Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary information

A theoretical insight on the rigid hydrogen-bonded network in the solid state structure of two zinc(II) complexes and their strong fluorescence behaviors

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Table S1. Selected Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex 1.

MO	energy	contribution				assignment (major)
		SB	N_3	Ac	Zn	
L+13	2.41	94	1	1	4	π*(SB)
L+12	2.29	83	7	2	8	π*(SB)
L+9	1.71	23	20	3	54	π*(SB)+ π*(N_3)+d*(Zn)
L+5	1.03	33	6	8	53	π*(SB)+d*(Zn)
L+4	0.81	11	1	77	11	π*(SB)+π*(Ac)+d*(Zn)
L+3	0.07	100	0	0	0	π*(SB)
L+2	-0.09	99	0	0	1	π*(SB)
L+1	-0.33	98	0	0	2	π*(SB)
LUMO	-0.46	99	0	0	1	π*(SB)
	energy gap = 4.69 eV					
HOMO	-5.15	1	97	0	2	π(N_3)
H-1	-5.35	5	91	1	4	π(N_3)
H-2	-6.29	99	0	0	0	π(SB)
H-3	-6.41	92	0	7	0	π(SB)
H-4	-6.73	6	1	91	2	π(Ac)
H-5	-6.96	97	0	2	0	π(SB)

Ac = CH_3COO, SB= reduced Schiff base

Table S2. Selected Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex 2.

MO	energy	contribution				assignment (major)
		SB	NCS	Ac	Zn	
L+12	2.4	79	16	1	3	π*(SB)+ π*(NCS)
L+10	2.16	59	18	2	21	π*(SB)+ π*(NCS)+d*(Zn)
L+5	0.96	38	1	6	55	π*(SB)+d*(Zn)
L+4	0.67	9	1	78	12	π*(Ac)+d*(Zn)
L+3	0.01	100	0	0	0	π*(SB)
L+2	-0.18	99	0	0	1	π*(SB)
L+1	-0.39	98	0	0	2	π*(SB)
LUMO	-0.56	99	0	0	1	π*(SB)
energy gap = 4.69 eV						
HOMO	-5.25	1	99	0	1	π(NCS)
H-1	-5.28	1	98	0	1	π(NCS)
H-2	-6.35	100	0	0	0	π(SB)
H-3	-6.51	94	0	6	0	π(SB)
H-4	-6.88	8	1	90	2	π(Ac)
H-5	-7.02	97	0	3	0	π(SB)

Ac = CH_3COO, SB= reduced Schiff base

Table S3. Frontier molecular orbital energies (eV) and compositions (%) in the lowest singlet excited state (S_1) for complex 1.

MO	energy	contribution				assignment (major)
		SB	N_3	Ac	Zn	
L+5	1.04	35	6	50	10	π*(SB)+π*(Ac)+d*(Zn)
L+4	0.78	11	1	10	78	π*(SB)+π*(Ac)+d*(Zn)
L+3	0.12	99	0	1	0	π*(SB)
L+2	0.05	100	0	0	0	π*(SB)
L+1	-0.35	98	0	2	0	π*(SB)
LUMO	-0.84	99	0	1	0	π*(SB)
energy gap = 4.3 eV						
HOMO	-5.14	1	97	2	0	π(N_3)
H-1	-5.34	5	91	4	1	π(N_3)
H-2	-5.99	97	0	0	3	π(SB)

H-3	-6.31	99	0	0	0	π(SB)
H-4	-6.76	5	1	2	93	d(Ir)
H-5	-6.98	98	0	0	2	π(SB)

Ac = CH_3COO, SB= reduced Schiff base

Table S4. Frontier molecular orbital energies (eV) and compositions (%) in the lowest singlet excited state (S_1) for complex 2.

MO	energy	contribution				assignment (major)
		SB	NCS	Ac	Zn	
L+5	1.01	37	2	5	55	π*(SB)+d*(Zn)
L+4	0.62	7	1	82	10	π*(Ac)+d*(Zn)
L+3	0.04	99	0	0	1	π*(SB)
L+2	0.01	100	0	0	0	π*(SB)
L+1	-0.4	98	0	0	2	π*(SB)
LUMO	-0.92	99	0	0	1	π*(SB)
		energy gap = 4.35 eV				
HOMO	-5.27	1	99	0	1	π(NCS)
H-1	-5.29	1	98	0	1	π(NCS)
H-2	-6.06	97	0	2	0	π(SB)
H-3	-6.35	100	0	0	0	π(SB)
H-4	-6.93	8	1	89	2	π(Ac)
H-5	-7.03	96	0	4	0	π(SB)

Ac = CH_3COO, SB= reduced Schiff base

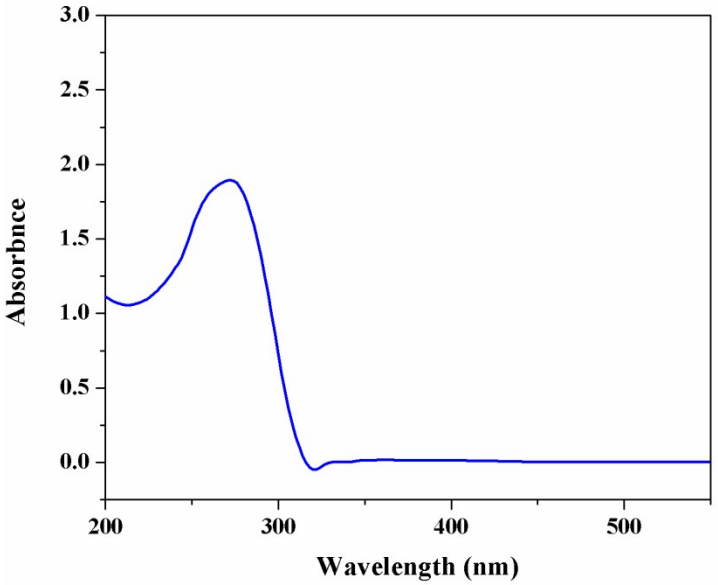


Fig. S1. UV-Vis spectrum of the ligand (H_2L).

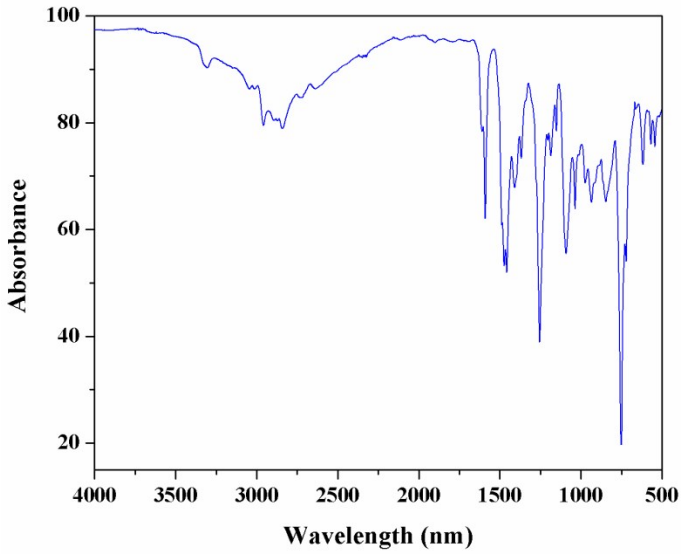


Fig. S2. IR spectrum of the ligand (H_2L)

