

Supporting information

Dual-mode highly selective and sensitive Schiff base chemosensor for fluorescent colorimetric detection of Ni²⁺ and colorimetric detection of Cu²⁺

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Sl.No.	Content	Figure No.
1.	Mass spectra of L	S1
2.	FT-IR spectra of L	S2
3.	¹ H-NMR spectra of L in DMSO-d ₆	S3
4.	Job's plot of L with Cu ²⁺ and Ni ²⁺	S4
5.	ESI-mass spectra of L -Cu ²⁺	S5
6.	ESI-mass spectra of L -Cu ²⁺	S6
7.	Association constants of (a) L -Cu ²⁺ and (b) L -Ni ²⁺	S7
8.	Absorption spectra of Ni ²⁺ in presence of Cu ²⁺ and Cys	S8
9.	Fluorometric Detection limit of L in presence of Ni ²⁺	S9
10.	IR spectra of L -Cu ²⁺ complex	S10
11.	Partial ¹ H NMR Spectra of L and L + Ni ²⁺ (2 equiv.)	S11
12.	IR Spectra of L and L + Ni ²⁺ in solid phase	S12
13.	Geometry obtained from crystal structure of the four stable conformers for L .	S13
14.	Selected HOMOs and LUMOs of 1 are shown. Positive values of the orbital contours are represented in yellow (0.03 au) and negative values in blue (-0.03 au).	S14
15.	Selected HOMOs and LUMOs of 2 ⁺ . Positive values of the orbital contour are represented in yellow (0.04 au) and negative values in blue (-0.03 au).	S15
16.	Crystallographically isolated conformational energies for L calculated at the level of DFT and their differences.	Table S1
17.	Selected experimental and optimized bond lengths (Å) and angles (°) of L and 1 are listed.	Table S2
18.	Selected optimized bond lengths (Å) and angles (°) of 2 is listed	Table S3
19.	The diagnostic experimental and calculated IR frequencies are shown for L , 1 and 2	Table S4
20.	Electronic transitions of L and 1 calculated in methanol using the TD-DFT method. The corresponding assignment is also given. Due to the open-shell electronic	Table S5

	configuration of the 1 , the assignment distinguishes between α and β molecular orbitals	
20.	Electronic transitions of L , 1 and 2 calculated in water using the TD-DFT method. Due to the open-shell electronic configuration of the L , 1 and 2 , the assignment distinguishes between α and β molecular orbitals	Table S6

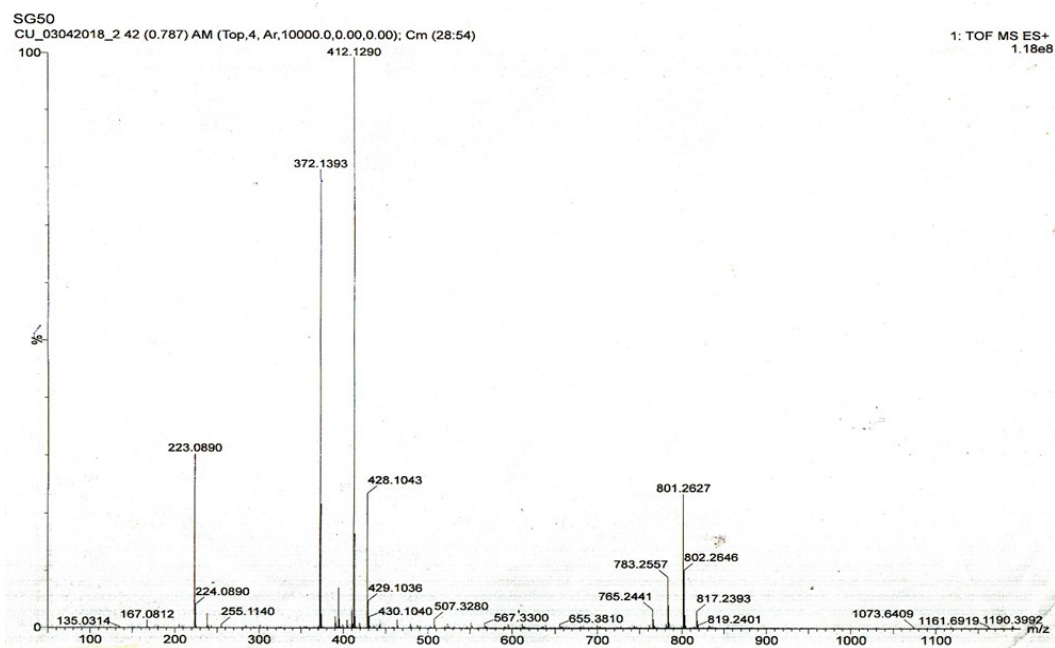


Fig. S1. ESI-mass spectra of **L**.

