Supporting Information

Design of Synthetic Superoxide Dismutase Mimetics: Seven-Coordinate Water Soluble Manganese(II) and Iron(II) Complexes and Their Superoxide Dismutase Like Activity Studies

Ovender Singh[a], Nidhi Tyagi[a], Marilyn M. Olmstead[b], Kaushik Ghosh[a]*

[a]Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee-247667 Uttarakhand INDIA. Fax: +91-1332-273560; Tel+91-1332-275547

E-mail: ghoshfcy@iitr.ernet.in

[b]Department of Chemistry, University of California, One Shields Avenue, Davis, CA 95616, USA.

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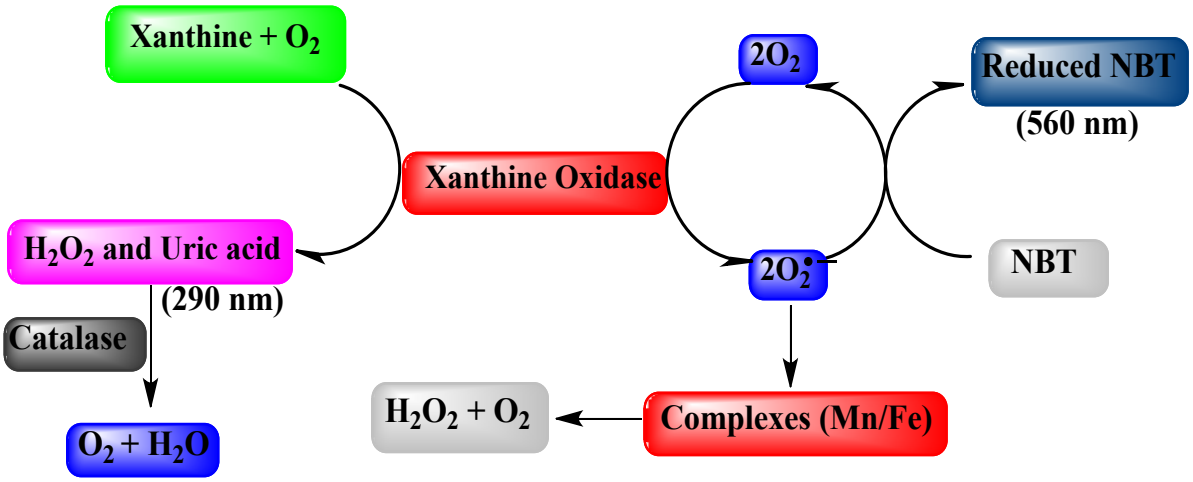

Chart S1. Schematic diagram of superoxide dismutase activity.