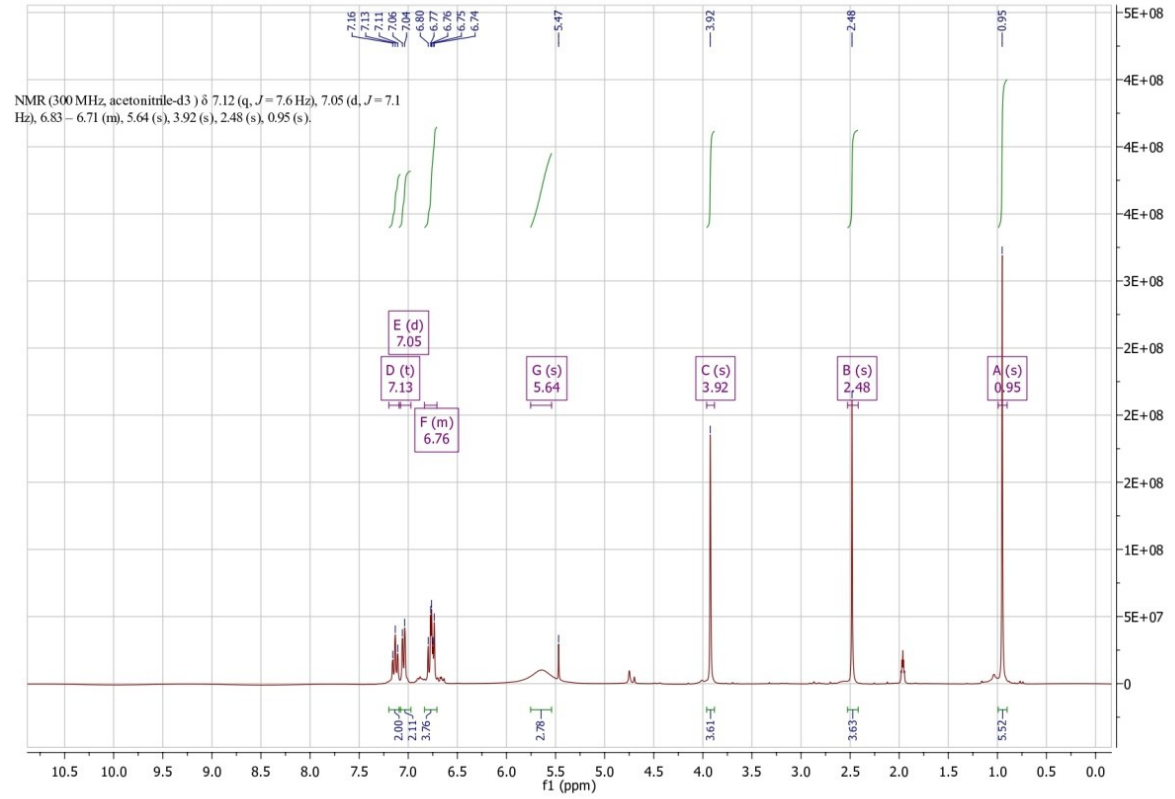


Fig. S3. NMR spectrum of the ligand (H_2L)

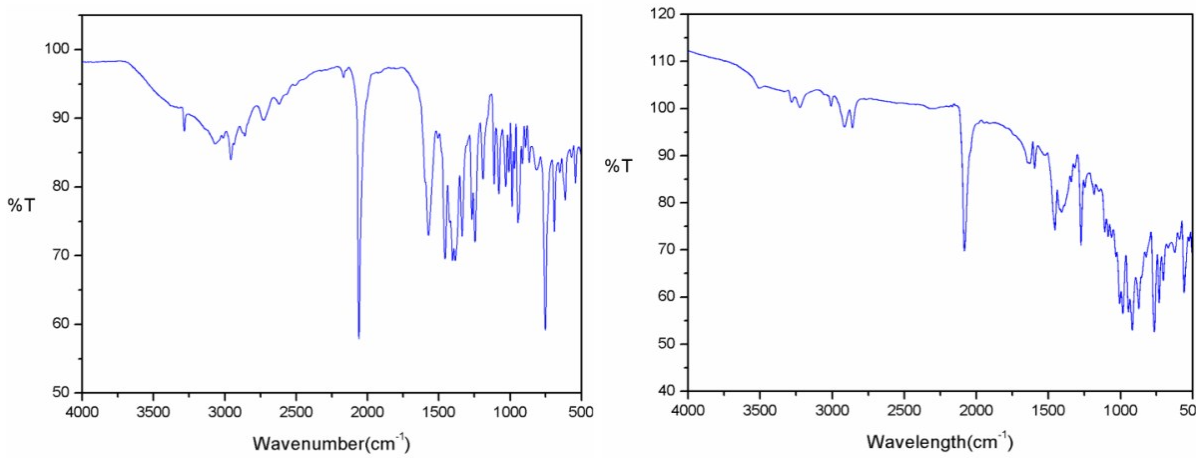


Fig. S4. IR spectra for complexes **1** (left) and **2** (right).

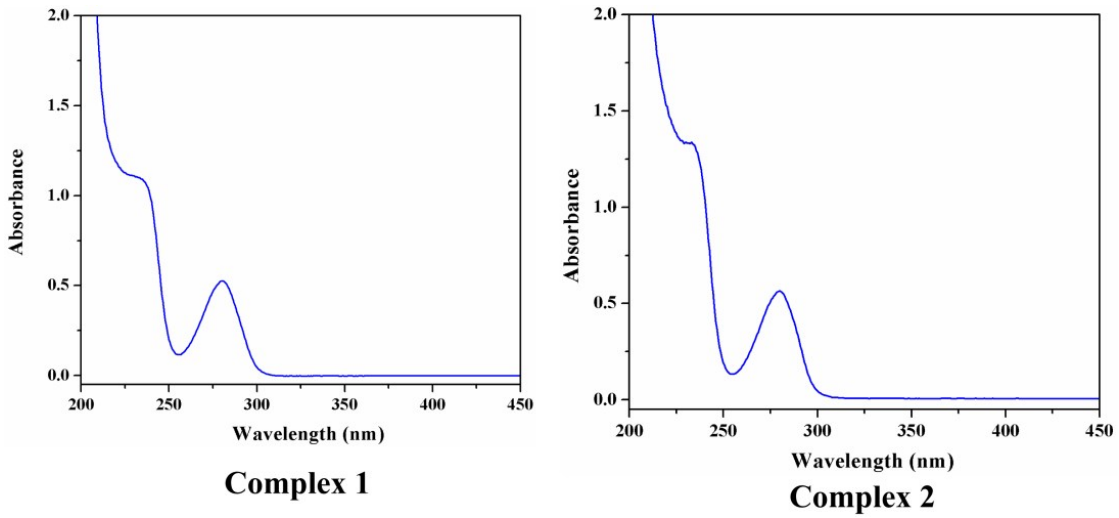


Fig. S5. UV-Vis absorption spectra of complexes **1** (left) and **2** (right).

