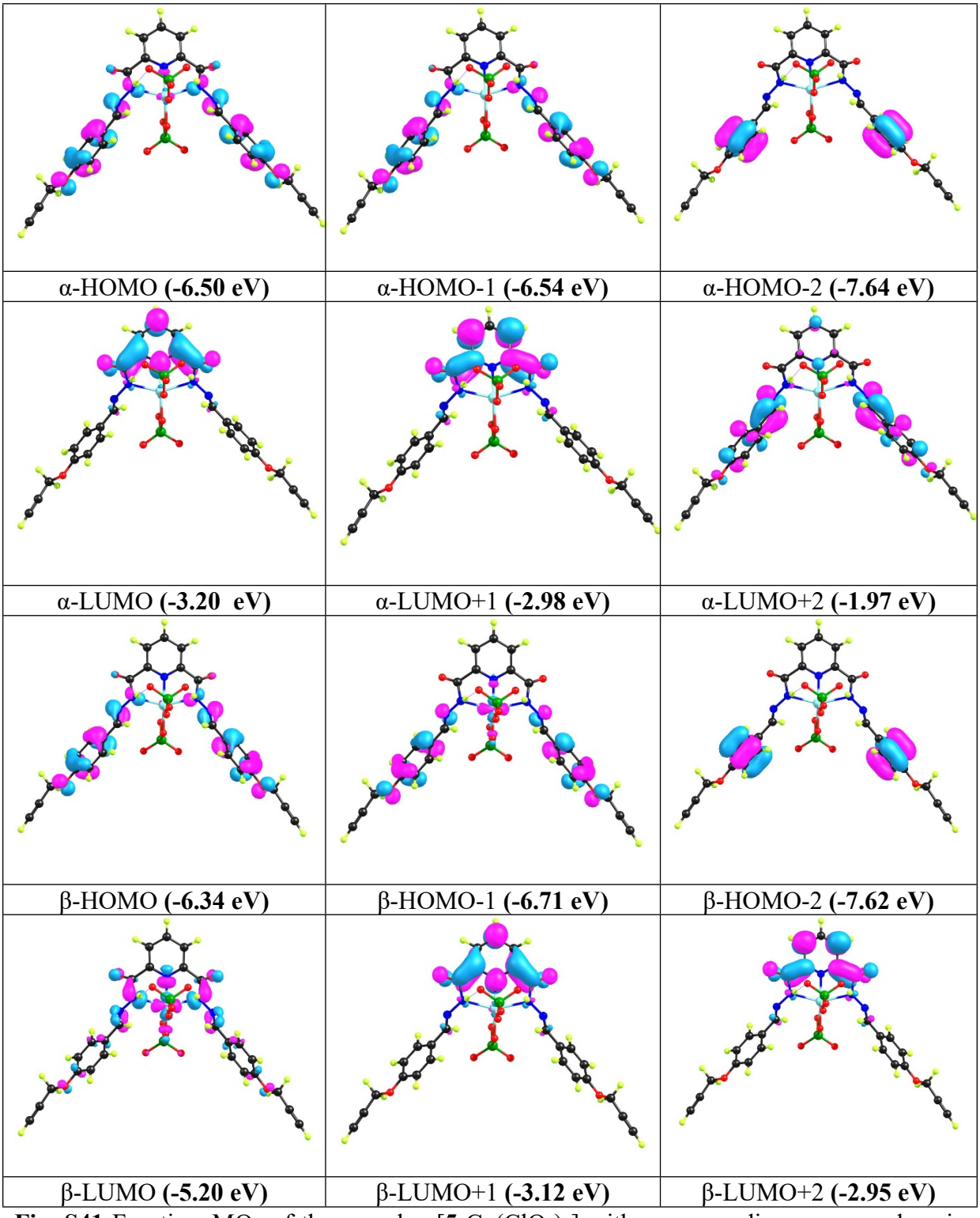
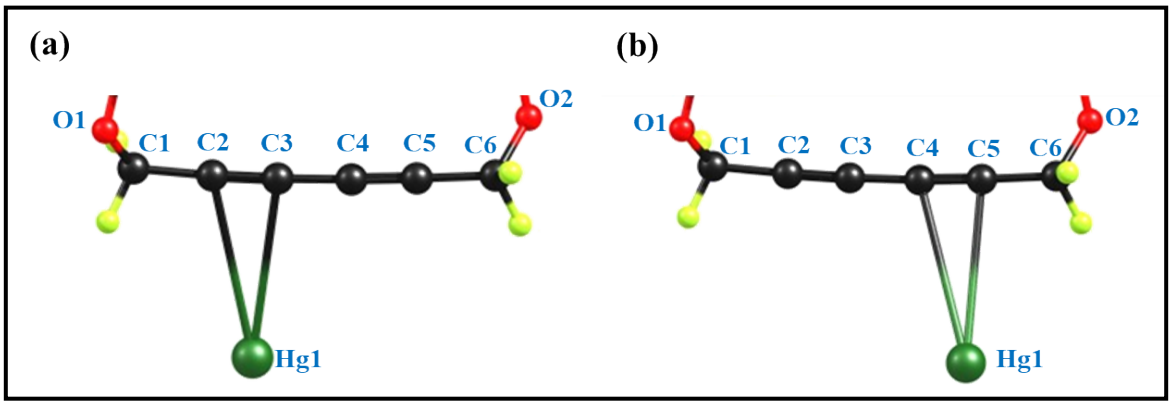


Fig. S41 Frontiers MOs of the complex [**5**·$Cu(ClO_4)_2$] with corresponding energy values in parenthesis. (isosurface value= 0.04).