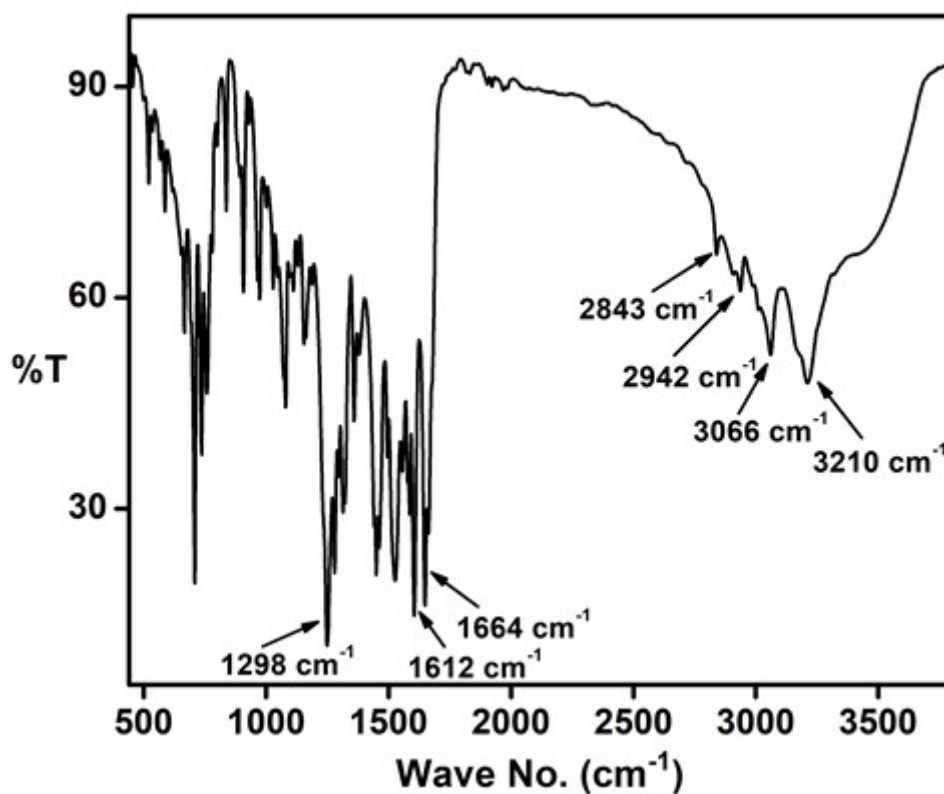


Fig. S2. FTIR spectra of L

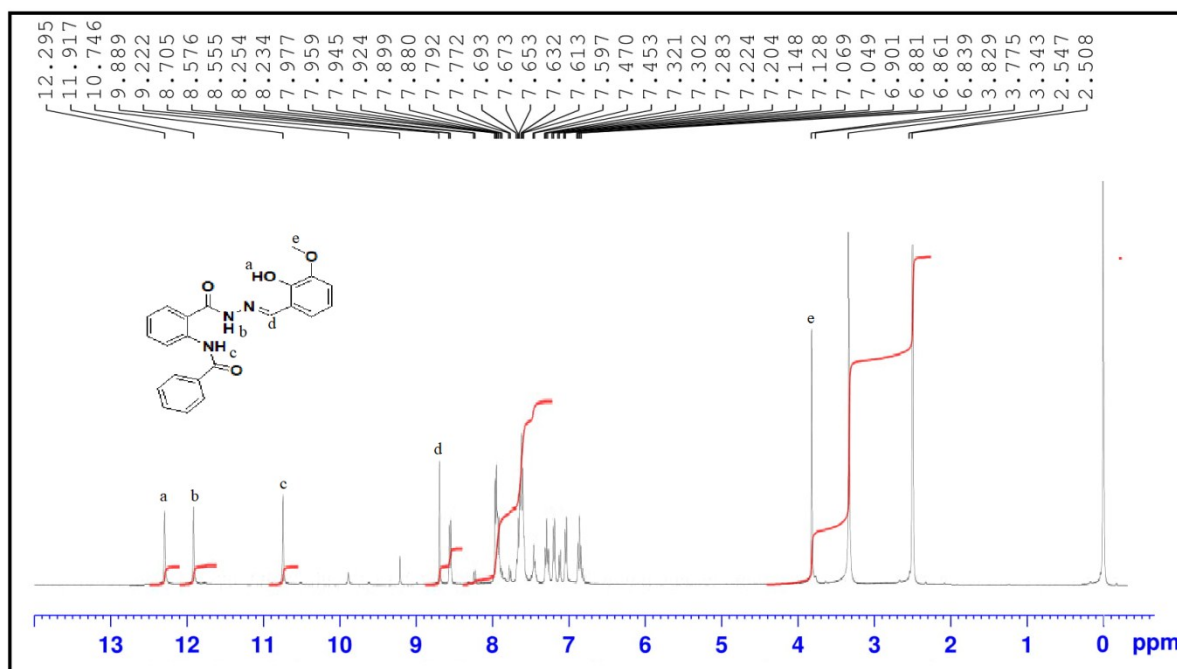


Fig. S3. ¹H NMR spectra of L in DMSO-d₆

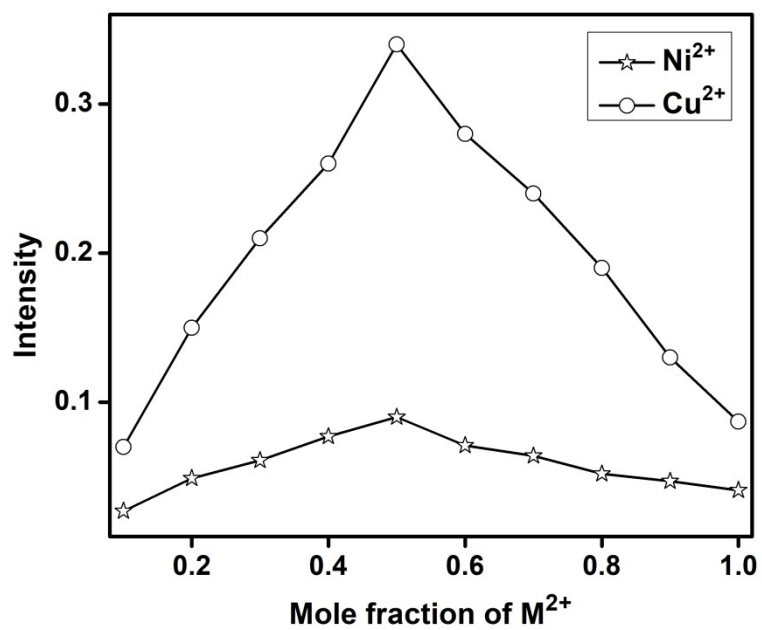


Fig. S4. Jobs plot of L- Cu^{2+} and L- Ni^{2+} complex formation

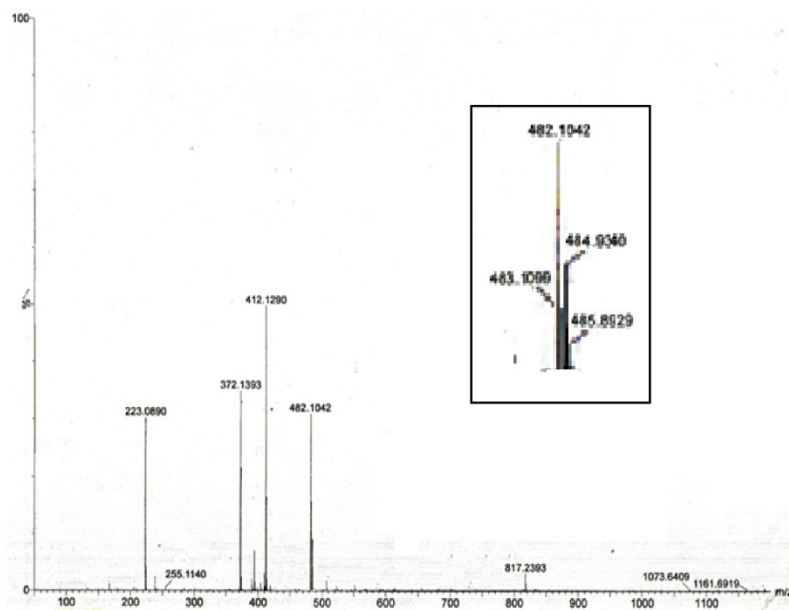


Fig. S5. ESI mass spectra of L- Cu^{2+} complex