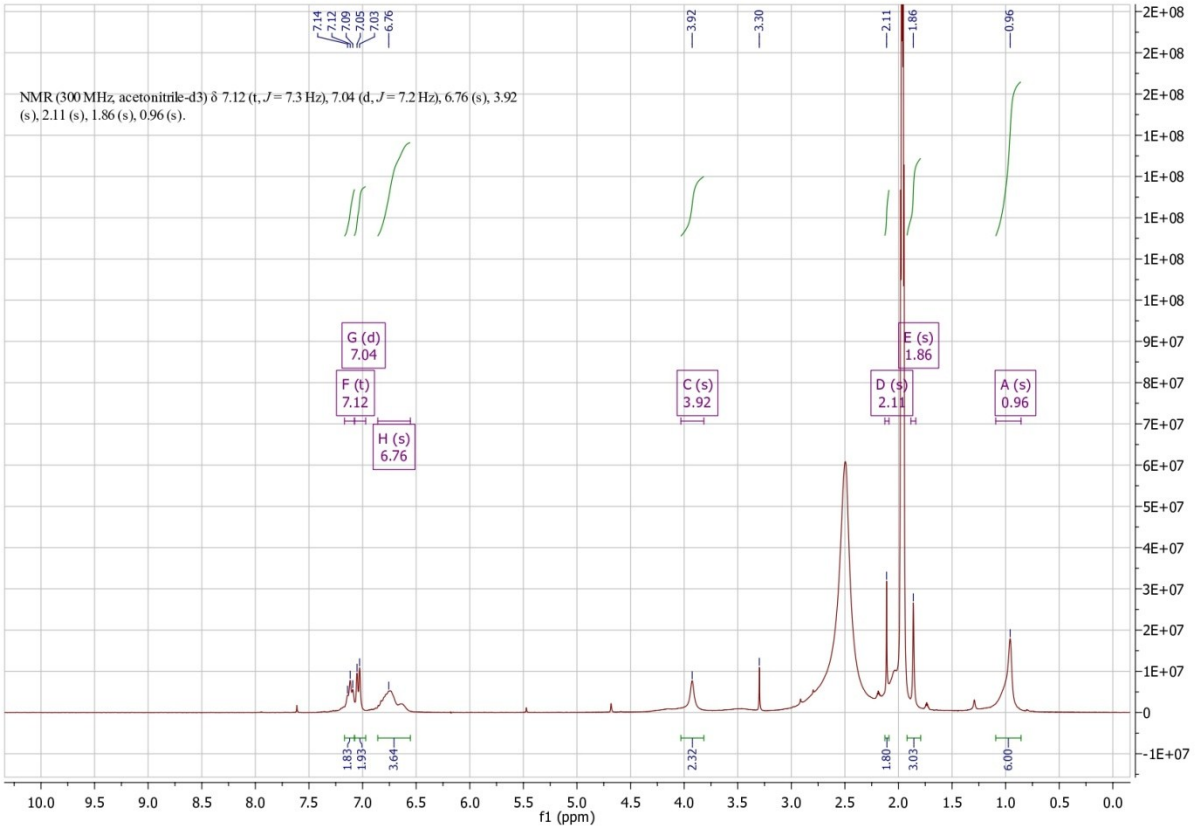


Fig. S6. NMR spectrum of complex **1**.

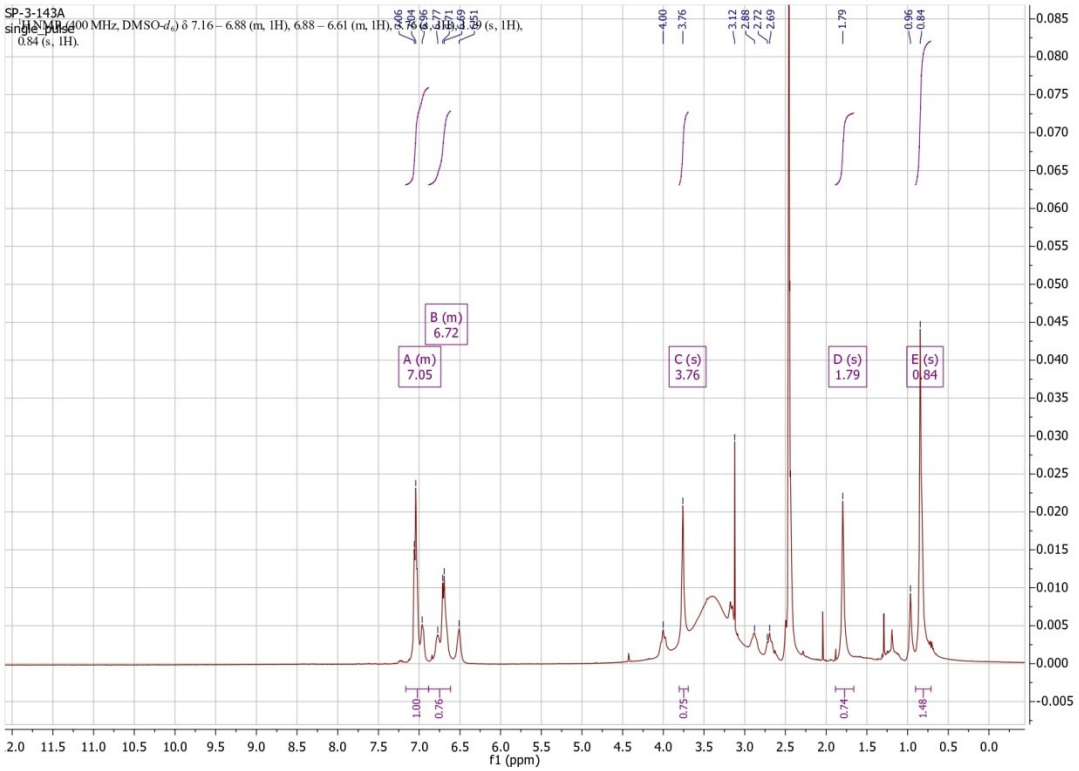
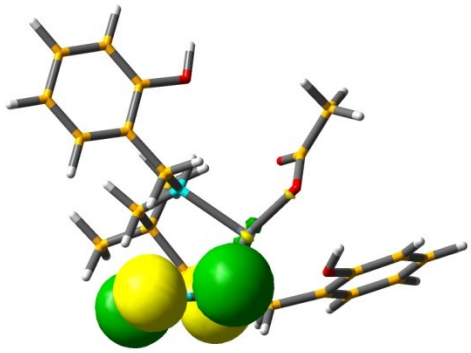


Fig. S7. NMR spectrum of complex **2**.



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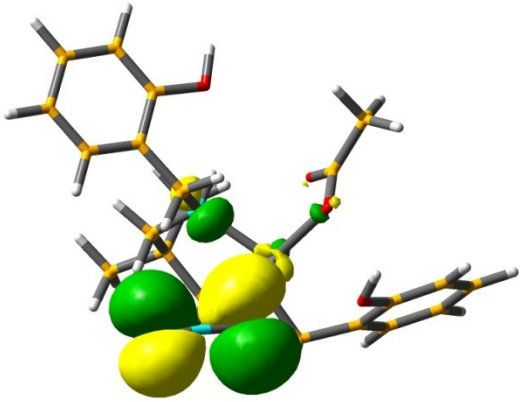

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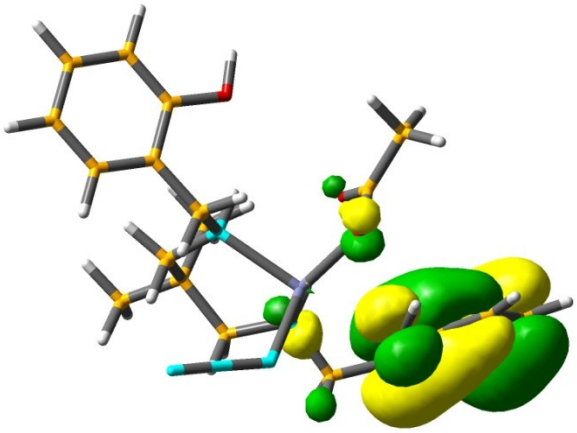