Table S5 The selected distances (Å) of complexes [**7**·Hg^{2+}] (left sided alkyne unit) and [**7**·Hg^{2+}] (left sided alkyne unit) calculated at B3LYP/6-311g(d)/lanl2dz(Hg)/cpcm (acetonitrile) level (The zoomed portions of the primary binding core of [**7**·Hg^{2+}] (left) and [**7**·Hg^{2+}] (right) with atom labeling are shown above the table).



Receptor [**7**·Hg^{2+}]		
contact	**Left side alkyne unit**	**Right side alkyne unit**
	distance(Å)	**distance(Å)**
C1-O1	1.43988	1.44038
C1-C2	1.46266	1.46169
C2-C3	1.21292	1.21154
C3-C4	1.36375	1.36346
C4-C5	1.21126	1.21245
C5-C6	1.46148	1.46242
C6-O2	1.43431	1.43355
C2-Hg1	3.67708	------
C3-Hg1	3.60429	------
C4-Hg1	------	3.73262
C5-Hg1	------	3.61795

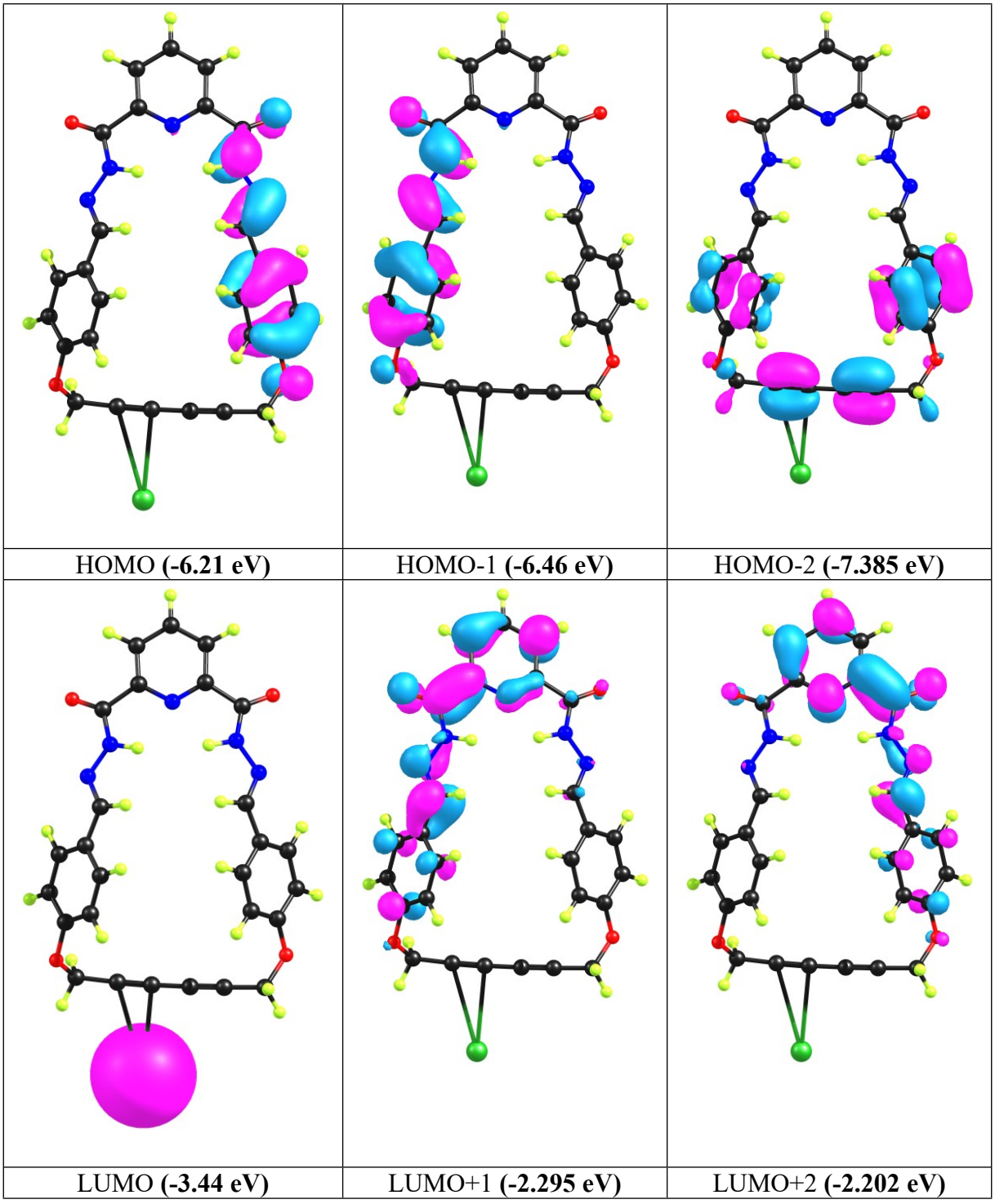


Fig. S42 Frontiers MOs of the complex [**7**·Hg^{2+}] (left sided alkyne unit) with corresponding energy values in parenthesis (isosurface value= 0.04)