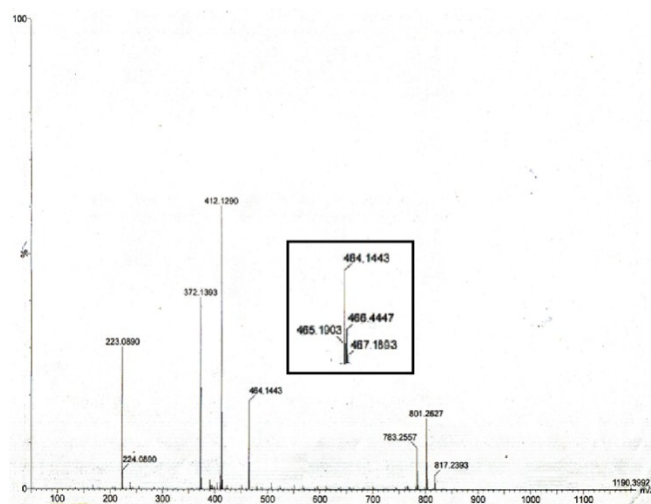


Fig. S6. ESI mass spectra of L-Ni²⁺ complex

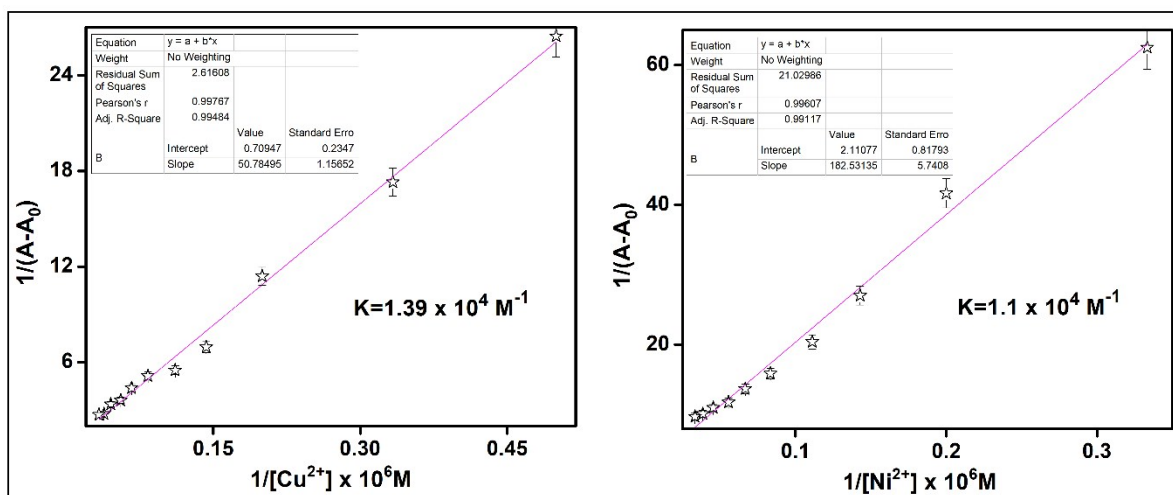


Fig. S7. Association constants of (a) L-Cu²⁺ and (b) L-Ni²⁺ complexes.

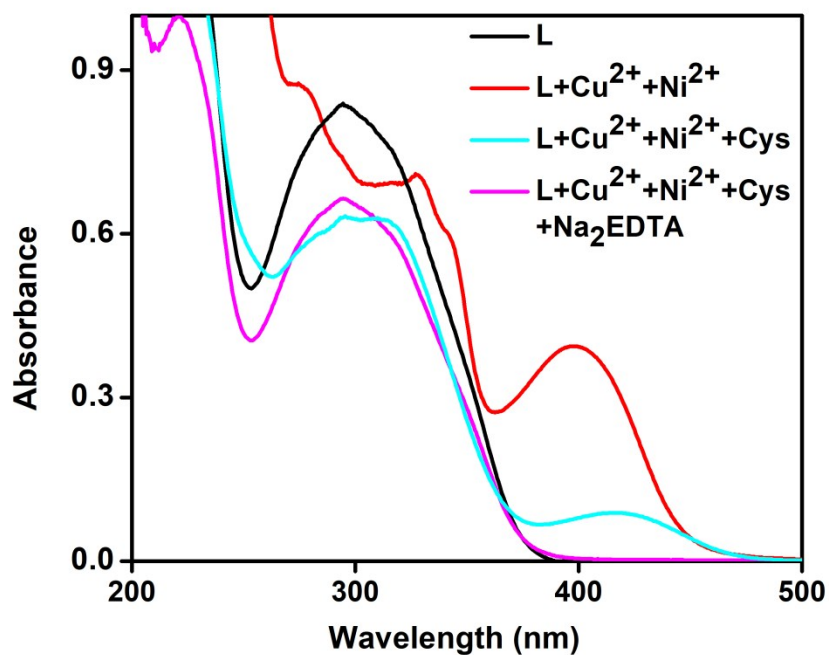


Fig. S8. Absorption spectra of Ni²⁺ in presence of Cu²⁺ and Cys.