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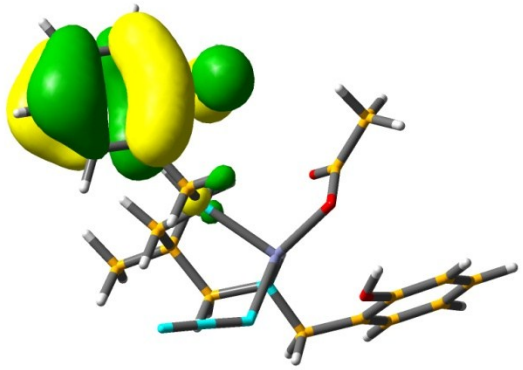

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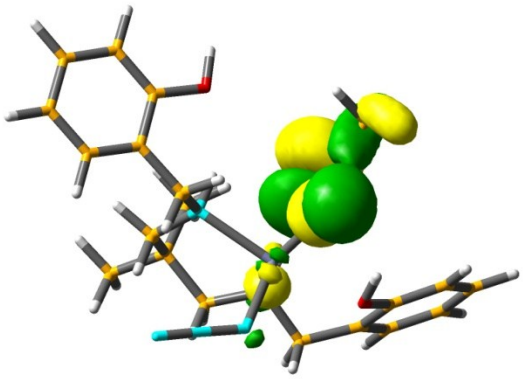

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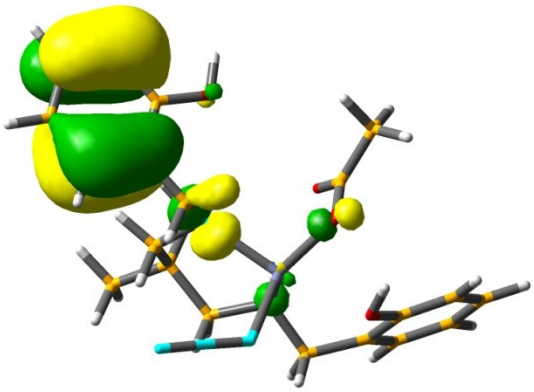

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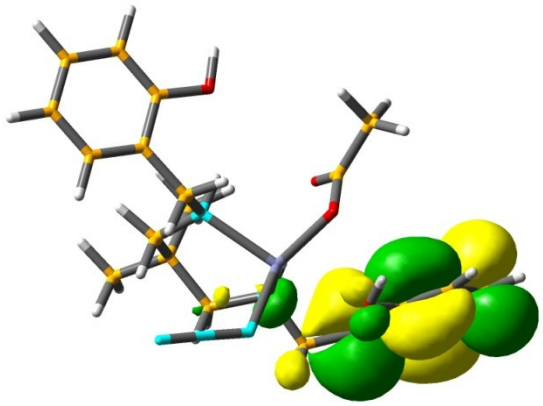

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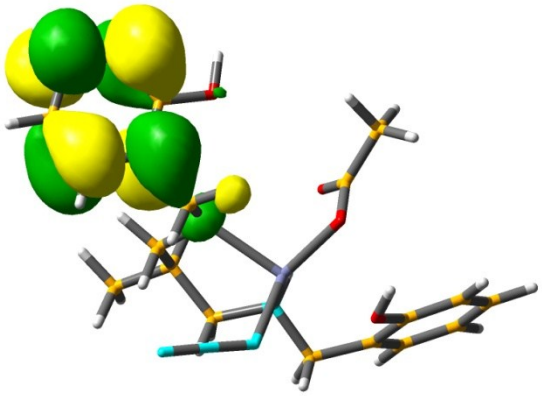

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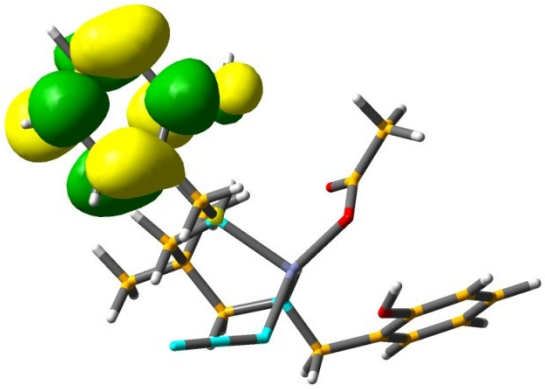

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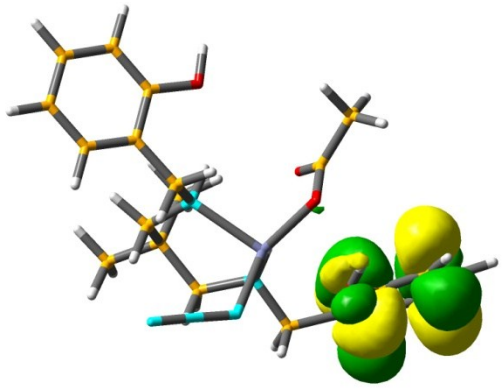

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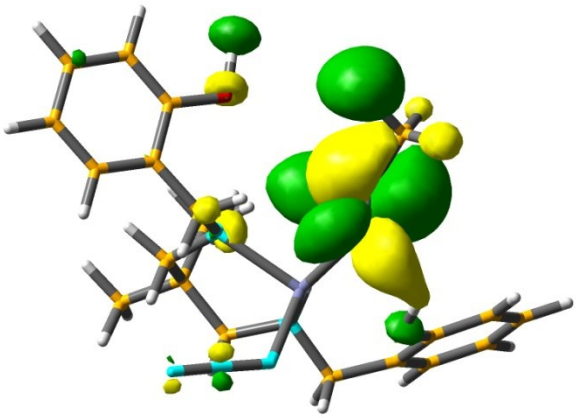

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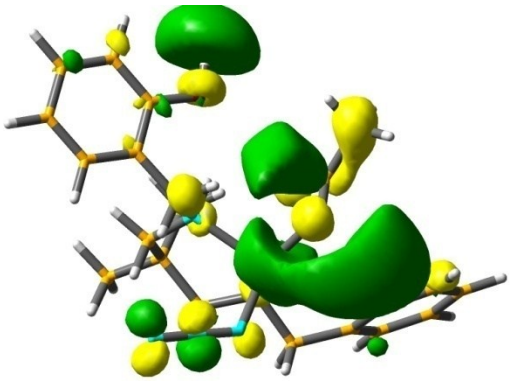

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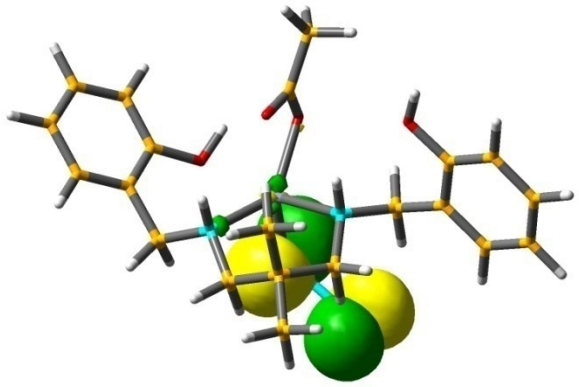
Fig. S8. Excited states of the complex **1**