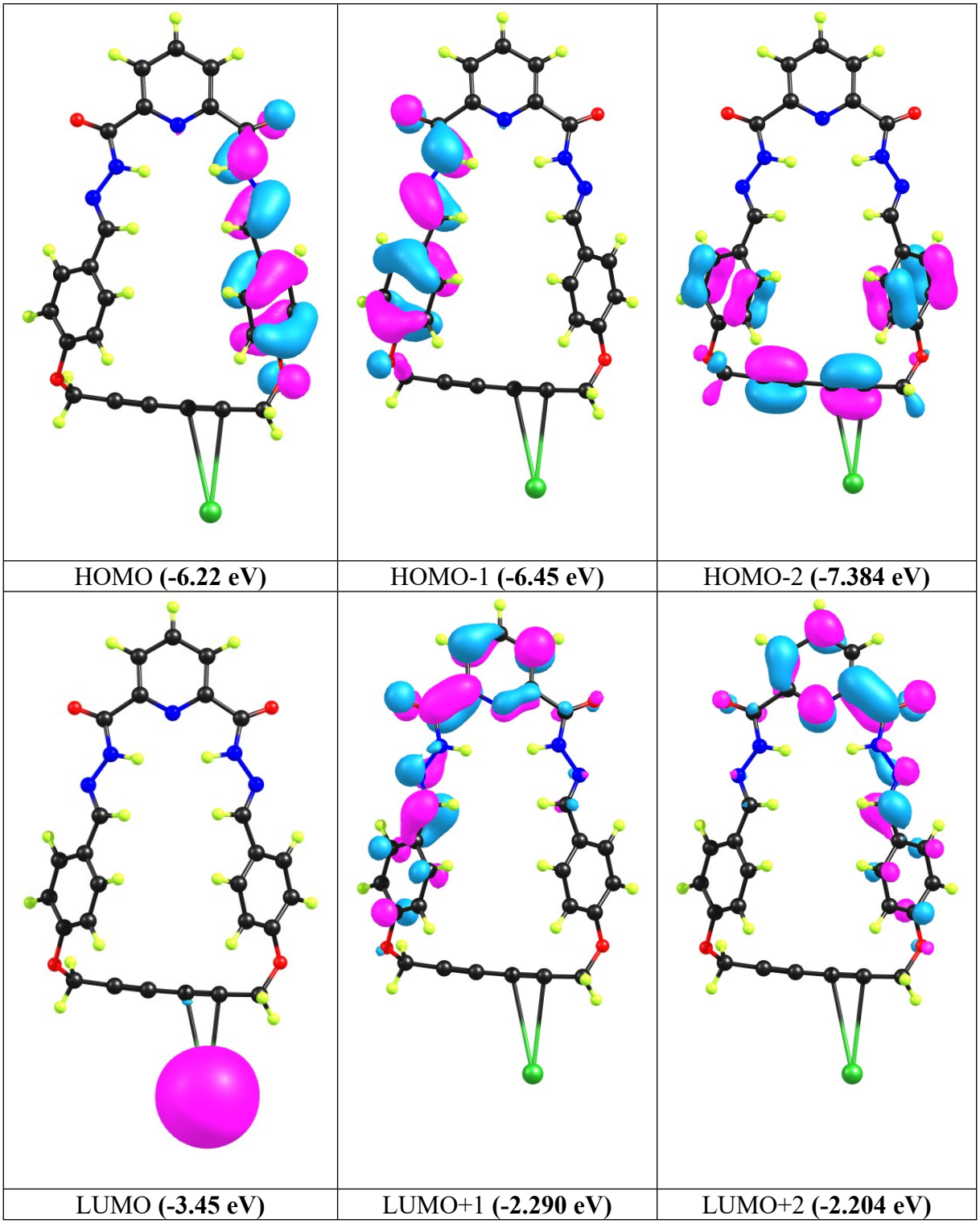


Fig. S43 Frontiers MOs of the complex [**7**·Hg^{2+}] (right sided alkyne unit) with corresponding energy values in parenthesis (isosurface value= 0.04)

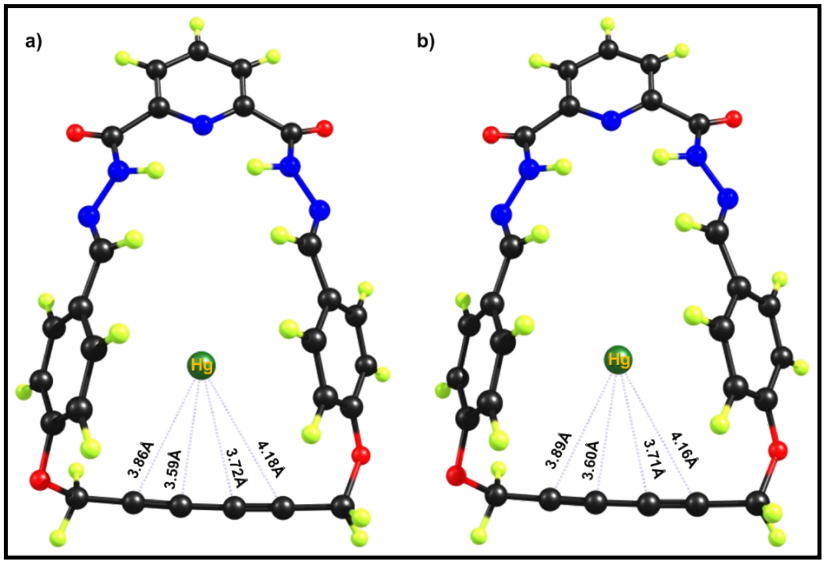


Fig. S44 Optimized structure of the complexes considering endocyclic binding mode: **a**) [7·Hg^{2+}] (left sided alkyne unit), and **b**) [7·Hg^{2+}] (right sided alkyne unit).