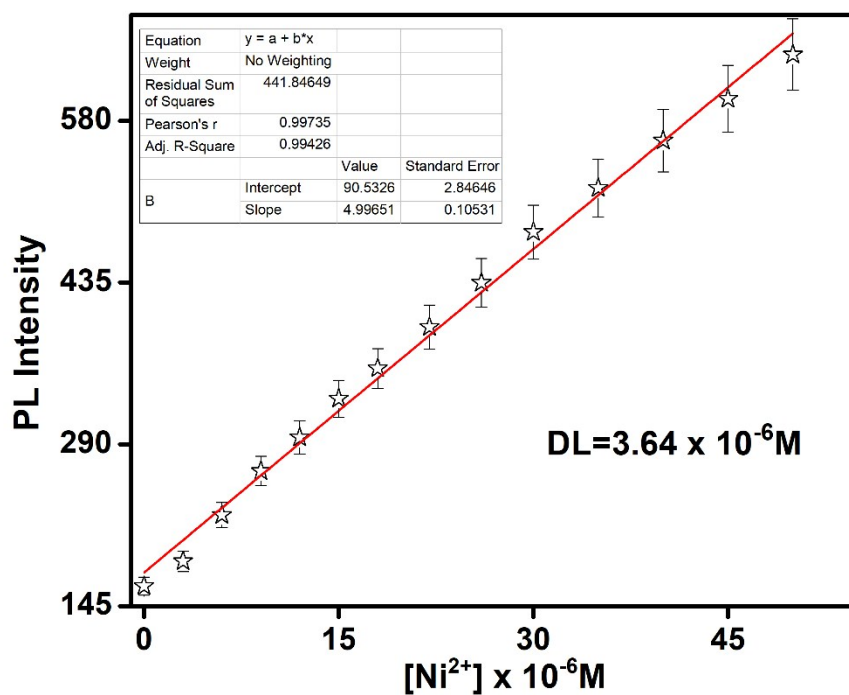


Fig. S9. Fluorometric Detection limit of L in presence of Ni²⁺

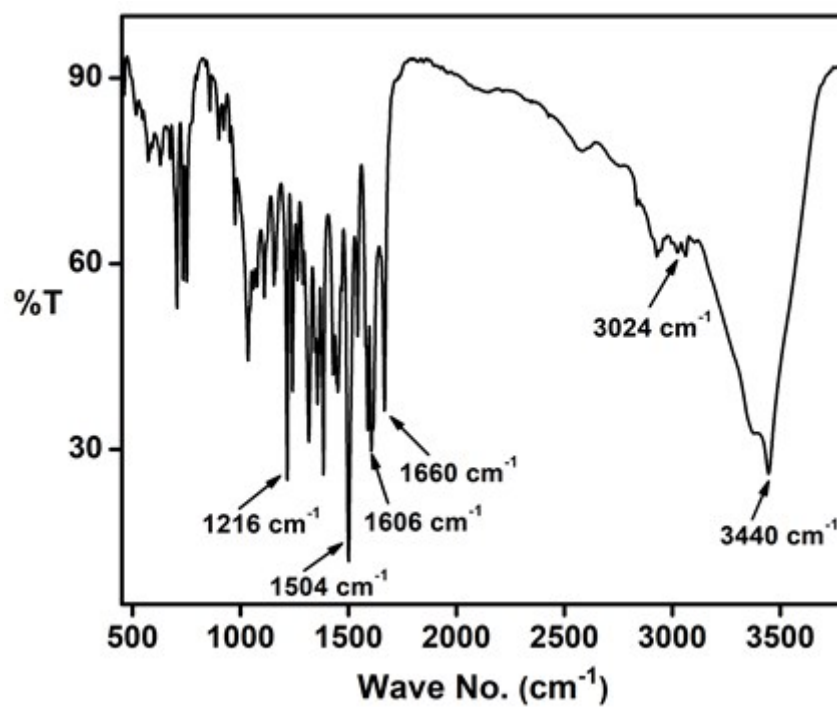


Fig. S10. IR spectra of L-Cu²⁺ complex

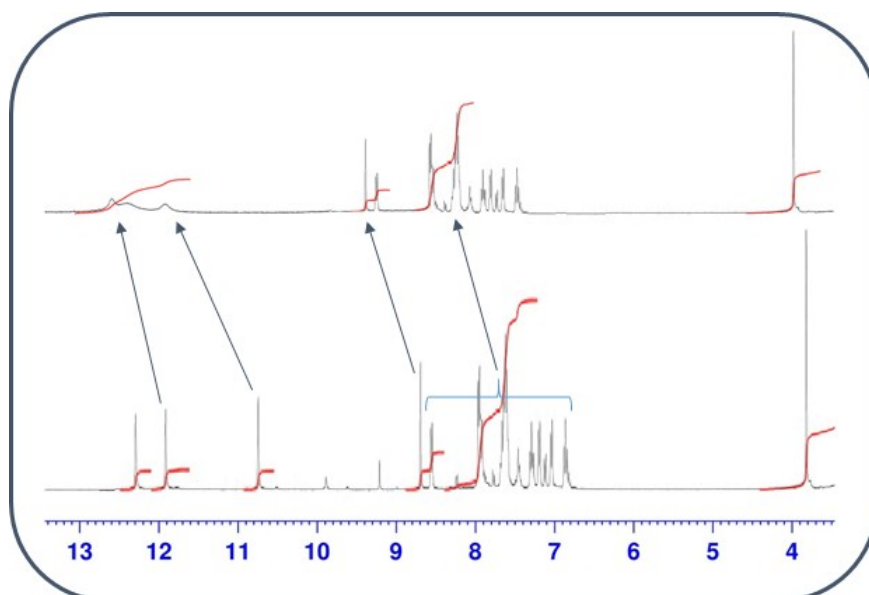


Fig. S11. Partial ¹H NMR Spectra of L and L+ Ni²⁺ (2 equiv.)