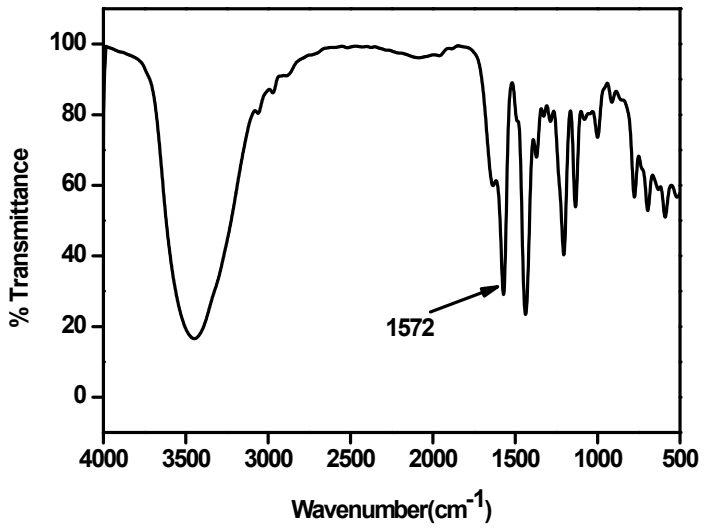

Fig. S1 IR spectrum of ligand N_5Py

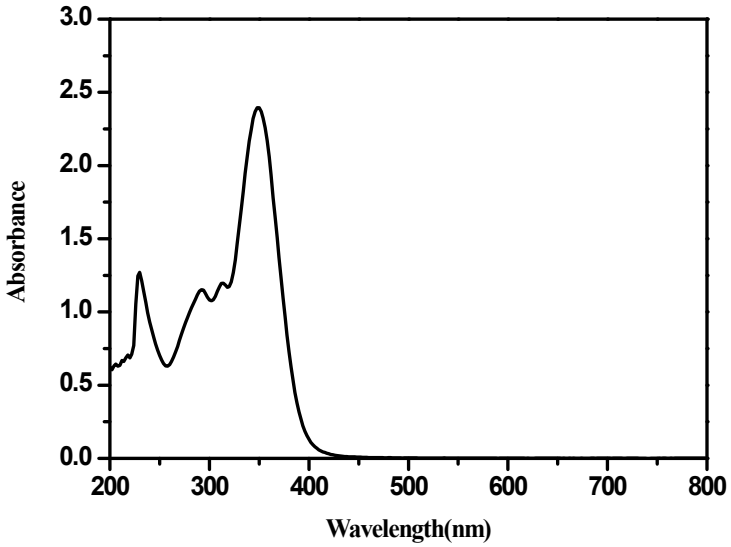

Fig. S2 UV-visible spectrum of ligand N_5Py

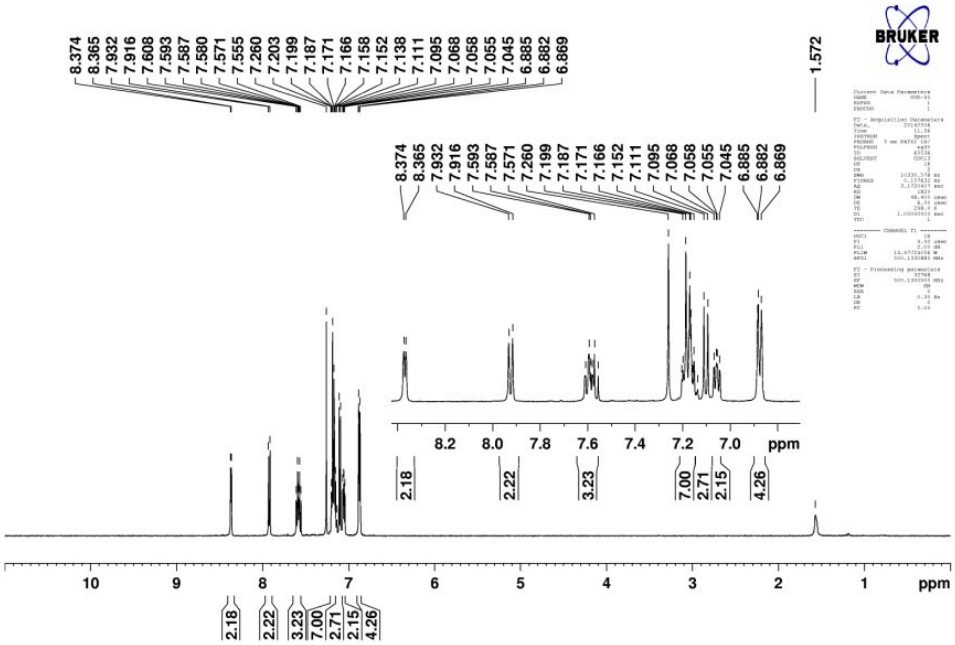

Fig. S3 ^1H NMR spectra of ligand N_5Py in $CDCl_3$

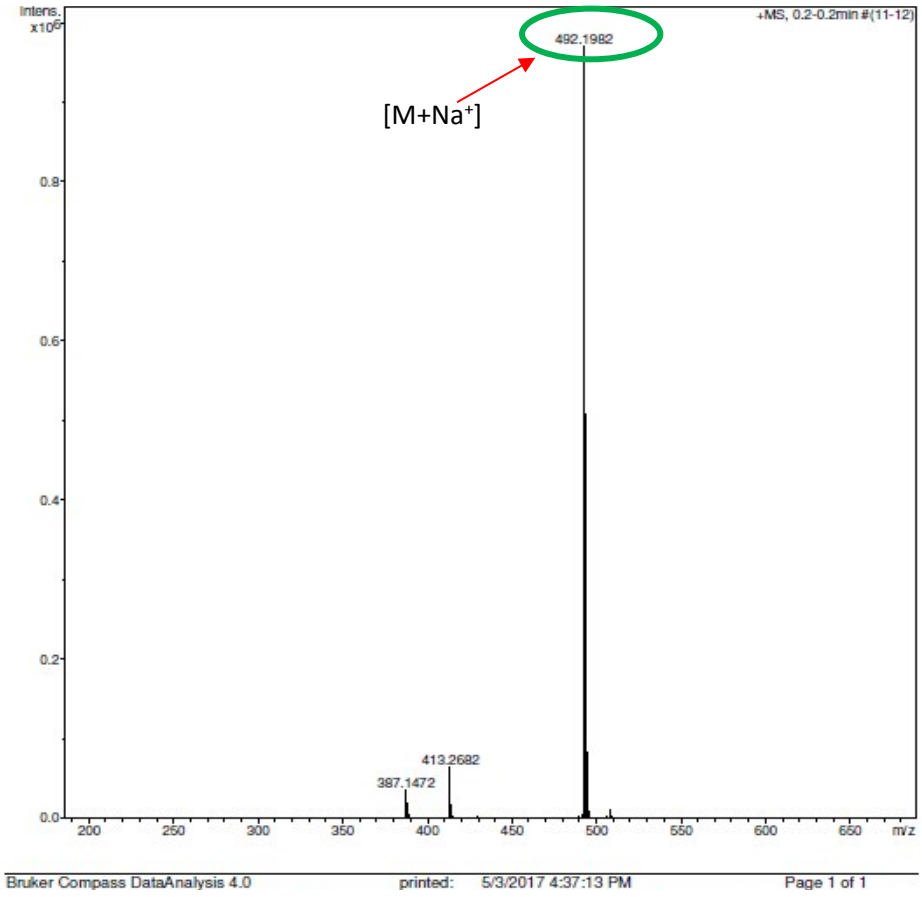

Fig. S4HRMS spectra of ligand N_5Pyin acetonitrile

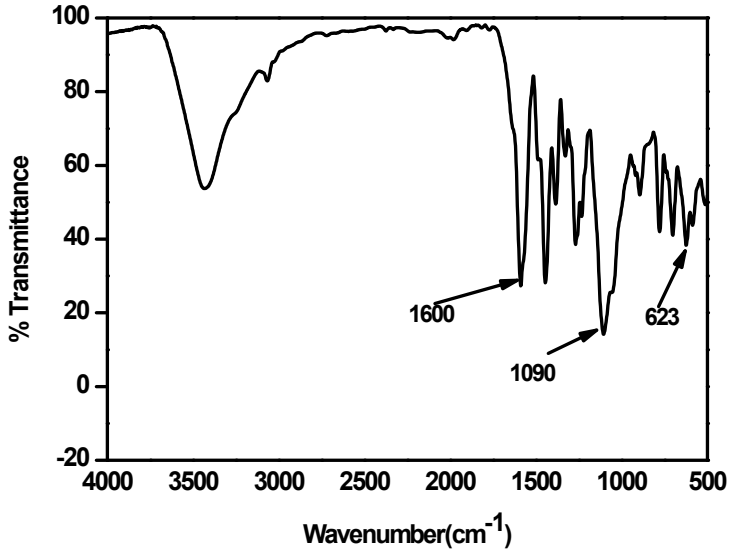

Fig. S5 IR spectrum of complex **1**

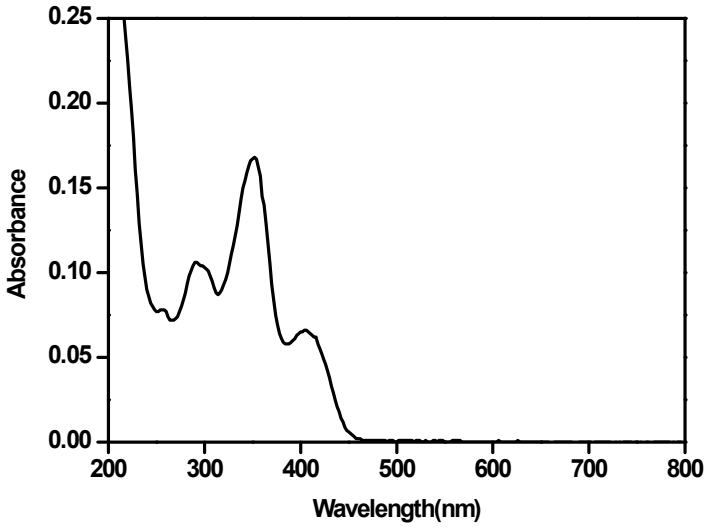

Fig. S6UV-visible spectrum of complex **1** $[Mn(N_5Py)(H_2O)(CH_3OH)](ClO_4)_2$

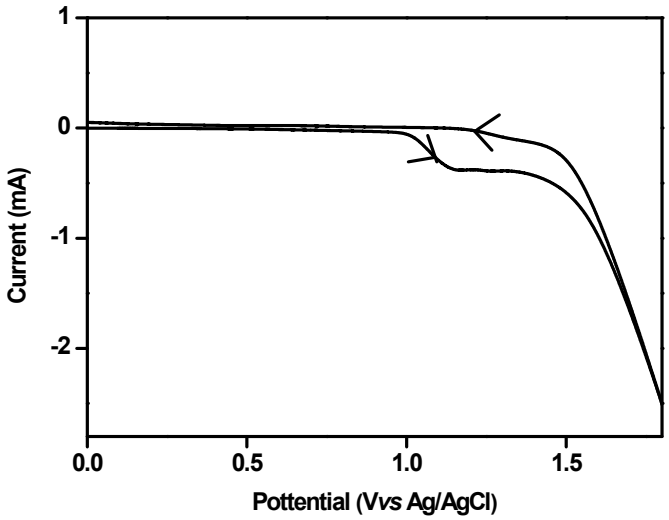

Fig. S7 Cyclic voltammograms of a 10^{-3} M solution of complex **1** in DMSO in presence of 0.1 M tetrabutylammonium perchlorate (TBAP), using working electrode: glassy-carbon, reference electrode: Ag/AgCl; auxiliary electrode:platinum wire, scan rate 0.1 Vs^{-1}.

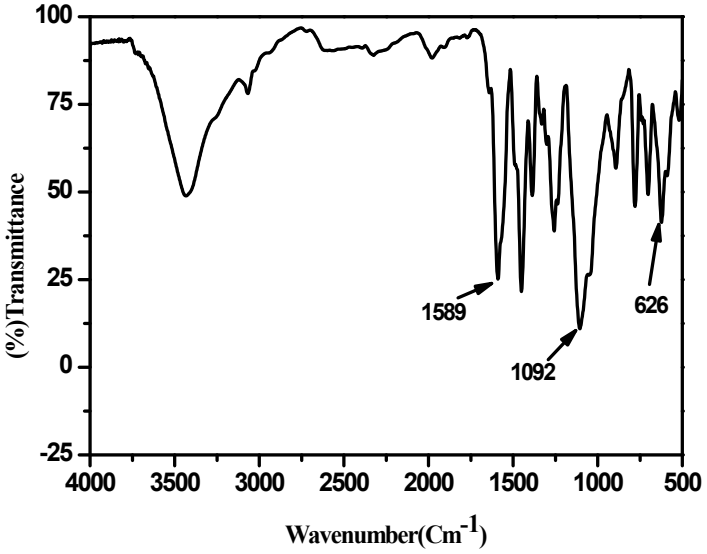

Fig. S8 IR spectrum of complex **2**

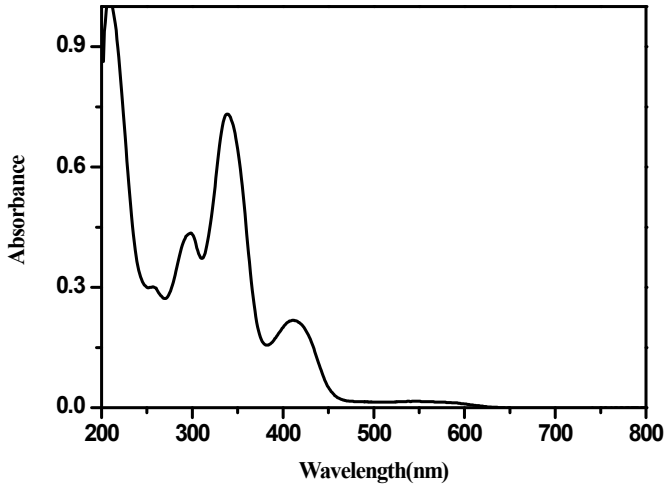