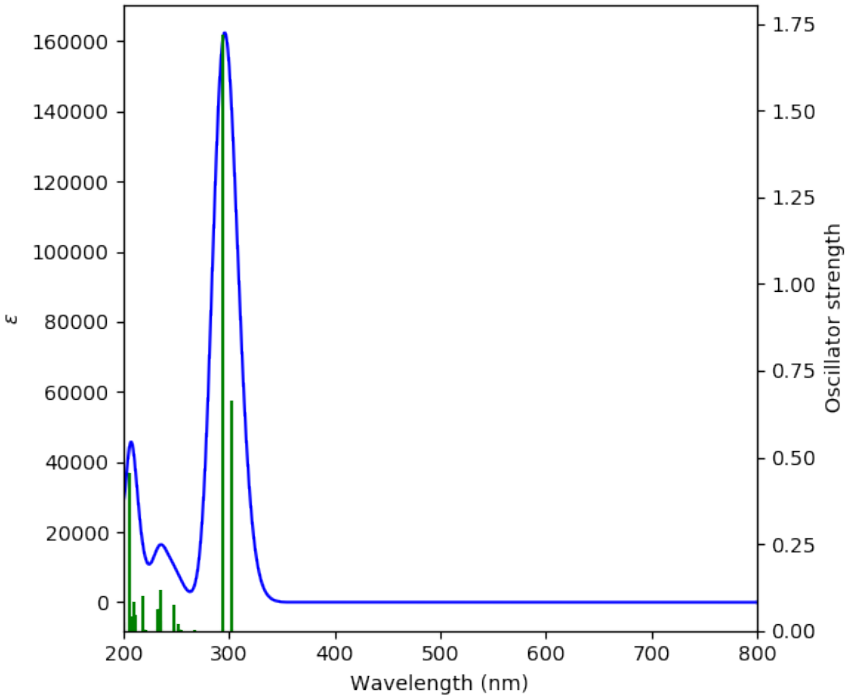


Fig. S45 Calculated absorption spectrum of the acyclic receptor **5**

Table S6 Major excited state transitions of the acyclic receptor **5** with Osc. Strength and λ_{ex}.

λ_{ex} (nm) (Exp.)[a]	λ_{ex} (nm) (Calc.)[b]	Oscillator Strength (f)	Major Transitions[c]
321	293.7	1.7195	H-1 → L+1 (35%), H → L (45%)
263	235.6	0.1162	H-1→ L (12%), H-1 → L+3 (31%), H → L+2 (36%)
[a]Experimental wavelength in DMSO. [b]TD-DFT calculated wavelength of acyclic receptor **5** in DMSO. [c]Transitions with greater than 10% contribution are represented.			

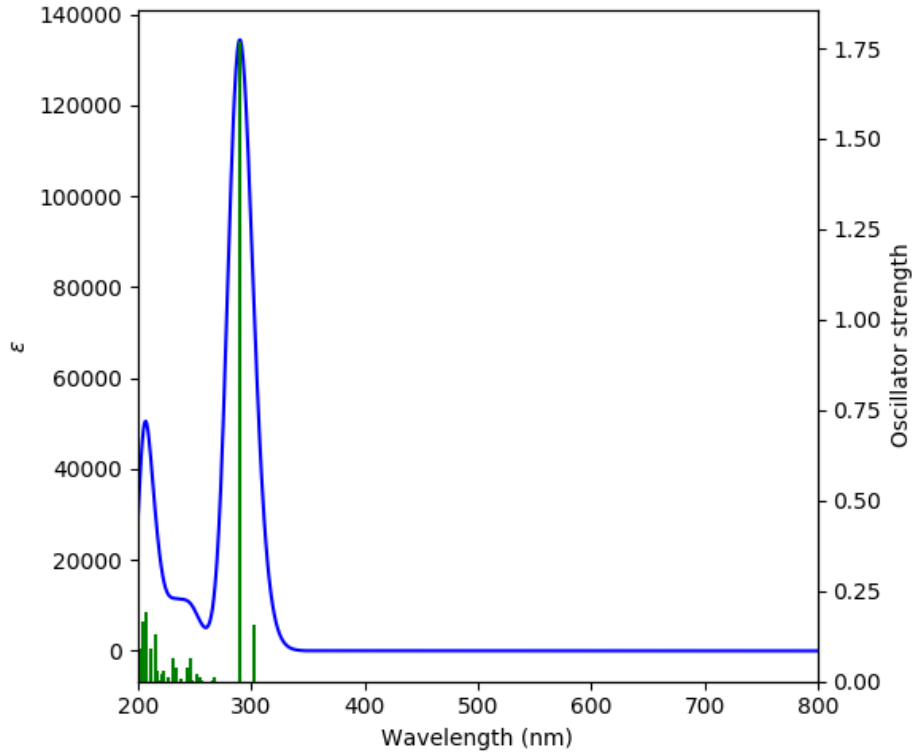


Fig. S46 Calculated absorption spectrum of the cyclic receptor **7.**

Table S7 Major excited state transitions of the cyclic receptor **7** with Osc. Strength and λ_{ex}.

λ_{ex} (nm) (Exp.)[a]	λ_{ex} (nm) (Calc.)[b]	Oscillator Strength (f)	Major Transitions[c]
321	289.4	1.769	H-1 → L (53%), H-1 → L+1 (9%), H → L+1 (17%)
[a]Experimental wavelength in DMSO. [b]TD-DFT calculated wavelength of cyclic receptor **7** in DMSO. [c]Transitions with greater than 10% contribution are represented.			