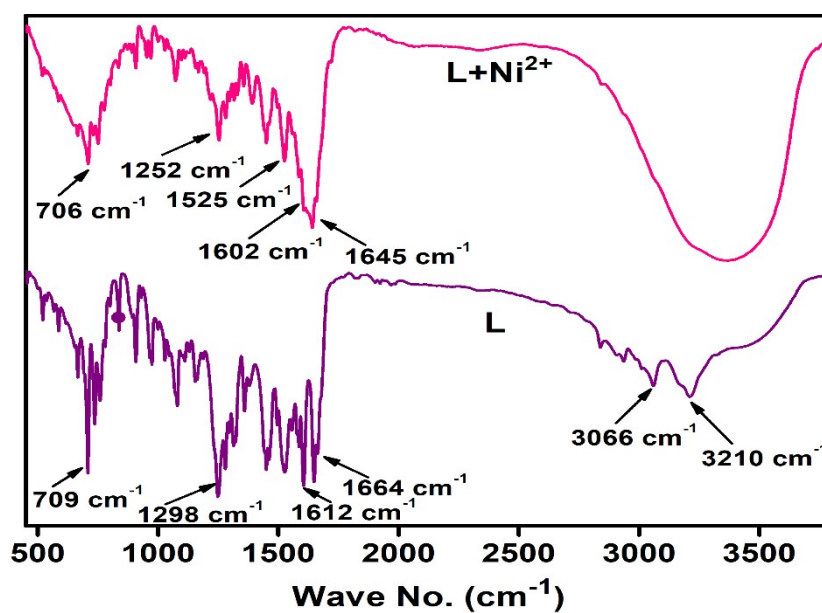


Fig. S12. IR Spectra of L and L+ Ni²⁺ in solid phase

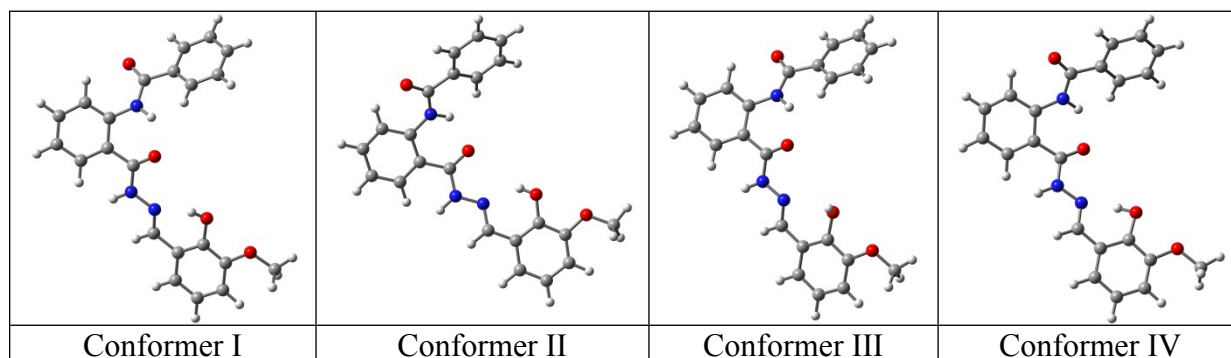
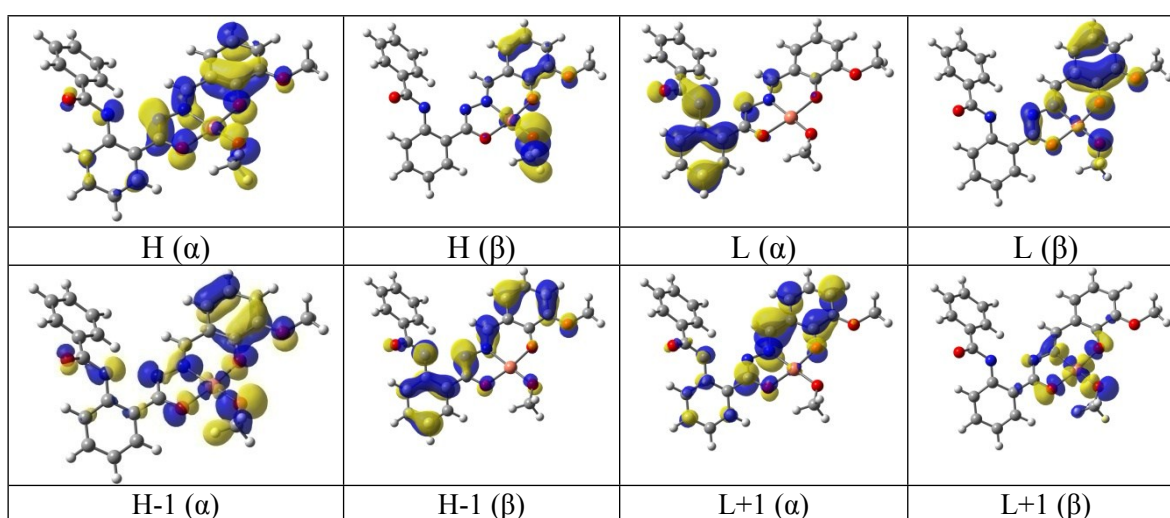


Fig. S13. Geometry obtained from crystal structure of the four stable conformers for L.