Fig. S9UV-visible spectrum of complex**2**, $[Fe(N_5Py)(H_2O)(ClO_4)]ClO_4$.

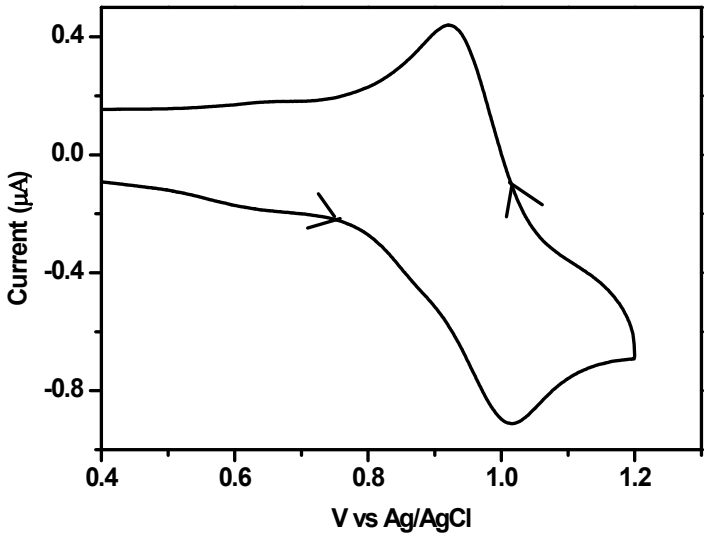

Fig. S10 Cyclic voltammograms of a 10^{-3} M solution of complex **2** in DMSO in presence of 0.1 M tetrabutylammonium perchlorate (TBAP), using working electrode: glassy-carbon, reference electrode: Ag/AgCl; auxiliary electrode:platinum wire, scan rate 0.1 Vs^{-1}.

Table S1. Electrochemical data for M^{II}/M^{III} redox couple 298 K[a] vs Ag/ AgCl. (M = Mn and Fe)

Complexes	M^{II}/M^{III}			
	E_{pa}/V	E_{pc}/V	$E_{1/2}$ [b],V (ΔE_p[c], mV)	[d]n = i_{Pa}/i_{Pc}
1	1.14	.....	.....	.....
2	1.01	0.92	0.96(90)	2.068

[a] Electrochemical data measured in DMSO with 0.1m tetrabutylammonium perchlorate (TBAP). [b]Data from cyclic voltammetric measurements; $E_{1/2}$ is calculated as average of anodic (E_{pa}) and cathodic (E_{pc}) peak potentials $E_{1/2}=1/2(E_{pa}+E_{pc})$; and [c] $\Delta Ep = E_{pa} - E_{pc}$ at scan rate 0.1 Vs^{-1}, [d] Constant-potential coulometric data $n=i_{pa}/ i_{pc}$ calculated for $1e^-$transfer.