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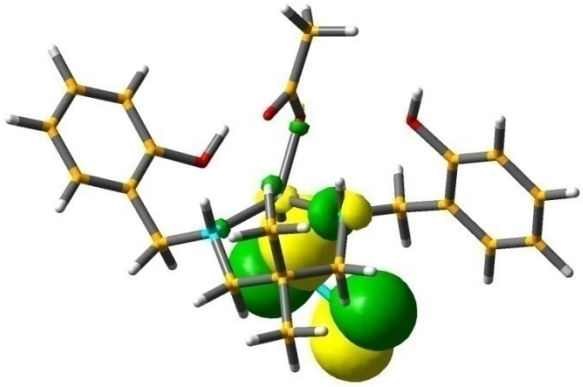

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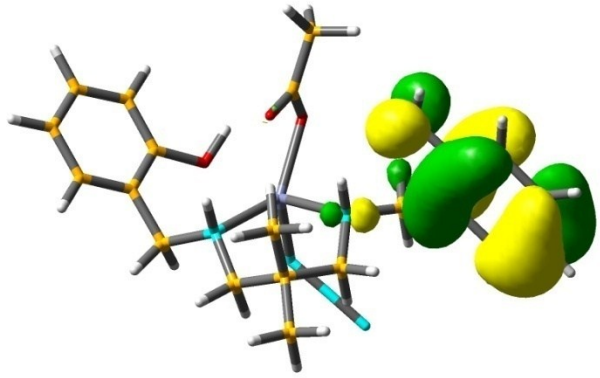

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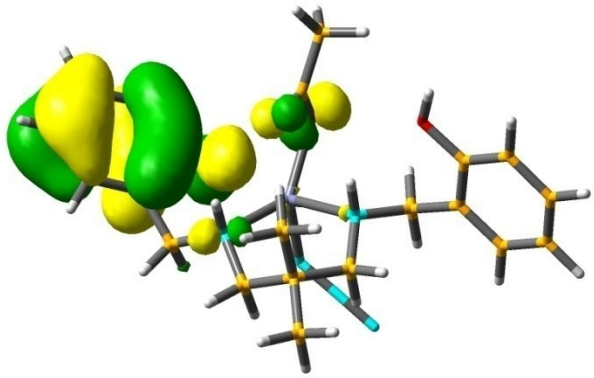

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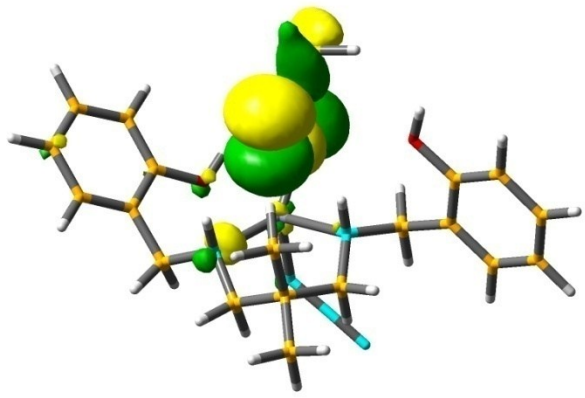

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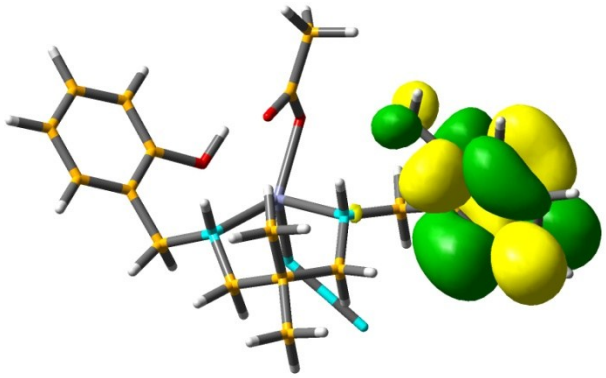

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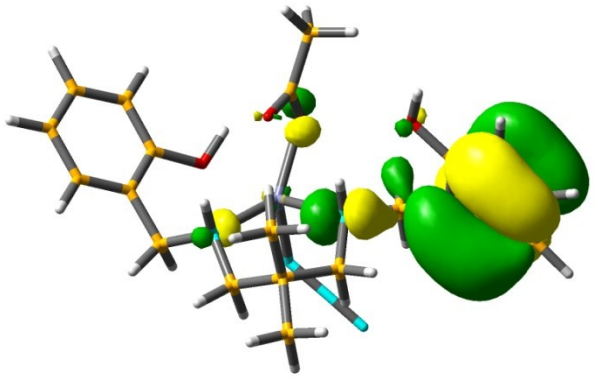

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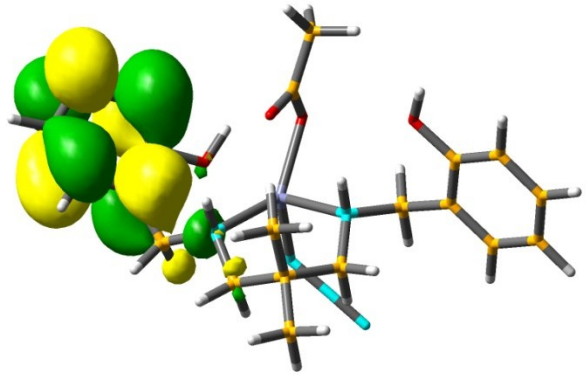

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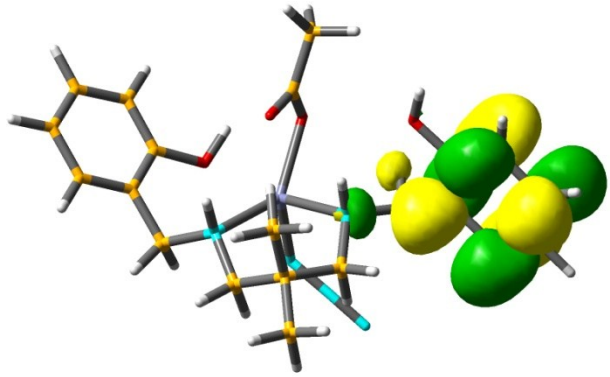

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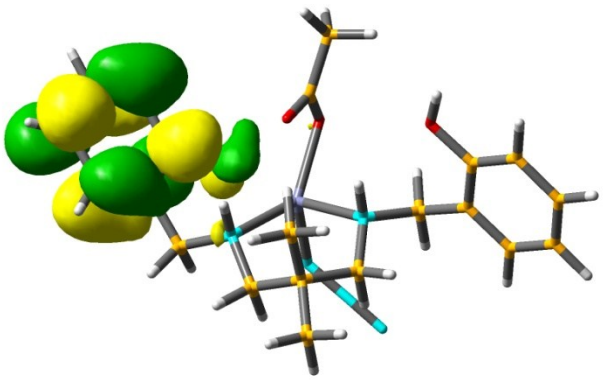

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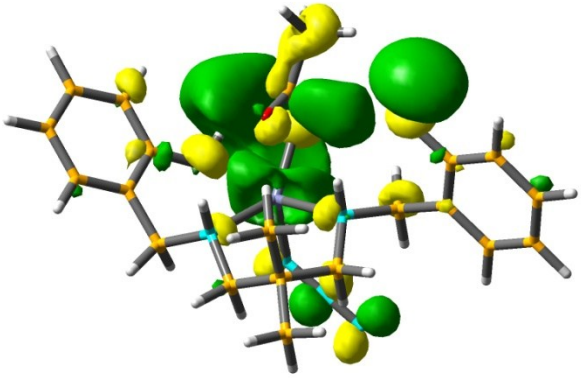