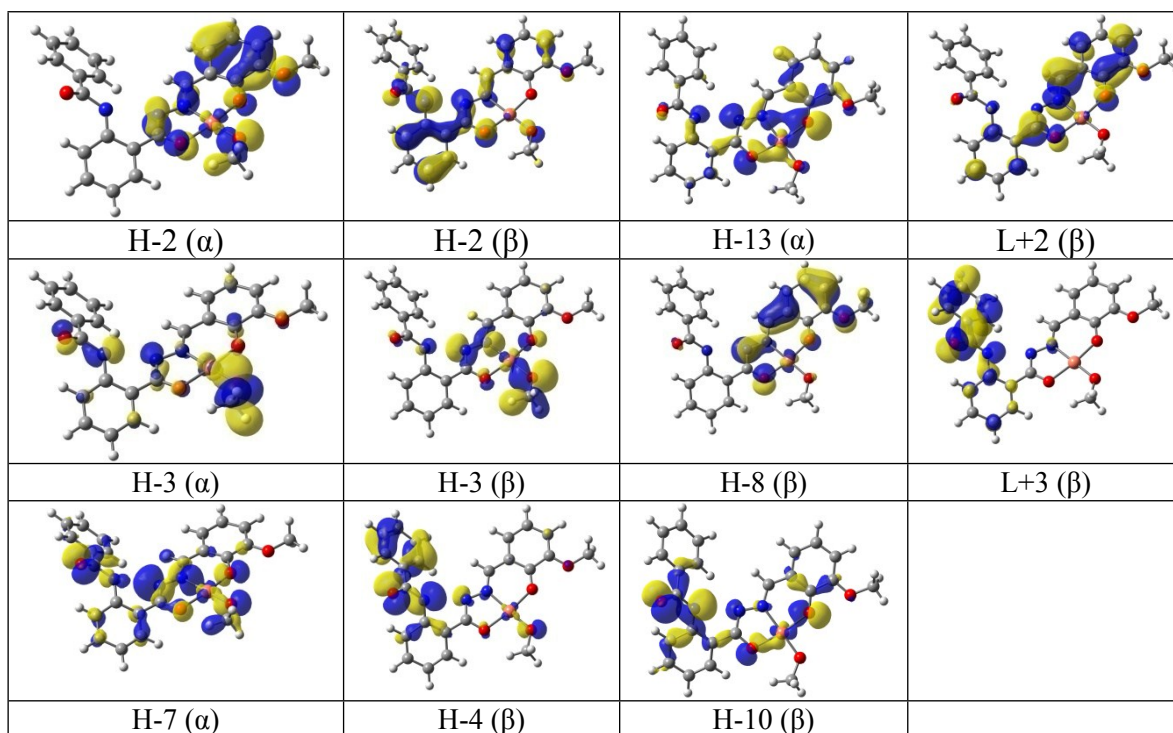


Fig. S14. Selected HOMOs and LUMOs of **1** are shown. Positive values of the orbital contours are represented in yellow (0.03 au) and negative values in blue (−0.03 au).

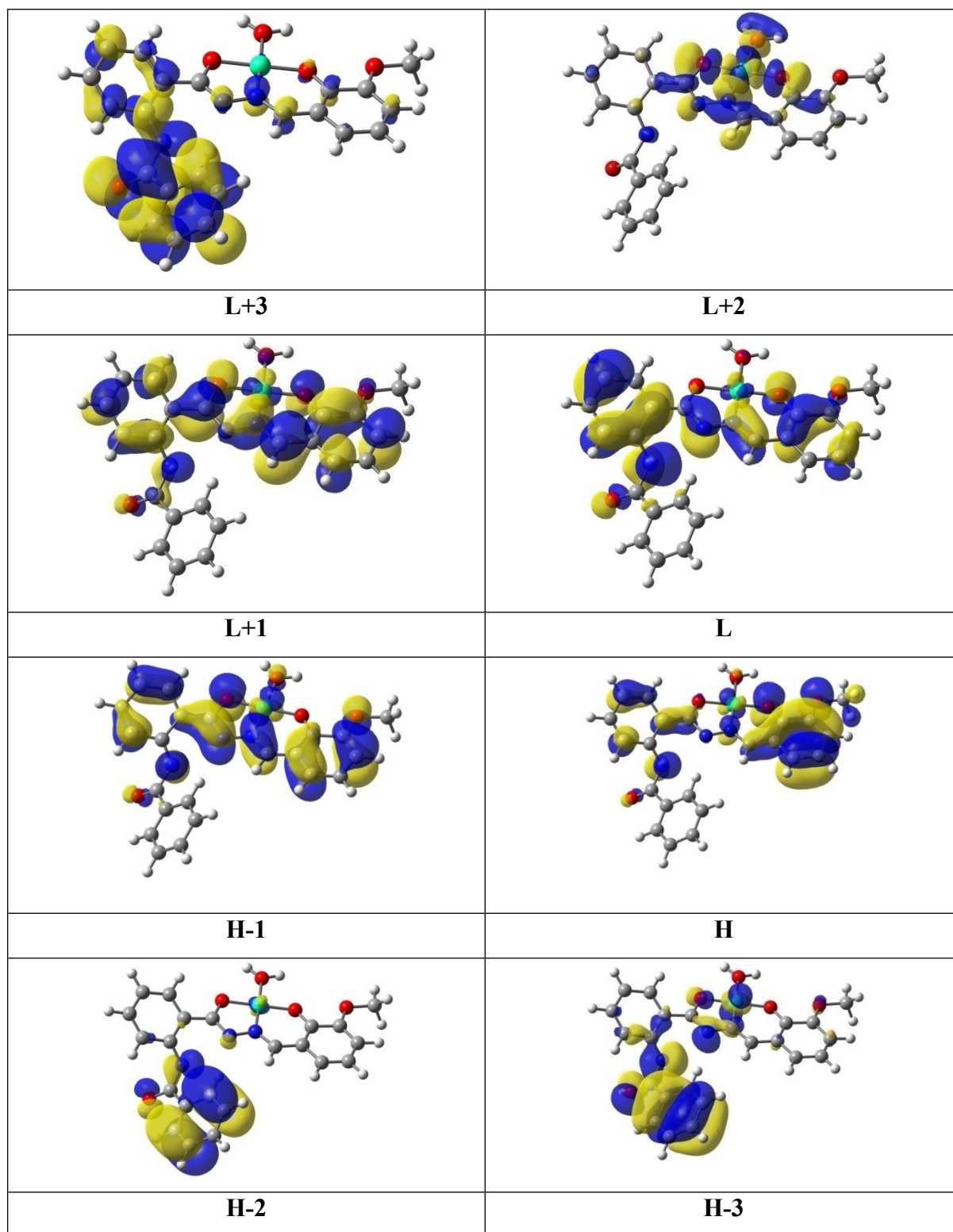


Fig. S15. Selected HOMOs and LUMOs of 2^+ . Positive values of the orbital contour are represented in yellow (0.04 au) and negative values in blue (-0.03 au).

Table S1 Crystallographically isolated conformational energies for **L** calculated at the level of DFT and their differences.

L	<i>E</i> (Hartree)	ΔE (kJ/mol)
Conformer I	-1314.9432216	43.95
Conformer II	-1314.9599612	0.0
Conformer III	-1314.9286518	82.02
Conformer IV	-1314.9588617	2.89

Table S2 Selected experimental and optimized bond lengths (Å) and angles (°) of **L** and **1** are listed.