Table S2. Crystallographic parameters of complex **1** and **2**

Complex	**Complex 1**	**Complex 2**
Colour	Orange	Red
Empirical formula	C30 H29 Mn N7 O2, 2(Cl O4)	C29 H25 Cl Fe N7 O5, (Cl O4)
Formula weight [g mol^{-1}]	773.44	742.31
Temperature [K]	90(2)	296(2)
λ [Å] (Mo-Kα)	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	*P-1*	*P21/n*
a [Å]	9.3017(5)	16.2831(10)
b [Å]	14.0136(7)	8.1985(5)
c [Å]	14.6344(8)	24.4790(14)
α [º]	111.6887(7)	90.00
β [º]	103.5835(7)	101.909(3)
γ [º]	100.6113(7)	90.00
V [Å^3]	1643.62(15)	3197.5(3)
Crystal size[mm]	0.440x 0.200x 0.120	0.22x 0.22x 0.22
Z	2	4
ρcalc [gcm^{-3}]	1.563	1.542
F(000)	794	1520
θ range for data Collection	2.361-31.501	1.38-27.89
Index ranges	-13<h<13, -20<k<21, -21<l<21	-21<h<21, -10<k<10, -32<l<32
Refinement method	Full matrix least-squares on F^2	Full matrix least-squares on F^2
Data/restraints/parameters	10848/4/511	7637/0/441
GOF on F^2	1.057	1.094
R_1[b][I>2σ(I)]	0.0326	0.0431
R_1[all data]	0.0344	0.0710
wR_2[c][I> 2σ(I)]	0.0872	0.1239
wR_2 [all data]	0.0857	0.1490

[a]GOF = $[\Sigma[w(F_o^2-F_c^2)^2]/M-N)]^{1/2}$ (M = number of reflections, N = number of parameters refined). [b] $R_1 = \Sigma \| F_o| - |F_c| / \Sigma |F_o|$, [c] $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma [w(F_o^2)^2]]^{1/2}$

Table S3. Selected bond distances (Å) of complex **1**		
Bond type	**Experimental**	**Theoretical**
Mn1-O1	2.154(4)	2.244
Mn1-O2	2.220(5)	2.250
Mn1-N4	2.311(4)	2.328
Mn1-N2	2.321(3)	2.336
Mn1-N7	2.341(4)	2.395
Mn1-N6	2.356(4)	2.359
Mn1-N1	2.394(2)	2.378

Table S4. Selected bond distances (Å) of complex **2**		
Bond type	**Experimental**	**Theoretical**
Fe1-O10	2.137 (3)	2.137
Fe1-N5	2.218 (4)	2.230
Fe1-N6	2.222 (4)	2.221
Fe1-N7	2.231 (4)	2.218
Fe1-O4	2.276 (3)	2.275
Fe1-N4	2.286 (3)	2.306
Fe1-N3	2.306(3)	2.285

Table S5. Selected bond angels(°)				
Complex **1**			Complex **2**	
1	O1—Mn1—O2	173.03(13)	O10—Fe1—N6	88.95(10)
2	O1—Mn1—N4	97.68(13)	O10—Fe1—N5	94.21(10)
3	O2—Mn1—N4	87.68(10)	N6—Fe1—N5	69.50(9)
4	O1—Mn1—N2	84.58(14)	O10—Fe1—N7	86.22(10)
5	O2—Mn1—N2	93.42(10)	N6—Fe1—N7	69.33(8)
6	N4—Mn1—N2	67.68(9)	N5—Fe1—N7	138.81(9)
7	O1—Mn1—N7	83.79(13)	O10—Fe1—O4	171.92(9)
8	O2—Mn1—N7	95.7(1)	N6—Fe1—O4	88.12(9)
9	N4—Mn1—N7	134.00(9)	N5—Fe1—O4	77.71(9)
10	N2—Mn1—N7	156.7(1)	N7—Fe1—O4	99.76(9)
11	O1—Mn1—N6	105.33(14)	O10—Fe1—N4	104.67(10)
12	O2—Mn1—N6	80.84(11)	N6—Fe1—N4	136.99(9)
13	N4—Mn1—N6	66.78(10)	N5—Fe1—N4	146.39(9)
14	N2—Mn1—N6	134.26(11)	N7—Fe1—N4	71.10(9)
15	N7—Mn1—N6	68.55(10)	O4—Fe1—N4	82.53(9)
16	O1—Mn1—N1	90.79(13)	O10—Fe1—N3	80.69(10)
17	O2—Mn1—N1	82.25(10)	N6—Fe1—N3	138.43(8)
18	N4—Mn1—N1	135.35(10)	N5—Fe1—N3	71.27(8)
19	N2—Mn1—N1	69.66(10)	N7—Fe1—N3	148.33(9)
20	N7—Mn1—N1	90.38(10)	O4—Fe1—N3	96.58(9)
21	N6—Mn1—N1	151.34(10)	N4—Fe1—N3	84.46(9)

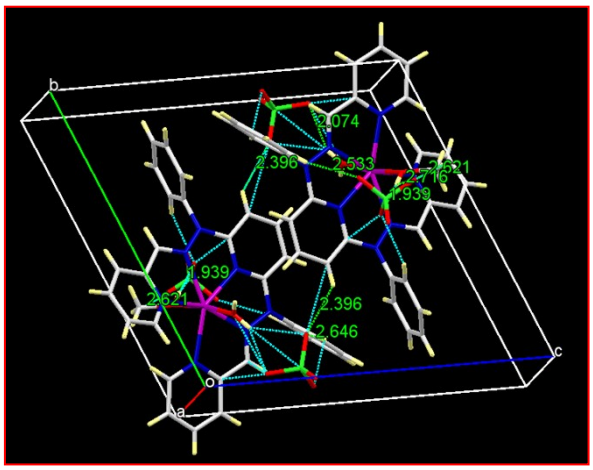

Fig. S11 Packing diagram of complex **1** showing the short interaction and hydrogen bonding with the neighbor atoms**.**

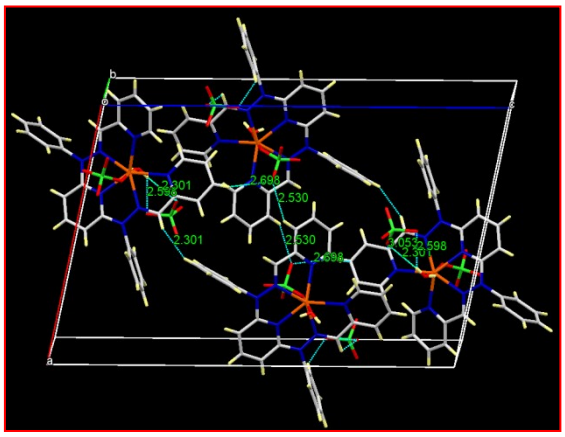

Fig. S12 Packing diagram of Complex **2**showing the short interaction and hydrogen bonding with the neighbor atoms.