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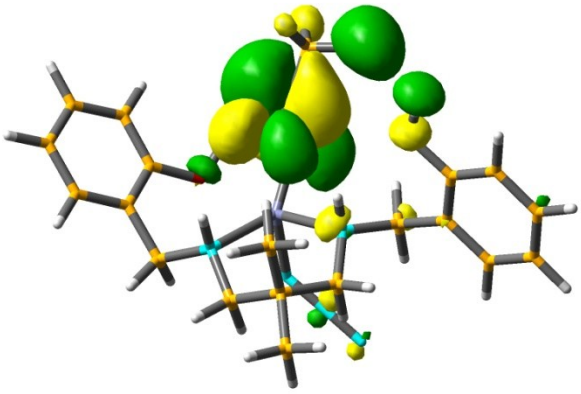

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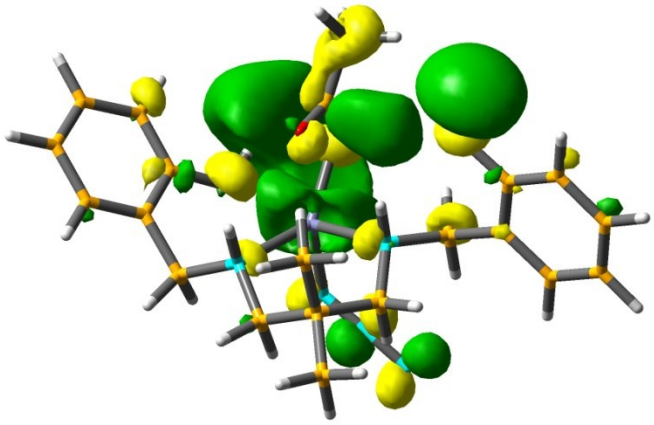

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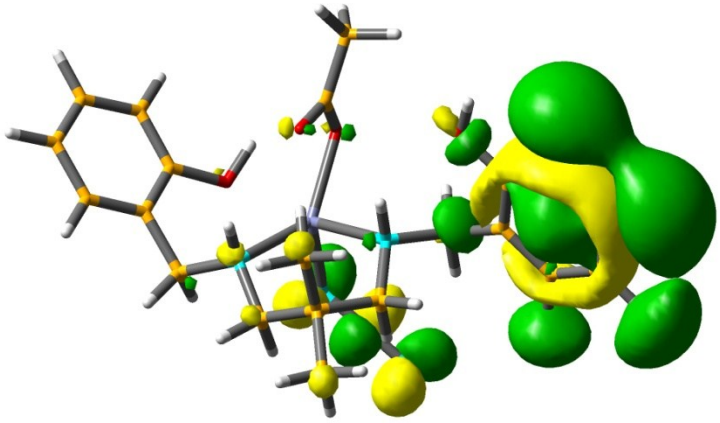

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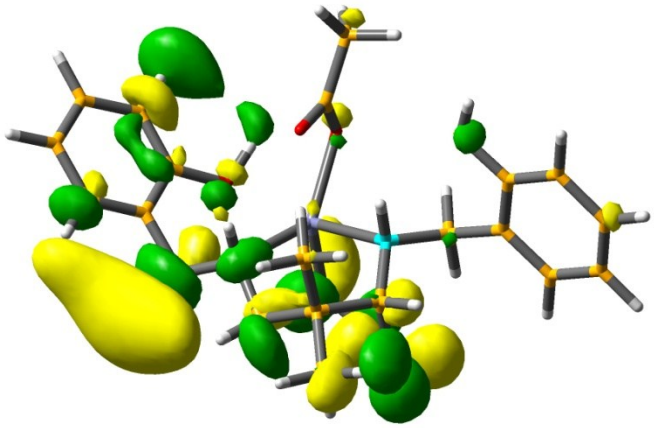

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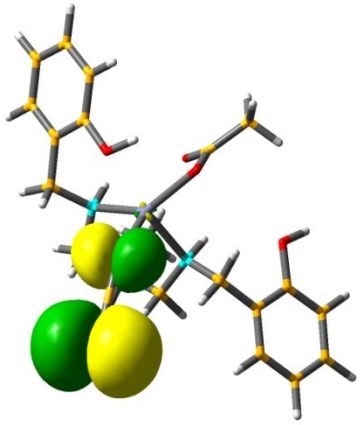
Fig.S9. Ground states of the complex **1.**



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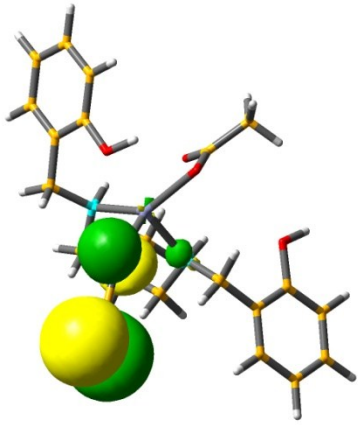

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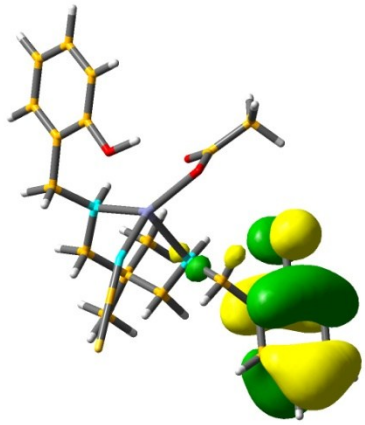

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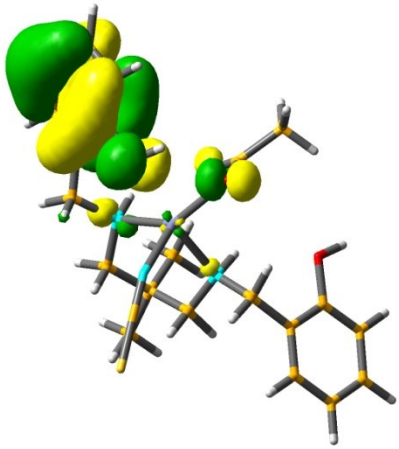

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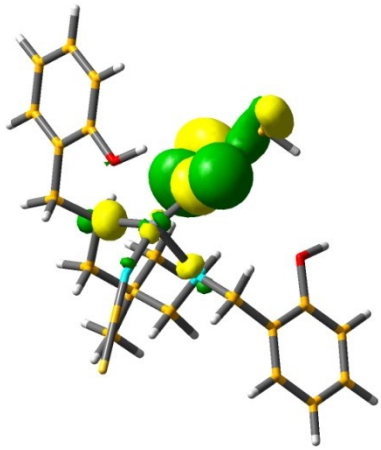

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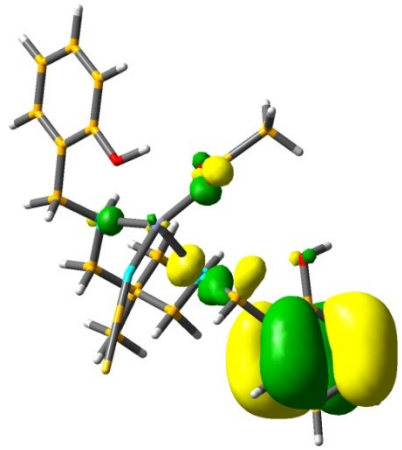

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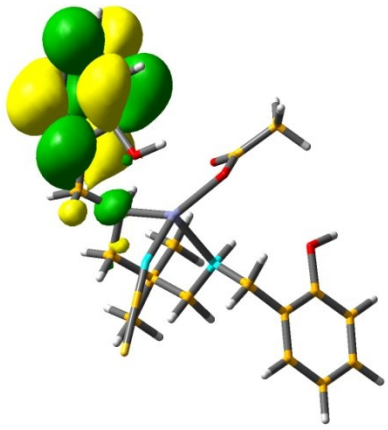