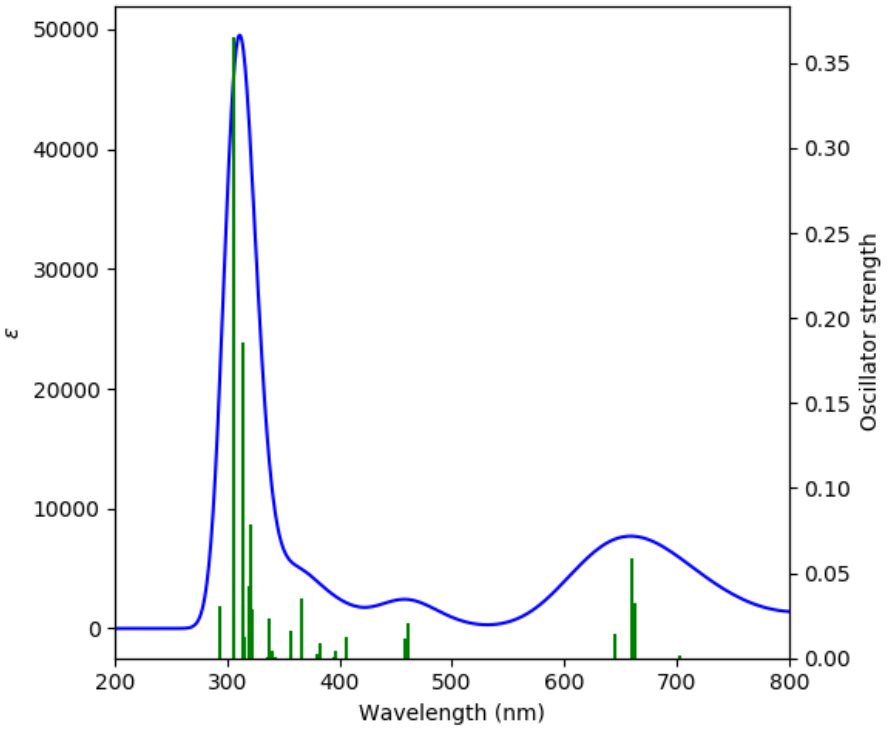


Fig. S47 Calculated absorption spectrum of the complex [**5**·$Cu(ClO_4)_2$]

Table S8 Major excited state transitions of the complex [**5**·$Cu(ClO_4)_2$] with Osc. Strength and λ_{ex}.

λ_{ex} (nm) (Exp.)[a]	λ_{ex} (nm) (Calc.)[b]	Oscillator Strength (f)	Major Transitions[c]
321	305.9	0.3656	H-1(B)->L+1(B) (23%), HOMO(B)->L+2(B) (42%)
[a]Experimental wavelength in DMSO. [b]TD-DFT calculated wavelength of complex [**5**·$Cu(ClO_4)_2$] in DMSO. [c]Transitions with greater than 10% contribution are represented.			

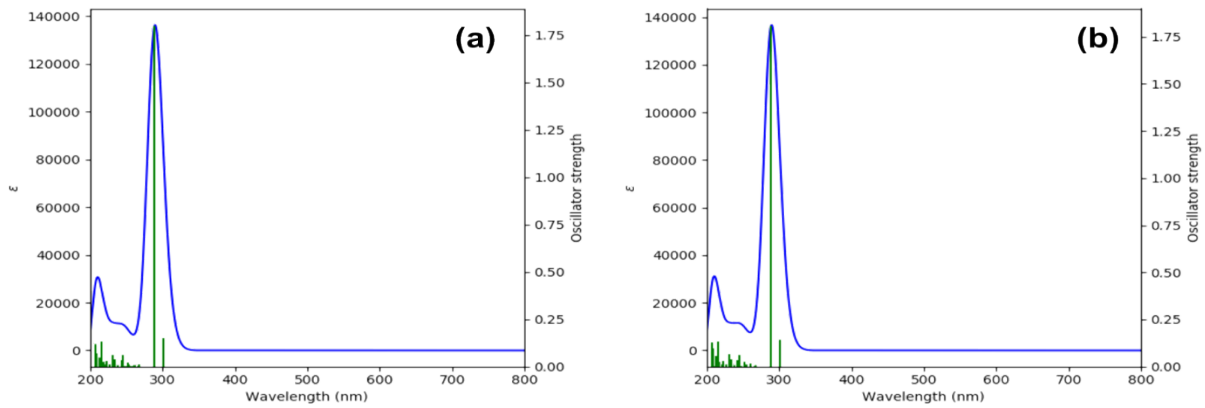


Fig. S48 Calculated absorption spectrum of the complex (a): [**7**·Hg^{2+}] (left side); (b): [**7**·Hg^{2+}] (right side).

Table S9 Major excited state transitions of the complex [**7**·Hg^{2+}] (involving left-sided alkyne as a binding unit) with Osc. Strength and λ_{ex}.

λ_{ex} (nm) (Exp.)[a]	λ_{ex} (nm) (Calc.)[b]	Oscillator Strength (f)	Major Transitions[c]
321	289.1	1.7992	H-1->L+1 (53%), HOMO->L+2 (18%)
[a]Experimental wavelength in DMSO. [b]TD-DFT calculated wavelength of complex **7**·Hg^{2+} ***(left)*** in DMSO. [c]Transitions with greater than 10% contribution are represented.			

Table S10 Major excited state transitions of the complex [**7**·Hg^{2+}] (involving right-sided alkyne as a binding unit) with Osc. Strength and λ_{ex}.