L						1		
Bond lengths/angles	Experimental				Optimized	Bond lengths	Exp.	Optimized
	Unit 1	Unit 2	Unit 3	Unit 4				
O4-C3	1.356(12)	1.370(12)	1.385(12)	1.349(12)	1.378	Cu1-O2	1.876(6)	1.98593
C3-C5	1.391(14)	1.387(15)	1.401(14)	1.406(14)	1.390	Cu1-N6	1.872(8)	1.98726
C5-C6	1.480(14)	1.416(15)	1.451(14)	1.397(15)	1.454	Cu1-O9	1.920(6)	1.97497
C6-N7	1.257(14)	1.319(12)	1.294(12)	1.301(14)	1.284	Cu1-O31	1.940(7)	1.86293
N7-N8	1.396(12)	1.375(12)	1.375(11)	1.379(11)	1.386	O2-C3	1.322(11)	1.30164
N8-C9	1.347(12)	1.365(12)	1.347(12)	1.385(12)	1.343	C4-C5	1.445(13)	1.43434
C9-O10	1.229(13)	1.234(13)	1.251(12)	1.217(12)	1.245	C5-N6	1.298(12)	1.32527
C2-O1	1.392(12)	1.384(13)	1.371(13)	1.376(13)	1.370	N6-N7	1.413(10)	1.39426
N13-C14	1.359(13)	1.344(14)	1.357(13)	1.357(13)	1.360	N7-C8	1.322(12)	1.35562
C14-O15	1.231(13)	1.249(14)	1.222(13)	1.222(13)	1.229	C8-O9	1.293(12)	1.32540
O1-C2-C3	114.7(9)	113.5(9)	116.6(9)	113.9(9)	116.48	O31-C32	1.437(12)	1.43585
C2-C3-O4	119.7(9)	119.0(9)	117.1(9)	118.5(9)	117.27	O29-C30	1.437(12)	1.45958
C3-C5-C6	122.1(9)	122.5(9)	122.4(9)	122.1(10)	122.11	O2-Cu1-N6	93.8(3)	89.93008
C5-C6-N7	119.5(9)	120.6(10)	119.9(9)	121.5(10)	119.94	N6-Cu1-O9	82.6(3)	80.14024
C6-N7-N8	117.2(9)	115.9(8)	115.9(8)	116.6(8)	116.34	O9-Cu1-O31	95.0(3)	99.13916
N7-N8-C9	117.5(8)	117.2(8)	117.2(8)	117.3(8)	117.17	O2-Cu1-O31	88.5(3)	90.90838
N8-C9-O10	122.7(9)	122.7(10)	122.4(9)	121.8(9)	122.65	O2-C3-C4	125.4(8)	123.79976
O10-C9-C11	123.8(9)	123.4(9)	122.1(9)	125.5(9)	122.60	C4-C5-N6	121.5(8)	125.37299
C9-C11-C12	120.2(9)	120.2(9)	121.2(9)	119.3(9)	120.88	C5-N6-N7	115.6(7)	116.34041
C11-C12-N13	117.3(9)	117.7(9)	117.4(9)	116.5(9)	117.57	N6-N7-C8	109.4(7)	109.82222
C12-N13-C14	125.5(9)	127.8(9)	127.0(9)	125.5(9)	126.51	N7-C8-O9	122.8(9)	122.56136

Table S3 Selected optimized bond lengths (Å) and angles (°) of **2** is listed.

Bondlengths	Optimized	Bond angles	Optimized
Ni1-O2	1.8312	O2-Ni1-N6	95.927
Ni1-N6	1.8442	N6-Ni1-O9	84.467
Ni1-O9	1.8605	O9-Ni1-O31	94.228
Ni1-O31	1.9044	O31-Ni1-O2	85.377
O2-C3	1.3166	O2-C3-C4	123.170
C3-C4	1.4572	C3-C4-C5	121.656

C4-C5	1.4170	C4-C5-N6	124.672
C5-N6	1.3397	N6-N7-C10	108.804
N6-N7	1.3814	N7-C8-O9	120.478
N7-C8	1.3593	N7-C8-C10	120.311
C8-O9	1.3411	C10-C11-N12	118.617
N12-C13	1.4244	N12-C13-O14	119.113
C13-O14	1.2574		

Table S4 The diagnostic experimental and calculated IR frequencies are shown for **L, 1** and **2**

Experimental (cm ⁻¹)	Theoretical (cm ⁻¹)	Assignments
Ligand (L)		
1675 s, 1664 vs	1731.84, 1693.47	$\nu_{C=O}$ (amides)
1649 vs	1639.08	$\nu_{C=N}$ (imine bonds)
2935 s, 3035 s, 3212 s	2996.49, 3065.88, 3105.75	ν_{C-H} of -OCH ₃
3435 br	3593.26	ν_{O-H}
1		
1616	1610.30	$\nu_{C=N}$
1667	1650.91	$\nu_{C=O}$ (coordinated amide)
1589	1547.91	$\nu_{C=O}$ (non coordinated amide)
3064 br, 3020 br, 2932 br	2980.39, 3048.70, 3095.14	ν_{C-H} (Coordinated -OCH ₃)
3454 br, 3364 br	3201.60, 3122.72	ν_{C-H} (Non Coordinated -OCH ₃)
2		
1610	1630.51	$\nu_{C=N}$
1642	1648.38	$\nu_{C=O}$ (coordinated amide)
1586	1583.80	$\nu_{C=O}$ (non coordinated amide)
1560	1594.45	δ_{H-O-H} (Coordinated water) bending
3066, 3210 br	3044.19, 3136.61, 3207.43	ν_{C-H} (OCH ₃)
3338 br	3211.11, 3214.91, 3220.10, 3223.45, 3229.73, 3234.17, 3236.90, 3242.75, 3250.32, 3254.22, 3259.28	ν_{O-H} , ν_{C-H} (Ar-H)

3742	3726.05	$\nu_{\text{O-H}}$ (Coordinated water) symmetric
3853	3896.97	$\nu_{\text{O-H}}$ (Coordinated water) asymmetric

Table S5. Electronic transitions of **L** and **1** calculated in methanol using the TD-DFT method. The corresponding assignment is also given. Due to the open-shell electronic configuration of the **1**, the assignment distinguishes between α and β molecular orbitals.