Theoretical calculation:

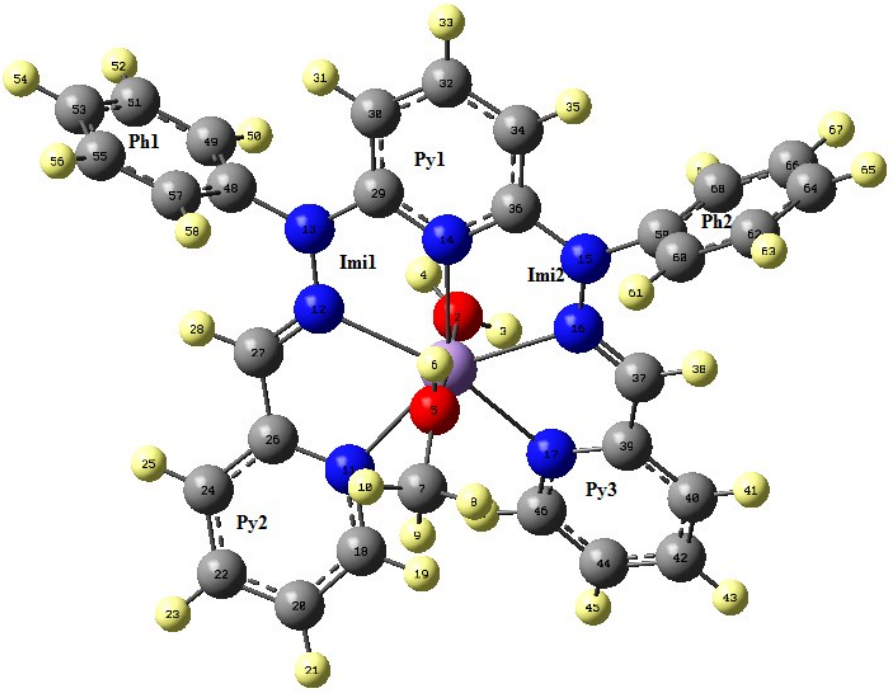

Fig . S13 Ground state optimized geometry of complex **1** usingB3LYP/LANL2DZ.

Table S6. Cartesian coordinates for complex **1**

Atomtypes=5

Charge=25.0 Atoms=1

Mn 0.011929000 0.849144000 -0.091194000

Charge=8.0 Atoms=2

O 0.316859000 0.906711000 -2.313883000

O -0.226238000 0.612828000 2.134154000

Charge=7.0 Atoms=7

N 1.571843000 2.570788000 0.417217000

N 2.175361000 -0.033833000 -0.100682000

N 2.351062000 -1.393556000 -0.243956000

N 0.004698000 -1.479282000 -0.056050000

N -2.344122000 -1.389811000 0.083616000

N -2.173418000 -0.039425000 -0.121373000

N -1.573020000 2.527772000 -0.731154000

Charge=6.0 Atoms=30

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C 2.304708000 4.811411000 1.012860000

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C 3.940950000 3.127526000 0.429302000

C 2.886403000 2.206951000 0.256551000

C 3.178106000 0.796750000 -0.021021000

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C 1.217253000 -3.575277000 -0.202853000

C 0.000007000 -4.268004000 -0.101490000

C -1.216176000 -3.574764000 0.010603000

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C -3.177848000 0.790328000 -0.181439000

C -2.888235000 2.186235000 -0.526143000

C -3.935153000 3.110376000 -0.722778000

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C 5.552665000 -2.813065000 -1.612292000

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C -5.508463000 -2.750712000 1.590059000

C -6.214100000 -3.131677000 0.431177000

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H 0.991019000 0.432831000 -2.836287000

H -0.294454000 -0.326026000 2.398959000

H -1.231191000 1.448439000 3.806080000

H -0.092343000 2.516865000 2.935052000

H 0.544581000 1.242591000 4.009485000

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H 2.032018000 5.812966000 1.327913000

H 4.446244000 5.171868000 0.946585000

H 4.968133000 2.806313000 0.284033000

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H -0.001419000 -5.353658000 -0.115853000

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H -2.017142000 5.715793000 -1.823162000

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H	3.737297000	-1.989943000	-2.473156000
H	6.017259000	-3.008603000	-2.574288000
H	7.218570000	-3.589545000	-0.466199000
H	6.146469000	-3.158627000	1.745529000
H	3.867312000	-2.139649000	1.852539000
H	-3.675746000	-1.884887000	2.369196000
H	-5.949292000	-2.904175000	2.570725000
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H	-6.184599000	-3.239934000	-1.734277000
H	-3.910199000	-2.224281000	-1.940888000

Table S7. Percentage contribution of complex **1** in different orbitals

Alpha molecular orbital percentage contribution											
Orbitals	**MeOH**	**Fe**	**Imi1**	**Ph1**	**Py1**	**Py2**	**Py3**	**Ph1**	**H2O**	**Imi2**	**Main bond type**
LUMO+2	0	19	2	33	6	3	5	30	0	1	3d (Fe) + π* L
LUMO+1	0	56	2	10	3	16	2	10	0	21	3d (Fe) + π* L
LUMO	0	16	1	2	1	31	40	6	0	2	3d (Fe) + π*L
HOMO	0	52	5	1	7	13	15	2	0	5	3d (Fe) + π L
HOMO-1	0	62	4	6	5	6	7	5	0	5	3d (Fe) + π L
HOMO-2	0	55	5	0	2	17	16	0	0	4	3d (Fe) + π L
Beta molecular orbital percentage contribution											
LUMO+2	0	55	5	0	2	17	16	0	0	4	3d (Fe) + π* L
LUMO+1	0	32	11	0	19	11	14	0	0	13	3d (Fe) + π* L
LUMO	1	47	10	0	4	15	14	0	0	8	3d (Fe) + π*L
HOMO	0	0	24	1	35	7	7	1	0	25	π L
HOMO-1	0	1	31	2	14	10	10	2	0	31	3d (Fe) + π L
HOMO-2	0	0	7	2	31	24	25	2	0	7	π L