λ_{ex} (nm) (Exp.)[a]	λ_{ex} (nm) (Calc.)[b]	Oscillator Strength (f)	Major Transitions[c]
321	289.08	1.8078	H-1->L+1 (51%), HOMO->L+2 (19%)
[a]Experimental wavelength in DMSO. [b]TD-DFT calculated wavelength of complex **7**·Hg^{2+} ***(right)*** in DMSO. [c]Transitions with greater than 10% contribution are represented.			

Table S11 DFT Optimized coordinates of all the compounds

Receptor **5** (Acyclic)					
C	-0.000014000	6.788843000	-0.000029000	H	7.559683000	-0.902606000	0.000564000
H	-0.000017000	7.872722000	-0.000045000	C	6.151638000	-2.523064000	-0.000228000
C	1.197266000	6.082655000	-0.000194000	C	4.802129000	-2.885547000	-0.000739000
H	2.158046000	6.579698000	-0.000353000	H	4.494441000	-3.922954000	-0.001097000
C	1.149371000	4.687792000	-0.000205000	C	3.826519000	-1.889890000	-0.000827000
N	-0.000007000	4.002783000	-0.000012000	H	2.781184000	-2.182721000	-0.001208000
C	2.452542000	3.923529000	-0.000457000	O	7.195340000	-3.398110000	-0.000079000
O	3.531826000	4.496426000	-0.001071000	C	6.903412000	-4.803110000	-0.000293000
N	2.290885000	2.569317000	-0.000136000	H	6.315562000	-5.065323000	-0.886770000
H	1.342681000	2.204501000	-0.000630000	H	6.314874000	-5.065449000	0.885688000
N	3.362494000	1.729821000	0.000014000	C	8.163609000	-5.534801000	0.000159000
C	3.107319000	0.472134000	-0.000481000	C	9.188389000	-6.161457000	0.000553000
H	2.076380000	0.101232000	-0.001007000	H	10.099137000	-6.714842000	0.000885000
C	4.165342000	-0.532594000	-0.000408000	C	-1.197290000	6.082649000	-0.000231000
C	5.531404000	-0.186645000	-0.000084000	H	-2.158073000	6.579686000	-0.000404000
H	5.812796000	0.859852000	-0.000409000	C	-1.149388000	4.687786000	-0.000200000
C	6.507199000	-1.162959000	-0.000172000	C	-2.452555000	3.923516000	-0.000425000

O	-3.531842000	4.496407000	C	-4.802107000	-2.885572000
0.001092000			0.000753000		
N	-2.290891000	2.569305000	H	-4.494413000	-3.922977000
0.000174000			0.001119000		
H	-1.342685000	2.204494000	C	-3.826502000	-1.889910000
0.000682000			0.000852000		
N	-3.362496000	1.729803000	H	-2.781165000	-2.182736000
0.000006000			0.001250000		
C	-3.107314000	0.472118000	O	-7.195314000	-3.398149000
0.000508000			0.000059000		
H	-2.076373000	0.101221000	C	-6.903382000	-4.803150000
0.001052000			0.000289000		
C	-4.165332000	-0.532616000	H	-6.315543000	-5.065353000
0.000423000			0.886777000		
C	-5.531396000	-0.186674000	H	-6.314831000	-5.065495000
0.000092000			0.885681000		
H	-5.812793000	0.859821000	C	-8.163566000	-5.534862000
0.000426000			0.000173000		
C	-6.507186000	-1.162993000	C	-9.188434000	-6.161375000
0.000191000			0.000576000		
H	-7.559671000	-0.902646000	H	-10.099545000	-6.714161000
0.000600000			0.000917000		
C	-6.151617000	-2.523096000			
0.000220000					

Receptor **7** (Cyclic)

C	-6.407551000	1.058947000	O	-4.671760000	3.391924000
0.552625000			0.620386000		
C	-5.068345000	1.066929000	N	-3.068400000	2.184737000
0.163472000			0.508712000		
N	-4.387264000	-0.060488000	C	-4.087601000	-2.466883000
0.059310000			0.064293000		
C	-4.977274000	-1.241518000	O	-4.427515000	-3.552060000
0.143718000			0.505799000		
C	-6.312918000	-1.346284000	N	-2.880051000	-2.180363000
0.530172000			0.506395000		
C	-7.039140000	-0.171858000	N	-1.757261000	-2.944155000
0.715318000			0.331026000		
C	-4.272126000	2.356813000	N	-1.975979000	2.981558000
0.112885000			0.272966000		