Experimental	Calculated		Assignment
λ nm (ϵ M ⁻¹ cm ⁻¹)	λ (nm)	Oscillator strength (a.u.)	Most important orbital excitations
L			
294 (8150)	325.68	0.1281	H→L, H-1→L
220 (11320)	228.22	0.3983	H-4→L+1, H-16→L, H-10→L
1			
390 (2350)	485.60	0.0256	H → L (β), H-3 → L+1 (β)
325 (4670)	387.72	0.0136	H-1 → L (α), H → L (α), H-1 → L (β)
277 (5830)	376.04	0.0106	H → L+1 (α), H-1→L+2 (β), H → L (β), H-2 → L+1 (β) H-2 → L+1 (α)
250 (7580)	286.61	0.0467	H-1 → L+1 (α), H → L+2(β), H-10 → L+1 (β)
230 (10750)	235.61	0.0315	H-3 → L +1 (α), H-2 → L+2 (β), H-4 → L+3 (β)
202 (19630)	225.27	0.1148	H-8 → L+1 (β), H-4 → L+3 (β), H-13 → L (α), H-7 → L+1 (α)

Table S6. Electronic transitions of **L**, **1** and **2** calculated in water using the TD-DFT method. Due to the open-shell electronic configuration of the **L**, **1** and **2**, the assignment distinguishes between α and β molecular orbitals

Most important orbital excitations	λ	f	Experimental λ (ϵ)
HL			
H \rightarrow L, H-1 \rightarrow L	325.68	0.1281	294 (8150)
H-2 \rightarrow L, H-3 \rightarrow L	304.64	0.0296	
H \rightarrow L, H-1 \rightarrow L, H-4 \rightarrow L	290.60	0.0803	
H-2 \rightarrow L+1, H-1 \rightarrow L+1, H-1 \rightarrow L	266.78	0.0310	
H-2 \rightarrow L+1, H-1 \rightarrow L+1, H-3 \rightarrow L+1	259.74	0.0069	
H \rightarrow L+3, H-2 \rightarrow L+2, H-5 \rightarrow L	239.22	0.0225	
H-4 \rightarrow L+1, H-16 \rightarrow L, H-10 \rightarrow L	228.22	0.3983	220 (11320)
H \rightarrow L+3, H-4 \rightarrow L+1, H-6 \rightarrow L+1	219.09	0.0966	
H-2 \rightarrow L+2, H-16 \rightarrow L, H-17 \rightarrow L	214.16	0.0517	
H-2 \rightarrow L+2, H-15 \rightarrow L, H-16 \rightarrow L	213.22	0.0063	
1			
H \rightarrow L (β), H-3 \rightarrow L+1 (β)	485.60	0.0256	390 (2425)
H \rightarrow L (α), H-2 \rightarrow L (β)	440.49	0.0187	
H-1 \rightarrow L (β), H-3 \rightarrow L (β), H \rightarrow L+1(α)	425.18	0.0026	
H-3 \rightarrow L (α), H-2 \rightarrow L (α), H-1 \rightarrow L+1(β)	402.88	0.0037	
H-1 \rightarrow L (α), H \rightarrow L (α), H-1 \rightarrow L (β)	387.72	0.0136	325 (4750)
H-2 \rightarrow L (α), H-1 \rightarrow L (β), H-3 \rightarrow L (β)	377.74	0.0011	
H \rightarrow L+1 (α), H-1 \rightarrow L+2 (β), H \rightarrow L (β), H-2 \rightarrow L+1 (β)H-2 \rightarrow L+1 (α)	376.04	0.0106	277 (5840)
H-4 \rightarrow L (β), H-3 \rightarrow L (β), H-2 \rightarrow L (α)	365.67	0.0045	
H-4 \rightarrow L (α), H-6 \rightarrow L (α), H \rightarrow L+2 (β)	314.43	0.1161	
H-1 \rightarrow L+1 (β), H-2 \rightarrow L+1 (β), H-3 \rightarrow L+1(α)	299.77	0.0398	
H-4 \rightarrow L (α), H-3 \rightarrow L (α), H-1 \rightarrow L+1 (β)	296.07	0.0037	
H-3 \rightarrow L (α), H-4 \rightarrow L (α), H-1 \rightarrow L+2 (β)	289.68	0.0232	
H-1 \rightarrow L+1 (α), H \rightarrow L+2(β), H-10 \rightarrow L+1 (β)	286.61	0.0467	250 (7580)
H-4 \rightarrow L (α), H-5 \rightarrow L (β)	283.12	0.0252	
H \rightarrow L+1 (α), H \rightarrow L+2 (α), H-7 \rightarrow L+1 (β)	276.20	0.0315	
H-5 \rightarrow L (α), H-8 \rightarrow L (α), H-9 \rightarrow L (β)	269.91	0.0255	
H-2 \rightarrow L+1 (α), H-1 \rightarrow L+1 (β), H-9 \rightarrow L (β)	263.70	0.0342	

H-2→L+1 (β), H-1→L+1 (β), H-5→L+1 (α), H-8→L+1 (α)	259.06	0.0194	
H-6→L (α), H-9→L (α), H-11→L (β)	246.80	0.0081	
H-8→L (α), H-6→L (β), H-9→L (β)	242.89	0.0278	
H-3 → L +1 (α), H-2 → L+2 (β), H-4 → L+3 (β)	235.61	0.0315	230 (10760)
H-8 → L+1 (β), H-4 → L+3 (β), H-13 → L (α), H-7 → L+1 (α)	225.27	0.1148	202 (20000)
H-8→L (β), H-7→L+1 (α), H-9→L (β)	221.81	0.0660	
H-4→L+1 (α), H-3→L+1 (β), H-19→L (β)	215.94	0.0376	
H-16→L (α), H-17→L+1 (α)	214.89	0.0390	
H-4→L+1 (β), H-3→L+1 (β), H-10→L+1 (α)	207.99	0.0460	
H-4→L+1 (α), H-3→L+1 (α), H-17→L (β)	205.32	0.0265	
2			
H → L, H → L+3	306.98437	0.0091	
H-1→L+1, H-1→L +2	306.11282	0.1275	
H-1→L +1, H-1→L+2, H-7→L+2	300.67384	0.1145	294
H-4→L+1, H-13→L	287.73969	0.0097	
H-3 → L+1, H-4 → L +1, H-5 → L+1	285.17407	0.0054	
H-13→L +1, H-14→L+1, H-15→L	280.20198	0.0073	
H-14 → L, H-15→ L, H-16→ L	275.8884	0.0581	
H-1→L +3, H→L +4, H-15→L	267.70465	0.0448	
H-1→L+3, H-5→L+1, H-2→L+1, H→L+4	265.66627	0.0592	
H→L+4, H-5→L+1, H-15→L	262.12991	0.0114	
H→L +4, H-15→L, H-16→L	256.14905	0.0879	
H-3→L +3, H-5→L+1, H-6→L+1	253.26601	0.0471	
H-2 → L+1, H → L+4, H-6 → L+1, H-15→ L	250.60429	0.1384	220
H-2→L +1, H-3→L +1, H-15→L	249.68153	0.0246	