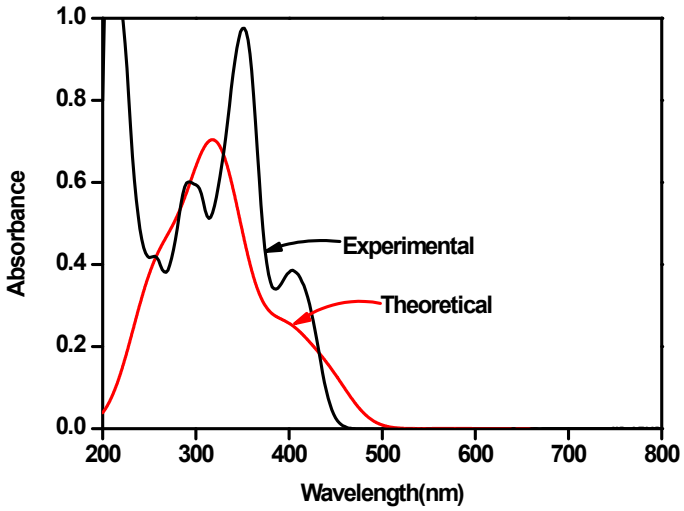

Fig . S14 UV-visible spectrum of complex **1** experimental as well as theoretical calculation

Table S8. Major transition along with their orbital contribution in complex **1**

λ_{max} (nm)	f (Osc. Strength)	Transition and their contributions
291	0.0011	H-8(A)→L+1(A) (34%), H-7(A)→L+1(A) (32%), H-2(A)→L+1(A) (15%) H-6(A)→LUMO(A) (6%), H-6(A)→L+1(A) (2%)
351	0.0041	H-6(A)→L+1(A) (17%), H-3(A)→L+1(A) (37%), H-2(A)→LUMO(A) (20%) H-8(A)→LUMO(A) (6%), H-4(A)→L+1(A) (4%), H-2(A)→L+1(A) (2%), H-1(A)→LUMO(A) (2%), H-1(A)→L+1(A) (6%)
441	0.1134	HOMO(A) →LUMO(A) (50%), HOMO(B)→LUMO(B) (50%)

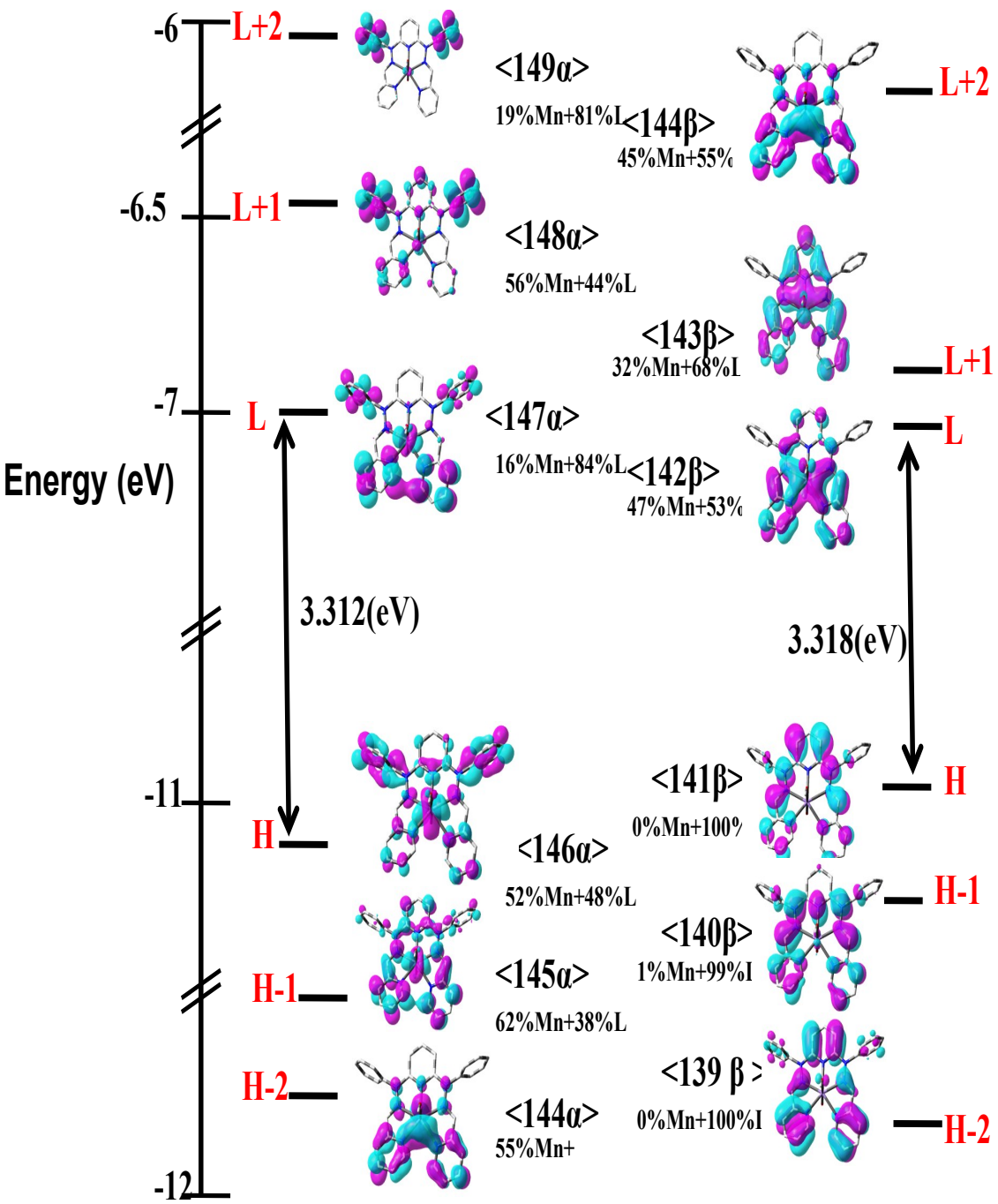

Fig.S15 Frontier molecular orbitals of complex **1** showing significant contribution of manganese and ligand (N_5Py) in molecular orbitals.