C -0.905282000 2.574649000 -0.856189000

C -0.711868000 -2.472696000 -0.909709000

C 0.429644000 3.091458000 -0.586601000

C 0.641986000 -2.978574000 -0.703522000

C 0.711776000 4.020193000 -0.433374000

C 2.019118000 4.325402000 -0.765365000

C 3.086186000 3.710468000 -0.088985000

C 2.823599000 2.835204000 0.966988000

C 1.504985000 2.530819000 1.287511000

C 1.675701000 -2.421207000 1.471793000

C 3.003166000 -2.752269000 1.230361000

C 3.313639000 -3.641442000 0.204206000

C 2.294748000 -4.238995000 -0.545659000

C 0.968940000 -3.911931000 -0.295084000

O 4.333622000 4.018714000 -0.551044000

C 5.470193000 3.323403000 -0.016159000

C 5.487845000 1.896432000 -0.328480000

O 4.640924000 -3.941491000 -0.043234000

C 5.226722000 -3.270966000 -1.177069000

C 5.355954000 -1.827787000 -0.988582000

C 5.479601000 0.709243000 -0.568440000

C 5.433306000 -0.634117000 -0.796437000

H -6.922664000 1.993310000 -0.734856000

H -6.752672000 -2.321619000 -0.693958000

H -8.081737000 -0.215707000 -1.008221000

H -2.900705000 1.247010000 0.858666000

H -2.762611000 -1.218915000 0.809827000

H -0.944128000 1.724920000 1.547093000

H -0.788489000 -1.590256000 1.554115000

H -0.104461000 4.467156000 -0.989319000

H 2.243776000 5.013312000 -1.572662000

H 3.621616000 2.359068000 1.520162000

H 1.312616000 1.817213000 2.082402000

H 1.438943000 -1.702162000 2.249482000

H 3.804245000 -2.313229000 1.812995000

H 2.549441000 -4.946902000 -1.326967000

H 0.178763000 -4.351529000 -0.892815000

H 4.643830000 -3.476423000 -2.081589000

H 6.209906000 -3.727411000 -1.302314000

H 5.535363000 3.475916000 1.066499000

H 6.329460000 3.819924000 -0.468276000

Complex **5·Cu(ClO$_4$)$_2$**

C 1.204020000 -5.489535000 -1.089960000
C 1.163520000 -4.125902000 -0.822595000
N 0.000062000 -3.479105000 -0.667773000
C -1.163421000 -4.125979000 -0.822045000
C -1.203918000 -5.489623000 -1.089389000
C 0.000049000 -6.181051000 -1.199987000
C 2.392448000 -3.264002000 -0.827669000
O 3.378194000 -3.529996000 -1.457187000
N 2.211544000 -2.053392000 -0.078255000
C -2.392499000 -3.264265000 -0.826740000
O -3.378341000 -3.530583000 -1.456003000
N -2.211666000 -2.053543000 -0.077609000
N -3.190462000 -1.093777000 -0.282780000
N 3.189884000 -1.093236000 -0.283792000
C 3.324715000 -0.228675000 -0.661424000
C -3.324154000 -0.228183000 -0.661632000
C 4.277743000 0.859097000 -0.573908000
C -4.277616000 0.859255000 -0.574181000
C 5.095856000 1.054237000 -0.552985000
C 5.999207000 2.102392000 -0.608976000
C 6.103532000 2.987991000 -0.477636000
C 5.292339000 2.805072000 -1.609666000
C 4.394472000 1.756861000 -1.653596000
C -4.393190000 1.758153000 -1.653037000
C -5.291326000 2.806142000 -1.609090000
C -6.103925000 2.987709000 -0.477860000
C -6.000776000 2.100959000 -0.607916000
C -5.097168000 1.053015000 -0.551894000
O 6.948249000 4.043597000 -0.532210000
C 7.812132000 4.298787000 -0.590848000
C 8.614886000 5.476376000 -0.292303000
O -6.948758000 4.043251000 -0.532335000
C -7.813772000 4.297315000 -0.590098000
C -8.616206000 5.475221000 -0.291934000
C 9.291433000 6.444437000 -0.074249000
C -9.292508000 6.443522000 -0.074183000

H	2.158360000	-5.982707000	-1.219203000	H	8.459135000	3.433496000	-0.766966000
H	-2.158277000	-5.982870000	-1.218200000	H	-8.460983000	3.431871000	-0.764704000
H	0.000039000	-7.245697000	-1.397440000	H	-7.214804000	4.464682000	-1.490925000
H	1.985945000	-2.262148000	0.907877000	H	9.889583000	7.304053000	0.123441000
H	-1.985216000	-2.262014000	0.908323000	H	-9.890431000	7.303359000	0.123232000
H	2.716453000	-0.278345000	-1.567867000	Cu	0.000112000	-1.515923000	-0.408380000
H	-2.714535000	-0.276567000	-1.567233000	O	0.000218000	0.446496000	-0.594764000
H	5.014701000	0.372946000	-1.391298000	Cl	-0.000307000	1.023975000	-2.049354000
H	6.611294000	2.223220000	-1.492780000	O	-0.000979000	-0.142521000	-2.971629000
H	5.387823000	3.499541000	-2.435910000	O	1.220817000	1.836080000	-2.200028000
H	3.772064000	1.624722000	-2.532510000	O	-1.221206000	1.836626000	-2.198928000
H	-3.769677000	1.627091000	-2.531330000	Cl	0.000945000	-2.161453000	2.876123000
H	-5.385925000	3.501478000	-2.434707000	O	-0.000799000	-0.999622000	1.895239000
H	-6.613951000	2.220725000	-1.491112000	O	-0.001210000	-1.658248000	4.257743000
H	-5.016925000	0.370832000	-1.389570000	O	1.228907000	-2.973589000	2.598443000
H	7.212258000	4.467071000	-1.490898000	O	-1.222816000	-2.979045000	2.596384000

Complex **7**·$\mathbf{Hg^{2+}}$ (left sided alkyne)

C	-6.411018000	1.058991000	-0.600764000	C	-4.983317000	-1.238139000	-0.164554000
C	-5.075605000	1.070102000	-0.198915000	C	-6.315238000	-1.346107000	-0.562751000
N	-4.396116000	-0.055525000	-0.037300000	C	-7.040399000	-0.173216000	-0.761599000