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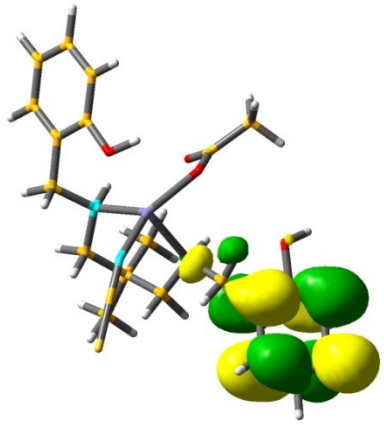

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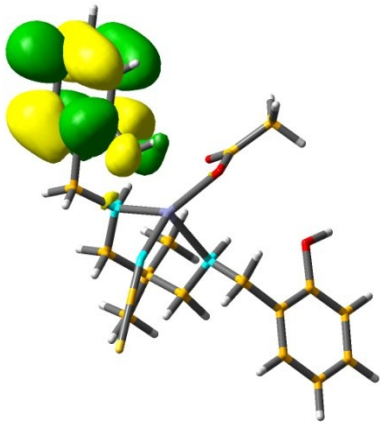

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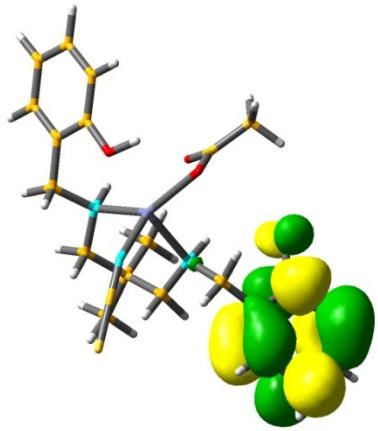

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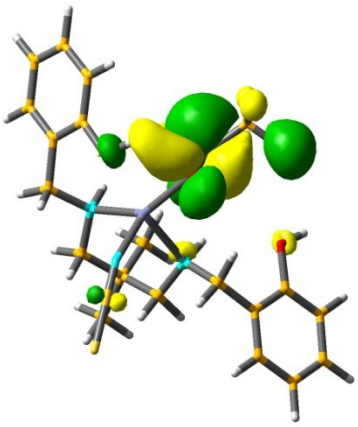

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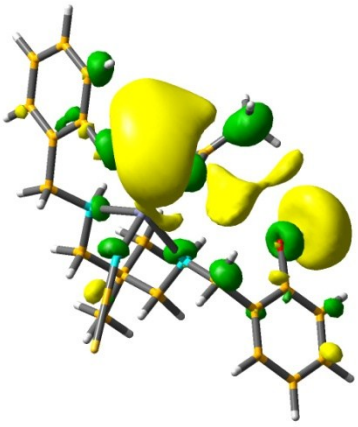
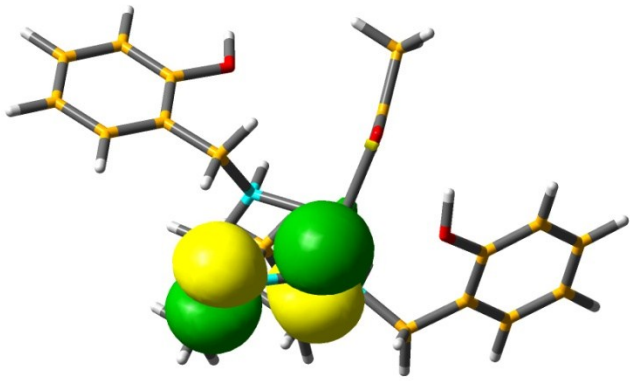


L+5

Fig. S10. Excited states of the complex **2**



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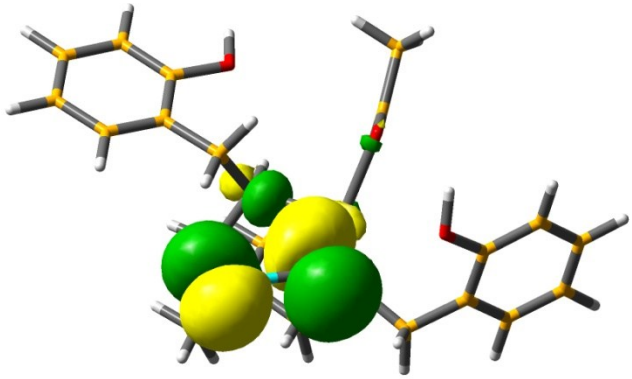
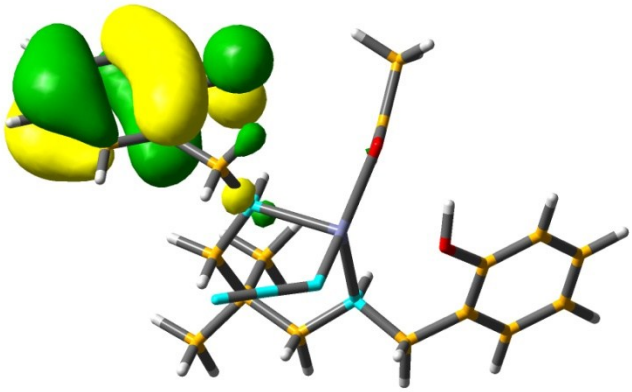
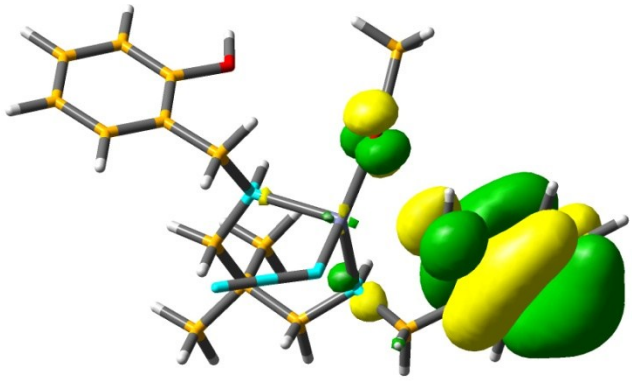