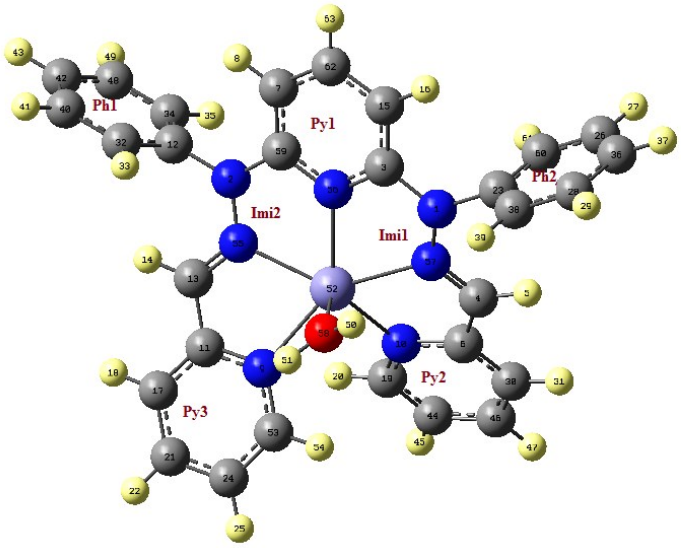

Fig. S16 Ground state optimized geometry of complex **2** using B3LYP/LANL2DZ.

Table S9. Cartesian coordinates for complex **2**

Atomtypes=5

Charge=26.0 Atoms=1

Fe -0.033807000 0.783410000 -0.250897000

Charge=8.0 Atoms=1

O 0.400083000 0.944042000 -2.340124000

Charge=7.0 Atoms=7

N 2.461994000 -1.078974000 -0.306041000

N -2.170975000 -1.464527000 0.195516000

N -1.567985000 2.397015000 -0.783914000

N 0.974047000 2.436019000 0.855091000

N -2.070650000 -0.111083000 -0.038826000

N 0.147236000 -1.387439000 -0.086803000

N 2.112550000 0.221030000 -0.016094000

Charge=6.0 Atoms=29

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C	-0.885539000	-3.569350000	0.090808000
C	-2.873468000	2.056815000	-0.527224000
C	-3.445364000	-2.122898000	0.430417000
C	-3.113414000	0.673090000	-0.115279000
C	1.527519000	-3.367647000	-0.267094000
C	-3.930886000	2.968520000	-0.719260000
C	0.372323000	3.478270000	1.482525000
C	-3.644601000	4.253579000	-1.214014000
C	3.846415000	-1.528823000	-0.289852000
C	-2.308709000	4.591140000	-1.505071000
C	5.788667000	-2.306761000	0.945155000
C	5.909047000	-2.011880000	-1.478375000
C	3.135103000	3.439526000	1.344786000
C	-4.202119000	-2.586794000	-0.664679000
C	-3.904190000	-2.276182000	1.753114000
C	6.518790000	-2.370026000	-0.259553000
C	4.566965000	-1.587546000	-1.497291000
C	-5.436636000	-3.218144000	-0.426107000

C -5.905146000 -3.378127000 0.894080000

C 1.096210000 4.533483000 2.066451000

C 2.500146000 4.524482000 1.976441000

C -5.140516000 -2.908795000 1.981194000

C -1.301674000 3.637086000 -1.267618000

C -0.956552000 -2.164966000 0.070704000

C 4.447184000 -1.884107000 0.935891000

C 0.376726000 -4.157812000 -0.095615000

Charge=1.0 Atoms=25

H 4.034617000 1.029413000 0.337338000

H -1.773093000 -4.172159000 0.231556000

H -4.131284000 0.326030000 0.045643000

H 2.503681000 -3.816215000 -0.397669000

H -4.951509000 2.671876000 -0.496708000

H -0.710458000 3.465440000 1.519857000

H -4.443447000 4.970818000 -1.375105000

H -2.047682000 5.566473000 -1.901584000

H 6.259267000 -2.589934000 1.882113000

H 6.471407000 -2.068572000 -2.405666000

H 4.217913000 3.387595000 1.282783000

H -3.829318000 -2.468254000 -1.679394000

H -3.302735000 -1.918638000 2.585072000

H	7.553276000	-2.700920000	-0.248563000
H	4.086478000	-1.321685000	-2.435463000
H	-6.024976000	-3.587500000	-1.260924000
H	-6.856848000	-3.869701000	1.074269000
H	0.568610000	5.335436000	2.571222000
H	3.087003000	5.333398000	2.400587000
H	-5.501008000	-3.039653000	2.997205000
H	1.170882000	0.553808000	-2.793664000
H	-0.246589000	1.310001000	-2.973209000
H	-0.259370000	3.870692000	-1.460813000
H	3.876464000	-1.843006000	1.860815000
H	0.466189000	-5.239850000	-0.101710000

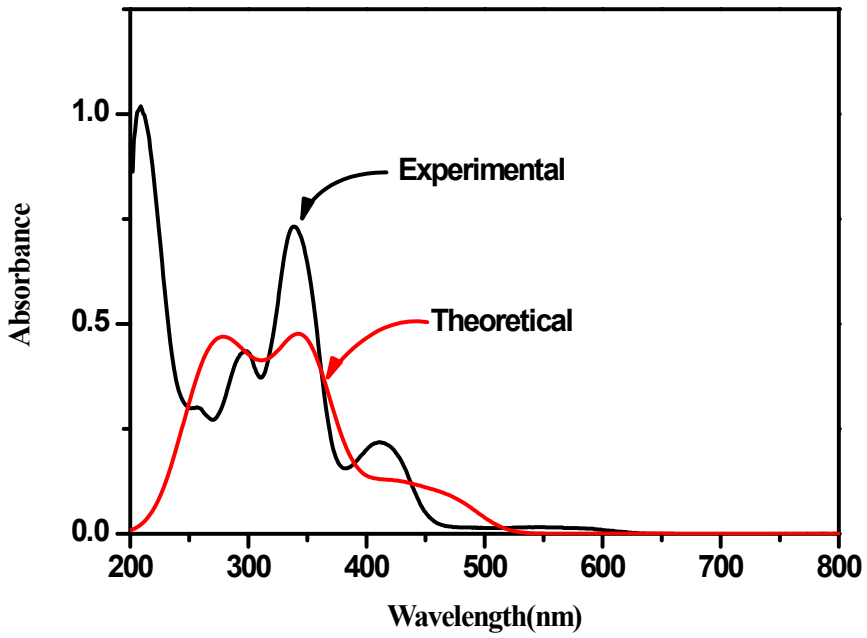

Fig. S17UV-visible spectrum of complex **2** experimental as well as theoretical calculation

Table S10. Major transition along with their orbital contribution in complex **2**