C	-4.279191000	2.359873000	-0.149754000
O	-4.670497000	3.390413000	-0.672243000
N	-3.083327000	2.192166000	0.488985000
C	-4.092497000	-2.461558000	-0.071139000
O	-4.425556000	-3.549338000	-0.510835000
N	-2.890309000	-2.170108000	0.509563000
N	-1.764917000	-2.931732000	0.346299000
N	-1.985630000	2.981789000	0.255415000
C	-0.921813000	2.575914000	-0.851488000
C	-0.723959000	-2.454885000	-0.928321000
C	0.417436000	3.085347000	0.588327000
C	0.631325000	-2.962381000	-0.734309000
C	0.710763000	4.007452000	-0.434424000
C	2.021779000	4.306323000	-0.757889000
C	3.080851000	3.691243000	-0.069735000
C	2.807338000	2.821791000	0.987921000
C	1.485067000	2.524148000	1.300203000
C	1.660885000	-2.398683000	-1.503360000
C	2.989471000	-2.734446000	-1.273962000
C	3.304491000	-3.635164000	0.259644000
C	2.289946000	-4.238499000	-0.491130000
C	0.963181000	-3.906217000	-0.252744000
O	4.333937000	3.993995000	-0.522949000
C	5.462704000	3.302041000	0.028700000
C	5.487110000	1.874390000	-0.282977000
O	4.633761000	-3.942616000	0.026333000
C	5.228564000	-3.297231000	-1.115135000
C	5.375520000	-1.852043000	-0.944190000
C	5.485911000	0.687413000	-0.524281000
C	5.447963000	-0.656399000	-0.753497000
H	-6.925008000	1.991818000	-0.793754000
H	-6.753076000	-2.322577000	-0.724878000
H	-8.080216000	-0.219494000	-1.063795000
H	-2.922384000	1.257700000	0.850639000
H	-2.777729000	-1.207272000	0.810481000
H	-0.969824000	1.732378000	1.549345000
H	-0.805302000	-1.567997000	1.565893000
H	-0.099569000	4.454880000	-0.998522000
H	2.255094000	4.989957000	-1.566353000
H	3.599090000	2.345984000	1.550397000

H	1.283889000	1.815862000	2.097629000	H	5.513341000	3.454109000	1.112173000
H	1.420346000	-1.671899000	-2.272604000	H	6.328462000	3.798388000	-0.411207000
H	3.787308000	-2.291740000	-1.858355000	H	4.644255000	-3.505373000	-2.018125000
H	2.547926000	-4.956081000	-1.262476000	H	6.205404000	-3.768433000	-1.233621000
H	0.176045000	-4.351143000	-0.850482000	Hg	8.595388000	-0.964937000	-2.482498000

Complex **7**·$\mathbf{Hg^{2+}}$ (right sided alkyne)

C	-6.426141000	1.054363000	-0.560272000	C	3.064271000	3.692070000	-0.111641000
C	-5.087574000	1.064437000	-0.169086000	C	2.805099000	2.820389000	0.947642000
N	-4.404661000	-0.061840000	0.053724000	C	1.487010000	2.518633000	1.274020000
C	-4.991769000	-1.243846000	-0.151799000	C	1.661490000	-2.409540000	1.476331000
C	-6.326647000	-1.350816000	-0.540271000	C	2.990072000	-2.740443000	1.240359000
C	-7.055033000	-0.177581000	-0.724925000	C	3.304725000	-3.630136000	0.216111000
C	-4.292156000	2.354594000	-0.117785000	C	2.289278000	-4.227867000	-0.538055000
O	-4.688089000	3.387983000	-0.630889000	C	0.962372000	-3.900754000	-0.292994000
N	-3.091032000	2.184313000	-0.510895000	O	4.311434000	4.000321000	-0.578124000
C	-4.098801000	-2.466934000	-0.073103000	C	5.451104000	3.329627000	-0.024613000
O	-4.434701000	-3.552502000	-0.516178000	C	5.497173000	1.899405000	-0.326299000
N	-2.892446000	-2.177330000	-0.499362000	O	4.633817000	-3.931960000	-0.023617000
N	-1.767413000	-2.937582000	-0.325787000	C	5.224924000	-3.270716000	-1.158533000
N	-1.995608000	2.974457000	-0.269275000	C	5.368033000	-1.827989000	-0.972515000
C	-0.925377000	2.566476000	-0.852081000	C	5.503214000	0.709738000	-0.560168000
C	-0.724428000	-2.463830000	-0.906802000	C	5.455048000	-0.634534000	-0.782988000
C	0.410303000	3.078093000	-0.574788000	H	-6.942952000	1.987810000	-0.742465000
C	0.631006000	-2.967494000	-0.704227000	H	-6.764377000	-2.326740000	-0.705938000
C	0.689808000	4.001544000	-0.450590000	H	-8.097158000	-0.223196000	-1.019164000
C	1.996259000	4.304263000	-0.788212000	H	-2.926486000	1.247849000	-0.865695000

H	-2.778649000	-1.215929000	H	3.788539000	-2.302048000
0.804341000			1.827125000		
H	-0.964995000	1.720460000	H	2.546815000	-4.936735000
1.547419000			1.317544000		
H	-0.804419000	-1.581741000	H	0.174719000	-4.341130000
1.551248000			0.893447000		
H	-0.127967000	4.447174000	H	5.500883000	3.489984000
1.005243000			1.057798000		
H	2.218891000	4.989247000	H	6.307310000	3.837244000
1.598532000			0.469961000		
H	3.604237000	2.345460000	H	4.640193000	-3.470777000
1.500398000			2.063049000		
H	1.296500000	1.808586000	H	6.203954000	-3.735932000
2.072495000			1.284356000		
H	1.421348000	-1.691006000	Hg	9.095788000	1.608142000
2.253437000			0.092458000		

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