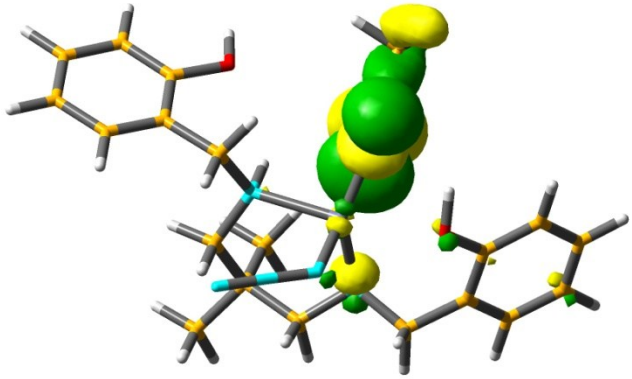
H-1



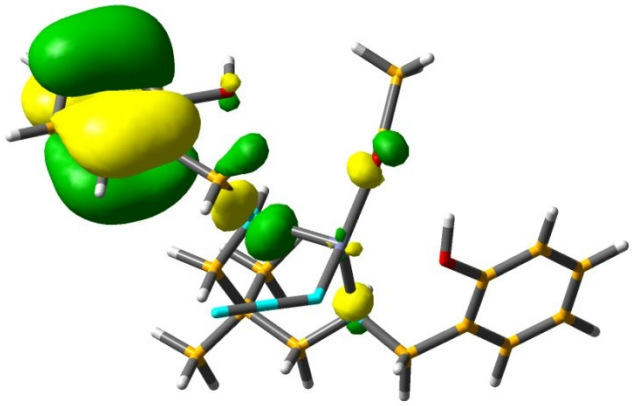
H-2



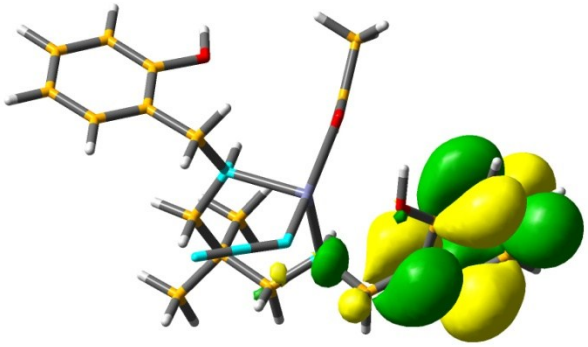
H-3



H-4



H-5



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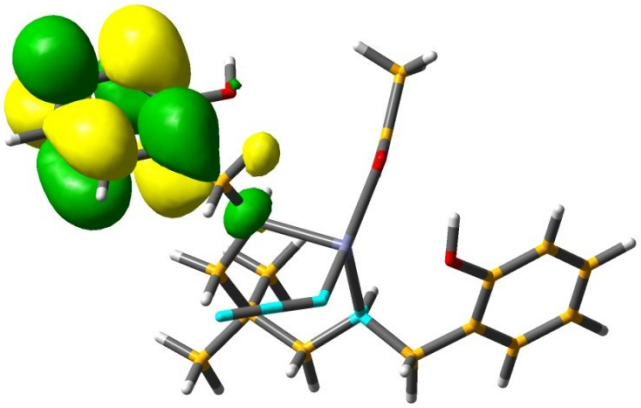
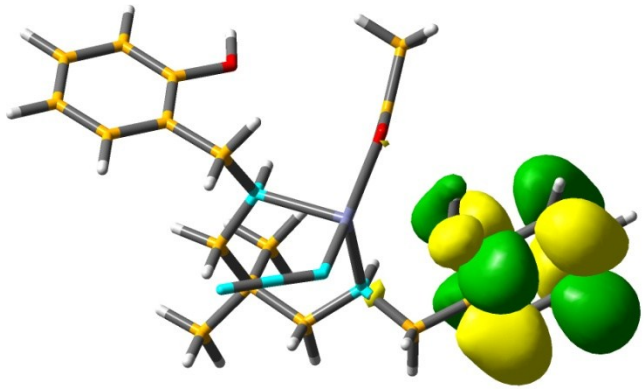
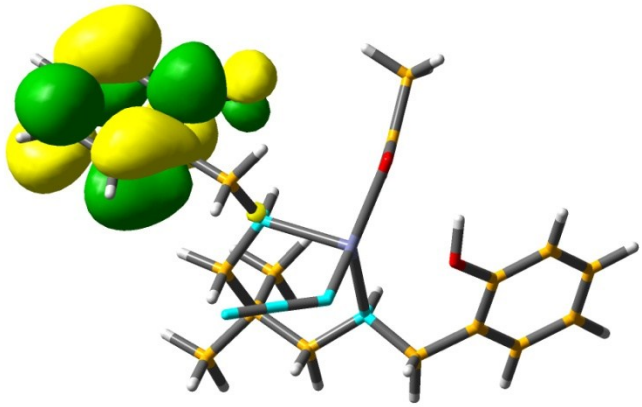


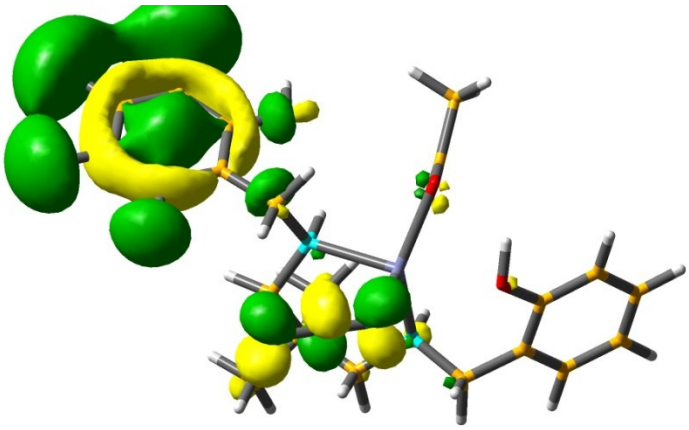
L+1



L+2



L+3



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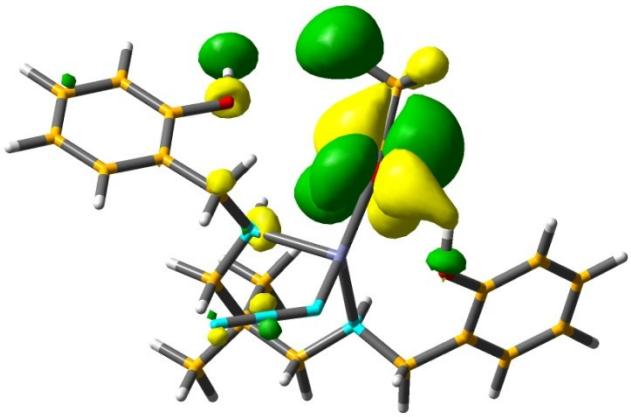

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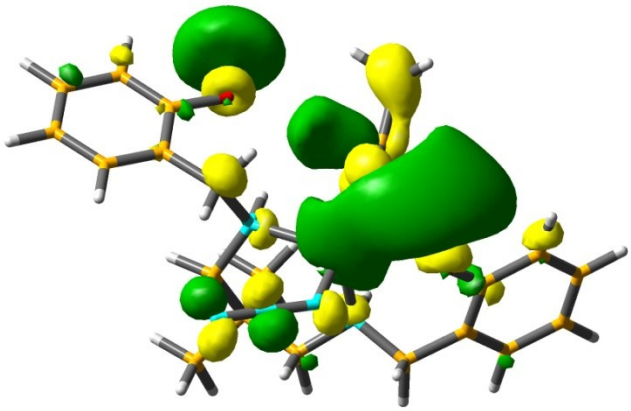
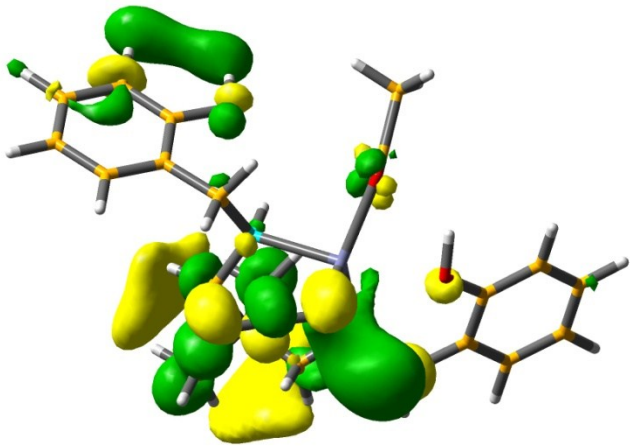


L+10



L+12

Fig. S11. Ground states of the complex **2**