λ_{max} (nm)	f (Osc. Strength)	Transition and their contributions
293	0.0534	HOMO(A)→L+3(A) (31%), HOMO(B)→L+6(B) (51%) H-11(A)→LUMO(A) (2%), H-10(A)→L+1(A) (2%)
347	0.1799	H-5(A)→LUMO(A) (22%), H-4(A)→LUMO(A) (12%) H-3(A)→L+1(A) (2%), H-2(A)→L+1(A) (5%), HOMO(A)→L+1(A) (2%), HOMO(A)→L+2(A) (2%), H-8(B)→LUMO(B) (2%), H-6(B)→LUMO(B) (9%), H-6(B)→L+1(B) (2%), H-5(B)→LUMO(B) (9%), H-5(B)→L+1(B) (2%), H-3(B)→L+1(B) (9%), HOMO(B)→L+2(B) (3%)
407	0.0663	H-1(A)→LUMO(A) (12%), HOMO(A)→L+1(A) (45%) H-5(A)→LUMO(A) (4%), H-4(A)→LUMO(A) (6%), H-2(A)→LUMO(A) (2%), HOMO(A)→LUMO(A) (2%), H-6(B)→LUMO(B) (3%), H-5(B)→LUMO(B) (4%), H-2(B)→LUMO(B) (5%), HOMO(B)→L+1(B) (3%), HOMO(B)→L+2(B) (5%)

Table S11. Percentage contribution of complex **2** in different orbitals

Alpha molecular orbital percentage contribution										
Orbitals	**Py2**	**Py3**	**Py1**	**H2O**	**Ph2**	**Imi2**	**Fe**	**Imi1**	**Ph1**	**Main bond type**
LUMO+2	49	41	2	0	0	3	2	3	0	3d (Fe) + π* L
LUMO+1	28	20	9	0	0	12	15	16	0	3d (Fe) + π* L
LUMO	14	23	10	1	0	14	26	12	0	3d (Fe) + π*L
HOMO	3	1	4	0	1	2	82	6	1	3d (Fe) + π L
HOMO-1	1	6	4	1	0	3	84	1	0	3d (Fe) + π L
HOMO-2	8	5	4	1	0	7	71	4	0	3d (Fe) + π L
Beta molecular orbital percentage contribution										
LUMO+2	1	6	4	1	0	3	84	1	0	3d (Fe) + π* L
LUMO+1	9	5	4	1	0	7	71	4	0	3d (Fe) + π* L
LUMO	3	2	2	1	0	3	88	1	0	3d (Fe) + π*L
HOMO	4	4	2	0	0	3	84	4	0	3d (Fe) + π L
HOMO-1	7	7	38	0	1	24	0	22	1	π L
HOMO-2	11	10	13	0	2	29	2	31	2	3d (Fe) + π L

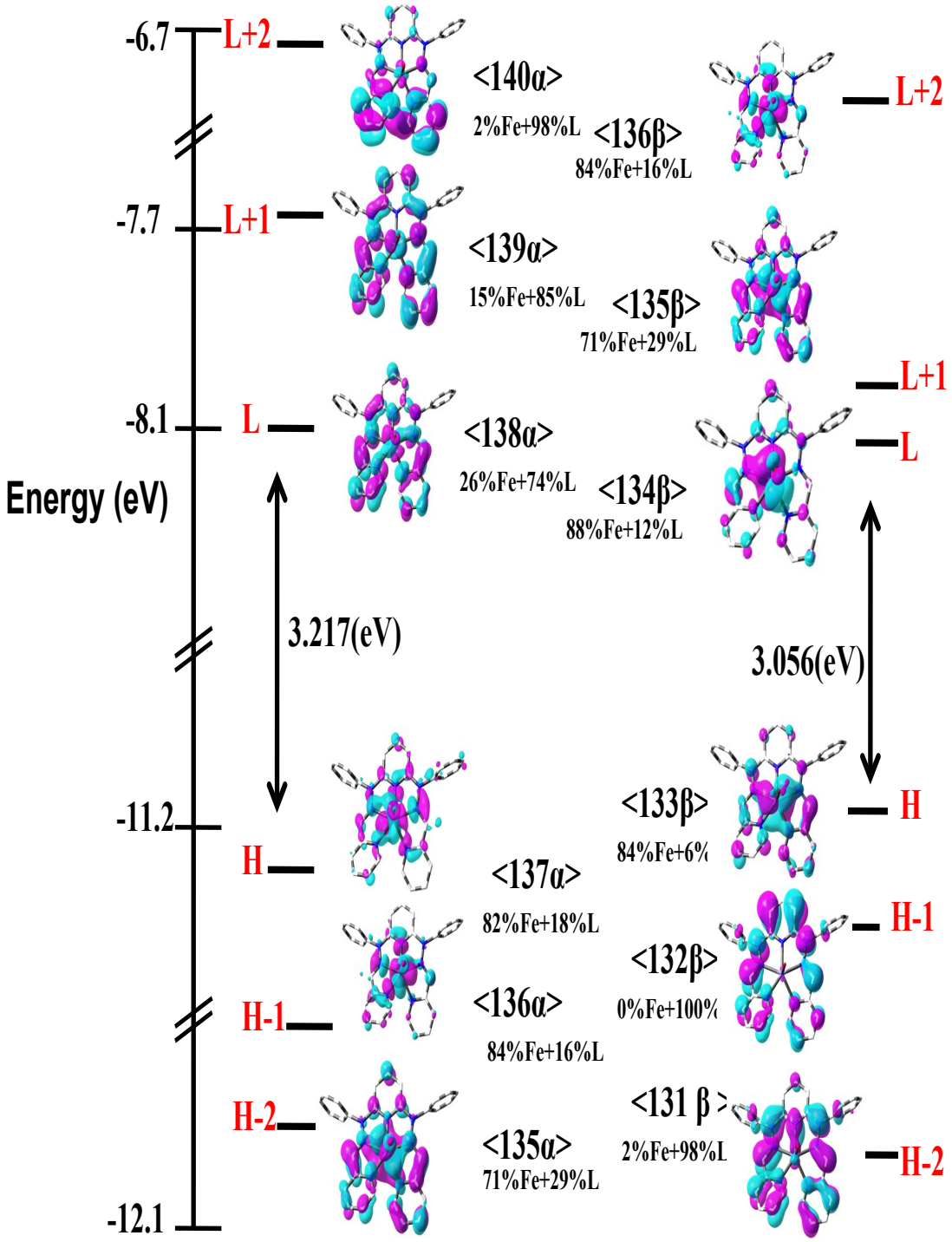

Fig.S18 Frontier molecular orbitals of complex **2** showing significant contribution of iron and ligand (N_5Py) in molecular orbitals.

-:END:-